

**ELMENTS**  
**AND THEIR**  
**EFFECT ON**  
**STEEL**

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# Aluminum

Atomic No : 13  
Density, 20 °C : 2.70 gm/cm<sup>3</sup>  
Atomic Wt : 26.98  
Melting Point : 660° C  
Boiling Point : 2467° C

## GENERAL

Aluminum finds use as a deoxidizer, grain refiner, nitride former and alloying agent in steels. Its ability to scavenge nitrogen led to its widespread use in drawing quality steels, especially for automotive applications. Since aluminum is so often added to high quality steels, it is interesting to note that prior to the 1930's, aluminum deoxidization was regarded as a way of compensating for sloppy steelmaking practice. Melters were even careful to add aluminum when no one was looking.

Aluminum extraction is extremely energy intensive, and prices for the metal are dependent to some extent on the cost of fuels and electric power. In addition, foreign producers of bauxite, long the principal ore, have controlled production and prices to some extent. All this has led to intensive evaluations of alternative ores, new extraction processes and stepped up reclamation programs. Most aluminum used in steelmaking is reprocessed from scrap, and secondary metal prices have stabilized in recent years. Steelmakers remain concerned with the efficiency of aluminum additions for both cost and quality reasons.

## AVAILABLE FORMS

Metallic aluminum is the most common addition agent. It is sold in the form of notch bars, or stick, and as shot, cones, small ingots, wire, "hockey pucks", briquettes and other convenient forms such as coiled machine fed wire. These standard products are supplied in bulk or packaged in bags or drums. Purity for deoxidation grades is usually over 95%, the major tramp elements being zinc, tin, copper, magnesium, lead and manganese. Coiled aluminum wire is normally made to 99% minimum specification.

Ferroaluminum, a dense and highly efficient aluminum addition, contains 30-40% Al. It is supplied in lump form, 8 in. x 4 in., 5 in. x 2 in., 5 in. x D, and 2 in. x D.

Finally, so-called "synthetic" slags containing calcium aluminate are available. These "aluminum" addition agents are valued for their desulfurization properties.

## ADDITION PRACTICE

Aluminum may be added to the furnace, ladle, LRFs, caster tundish or ingot mold. Each type of addition has its specific purpose, and each will produce characteristic results. Aluminum is a very powerful deoxidizer, but while fast, is at somewhat of a disadvantage because of its low density. It has been estimated that the density of liquid aluminum at steelmaking temperatures (1600 C, 2910 F) is only about 2 g/cm<sup>3</sup>. Steel's density at this temperature is greater than 7 g/cm<sup>3</sup>, depending on composition. Therefore, when aluminum is added to the bath, it will float at the steel/slag interface, where it quickly oxidizes.

Relatively small amounts actually make contact with the steel. Wire feeding has overcome this disadvantage by force feeding the aluminum deep into the bath.

Major additions of aluminum for deoxidation and grain refinement are made in the ladle or ladle furnace. Addition is made early in the tap, after ferrosilicon, if used, and before major alloying elements are introduced. Additions are made in the form of shot, pigs, stick, or ferroaluminum. The latter is preferred for its higher efficiency and better consistency. The amount added depends on composition, temperature, and tap carbon.

The amount of aluminum added to fully killed steels depends on carbon, manganese and silicon content. As these elements increase, less aluminum is needed. In AKDQ low carbon steels, aluminum additions will range from about 3-5 lbs./ton. Fine grained structural medium-to-high carbon killed steels need a little less, and the corresponding range is 1-3 lbs./ton.

Aluminum contents over 0.01% can cause nozzle blockage in open stream continuous billet casting machines.

Slab casters are less affected than billet casters by this problem but most of them use submerged casting where the aluminum content is not as critical. Feeding aluminum wire into the open pouring stream below the tundish nozzle eliminates nozzle blockage, but may produce poor surface quality if not carefully controlled.

Steel foundries typically add 0.03-0.07% Al to the furnace ladle (plus a few ounces per ton to the bull or shank ladles, in the event of fade) to ensure soundness. Deoxidation aluminum can be troublesome due to its erratic recovery behavior: too much produces poor surface quality, machining problems and embrittlement; not enough results in porosity. Ferroaluminum is the preferred ladle addition because of its consistent recovery. This guarantees better control over casting quality.

## **ROLLING/FORGING**

The amounts of aluminum needed for deoxidation and/or grain size control present no problems in hot working, aside from the surface quality considerations noted above. Larger amounts, such as those used in magnetic materials and high temperature alloys, will cause embrittlement through the formation of intermetallic compounds. Ferrous alloys containing up to 5% aluminum can be readily hot or cold worked; those with 5-10% aluminum can only be hot worked, and alloys with 10% aluminum cannot be worked at all.

Aluminum tends to produce a more refractory scale that is difficult to remove during pickling.

Aluminum deoxidation promotes the formation to "pancake" ferrite grains. This structure is particularly beneficial for deep drawing applications such as automotive body panels.

Aluminum improves strength in low-carbon steels by fixing the interstitial nitrogen.

## **HEAT TREATMENT**

Aluminum has a weak effect on hardenability (it is never added for this purpose) and, because of its grain refining properties, actually detracts from deep hardening. Heat treatable steels made to fine grain practice require slightly extra alloying to counteract this phenomenon. Aluminum is, however, a ferrite former and promotes graphitization during long-term holding at elevated temperatures. It also enhances creep, probably because of its grain refining property. Aluminum, therefore, should not be used in Cr-Mo or Cr-Mo-V steels specified for boiler or high temperature pressure vessel applications. Perversely, aluminum is otherwise beneficial to such materials since it reduces scaling through the formation of a more tightly adhering oxide film, particularly if chromium is present as well.

## **APPLICATIONS**

Beyond its important functions in deoxidation and grain size control, aluminum has several applications as an alloying agent. Nitriding steels, such as the Nitralloy family, contain up to 1.5% Al to produce a case with hardness as high as 1100 VHN (70 RC). The outer layer of this case must, however, be removed by grinding to prevent spalling in service. The oxidation (scaling) resistance imparted by aluminum is exploited in some stainless steels and various high temperature alloys. Precipitation hardening stainless steels (17/7 PH, 15/7 PH, etc.) make use of aluminum's ability to form strength-inducing particles of intermetallic compounds. Aluminum is found in many superalloys for the same reason.

Aluminum combines very readily with nitrogen, and this effect has important commercial uses. Aluminum killed deep drawing steels will be nonaging since AlN is extremely stable. Such steels will not exhibit stretcher strains (Lüder's lines) or a yield point, even after prolonged holding after cold rolling. Aluminum is also added to nitriding steels for its ability to form an extremely hard case.

Aluminum is an important addition to some HSLA steels, and AlN was the first nitride used to control grain size in normalised and heat treated steels. Again, Al removes nitrogen from solution and provides grain refinement. Both of these effects promote high toughness, especially at low temperatures.

Mention should be made of the effect of aluminum on nonmetallic inclusions, since these will always be present in AK steel. Because aluminum is among the strongest deoxidizers known, it can combine with, and partially or totally reduce, any other oxides present in steel. The subject is quite complex and depends not only on aluminum, but also on oxygen, nitrogen, sulfur, manganese, silicon, and calcium contents. For ordinary steels, however, the pattern is generally as follows: unkilld steels will contain oxides of iron, manganese and silicon, to the extent they are present. Steels deoxidized with silicon and aluminum will contain complex inclusions containing silica,

alumina and manganese and iron oxides. As aluminum is increased, it gradually replaces silicon in the inclusions, and the principal inclusions in aluminum killed steels will be alumina and iron-manganese aluminates. Calcium-aluminum deoxidized steels will contain calcium aluminates, the composition and properties of which will depend on oxygen content (see Calcium). The residual  $Al_2O_3$  in a ladle aluminum deoxidized steel will usually be in the range of 0.015-0.020%. This alumina range will be present regardless of the amount of aluminum used for deoxidation. It is assumed that the remaining alumina of iron aluminate is slagged off.

Aluminum also has a profound effect on the structure of sulfide inclusions. The three basic types of sulfides present in steels have been designated as Type I (fine, randomly distributed spheroids, usually oxysulfides), Type II (intergranular chains which are most harmful to mechanical properties) and Type III (large, globular particles with complex, multiphase structures). Incomplete deoxidation with aluminum results in Type I inclusions; complete, but not excessive deoxidation produces Type II inclusions, while excessive aluminum addition leads to the formation of the Type III particles.

High aluminum contents also promote the generation of interdendritic alumina galaxies, which can impair machinability. Aluminum is added in some stainless grades to improve machinability.

Aluminum as alumina in calcium aluminate slags has found extensive use as slag conditioners at LRF stations. These are used to remove sulfur and inclusions, to lower costs of dolomitic lime, fluorspar, aluminum and calcium carbide additions, to protect the refractory lining, and to improve castability. Applications include both aluminum- and silicon-killed steels.

# **Silicon**

Atomic number : 14  
Density, 20° C : 2.34 g/cm<sup>3</sup>  
Atomic weight : 28.09  
Melting point : 1412° C  
Boiling point : 2355° C

## **GENERAL**

Silicon, the second most abundant element in the Earth's crust (25.7%), is present in virtually all steels, either as a residual from ore, scrap or deoxidants, or as an intentional addition.

Silicon products used in steelmaking are produced from quartzite, silica sand or by a variety of processes, almost all of which currently use submerged arc electric furnaces as reaction vessels. Low grade ferrosilicon was once made in blast furnaces, but the practice has now been completely discontinued in the U.S. Ultrahigh purity silicon, not intended for steelmaking, may be produced by reducing intermediate silicon compounds with hydrogen.

## **AVAILABLE FORMS**

Because of its many uses, silicon is contained in a wide variety of addition agents. Some of these are simply used to add silicon and have general application; in others, the silicon serves as a carrier for other elements.

Ferrosilicon is by far the most common addition agent. It is available in several standard grades containing from 15 to 95% Si. Of these, the 75% grade is the most widely used. The 75% FeSi grade is exothermic while 50% FeSi is endothermic. Significant impurities in ferrosilicon include carbon (up to 0.25%, but generally less than 0.10%) and aluminum (generally 1-1.5%, but lower, 0.10%, or higher, to 2%, in certain grades). Manganese will usually be present as well, but not over 0.40% unless specified. In all cases, phosphorus and sulfur contents are restricted to low residual levels: in general they will not exceed 0.025 and 0.040%, respectively.

Standard foundry grades of ferrosilicon specify aluminum and calcium (0.50-1.50%). Silicon contents parallel those for steelmaking ferrosilicon. Ductile iron foundries also use magnesium ferrosilicon in both 5 and 9% magnesium grade with or without cerium, calcium and/or aluminum.

Silicon-bearing deoxidizers on the market include: calcium silicon, calcium barium silicon, calcium barium silicon aluminum (Hypercal®), calcium manganese silicon, silicon carbide and ferrosilicon zirconium. Silicon metal (97.5%) is used for superalloys, silicones, and nonferrous applications.

Ferrosilicon and related alloys are generally sold in lump or granular form. Standard sizes range from 8 in. x D to as fine as 8 mesh x D. Coarser lumps are used for better slag penetration during deoxidation; finer sizes insure rapid dissolution when used as an alloying addition. Ferrosilicon is fairly friable and excessive handling will generate unwanted fines. Calcium silicon is exceedingly friable and must be handled carefully.

Silicon carbide (SiC) is usually in a granular form. Sizing is 3/8 in. x D, 3/8 in. x 100 mesh, or 3/8 in. x 65 mesh depending on the need to control fines. Larger sizes are available up to 3 in. x 1 in., but only from producers using "big furnace" technology. Inerts are primarily silica and alumina. Petroleum coke and charcoal based silicon carbide usually runs 4-6% SiO<sub>2</sub> and less than 1% Al<sub>2</sub>O<sub>3</sub>. Coal based SiC has 2-4% SiO<sub>2</sub> and 2-5% Al<sub>2</sub>O<sub>3</sub>. The higher alumina in coal based SiC has proven to be a problem in continuous cast silicon killed steels.

## **ADDITION PRACTICE**

The way in which silicon is used in steelmaking depends on the intended purpose of the addition, the practice involved, the condition of the steel, the aim residual silicon level, and the experience and preference of the individual operator. All these factors are implicitly related to the strong deoxidizing power of silicon which, at 1600 C (2910 F), ranks between manganese and titanium, but well below calcium. The deoxidizing power of silicon relative to that of carbon depends on pressure, i.e., on the partial pressure of CO above the melt. At one atmosphere, as in the furnace or an open ladle, silicon is slightly stronger than carbon; at low pressures (0.10 atm or less), as in a vacuum degasser, the deoxidizing power of carbon is greater than silicon, especially at higher carbon concentrations.

Silicon is the first major element removed from hot metal during melt down and is a major source of heat. If the silicon from the blast furnace iron is too low, the steelmaker may add ferrosilicon or silicon carbide for additional heat. Residual silicon levels will not exceed about 0.02% after melt down. In stainless steel melting, silicon additions may be made to the furnace to maintain silicon levels above 0.3% to maximize chromium recovery. Two points should be emphasized here:

(1) Although silicon is a stronger deoxidizer than manganese, when the two elements are used together (either separately or as silicomanganese) they leave a much lower oxygen level in the steel. This is because their joint deoxidation product will be a manganese silicate, in which the activity of silicon is considerably less than it would be if silica were the only product formed. It should be noted that the effectiveness of manganese in increasing silicon's deoxidizing power decreases with increasing silicon content: the increase caused by 0.8% Mn is about ten times greater at 0.05% Si than at 0.2% Si.

(2) Preliminary furnace deoxidation with ferrosilicon should be done with care since silicon has the power to reduce P<sub>2</sub>O<sub>5</sub> in the slag. Thus, if slag phosphorus content is high and the slag is not flushed, it may remain insufficiently basic after the ferrosilicon addition. These conditions can lead to phosphorus reversion in the heat, especially if the slag is hot, and the bath analysis after block exceeds about 0.10% Si and 0.40% Mn at carbon levels over 0.15%.

Modern practice aims to keep expensive furnace time as short as possible, tapping the heat "open" and relying mostly on ladle deoxidation. Ferrosilicon and silicomanganese become the primary deoxidizers. The amount of silicon added will depend on tap temperature and oxygen content and the residual silicon level needed after solidification.

Fully killed steels usually contain silicon in the range 0.15-0.30% Si. Exceptions are steels in which silicon is also an alloying agent, in which case silicon content will be somewhat higher, or aluminum killed steels such as AKDQ, where it is not needed at all. As a general rule, alloy steels and most medium carbon steels will be fully killed with ferrosilicon, even if only as a protection against reoxidation.

Steels to which the elements titanium, zirconium, and rare earth metals are added (for inclusion shape control, or as nitrogen scavengers to protect subsequent or concurrent boron additions) will be deoxidized first with ferrosilicon for reasons of economy. These elements combine readily with oxygen and will be lost to the slag or remain trapped as oxide inclusions if the steel has been inadequately deoxidized. An inexpensive prior deoxidation therefore raises their ultimate recovery or improves their efficiency as nitrogen scavengers, as the case may be.

Silicon carbide is added in three areas. As a ladle addition for silicon killed steel, granular SiC is added to the stream or directly into the ladle after at least 10% filled. Silicon recovery will be similar to that of 75% FeSi, while carbon recovery will be near 100%. In furnace applications (slag reduction), SiC is injected into the slag at the end of the oxygen blow. Moderate foaming occurs, which aids arc energy transfer to final temperature. One pound SiC will reduce 5.8 lbs. of FeO, 5.6 lbs. MnO, or 3.8 lbs. Cr<sub>2</sub>O<sub>3</sub>. It will react first with whichever of these oxides is present in the highest concentration. As a BOF fuel, SiC is added as briquettes or 96% Lump product into the BOF after scrap melt down and preliminary oxygen blow. SiC fuel component may be added into the stream during the blow as the need for additional temperature becomes apparent or is predetermined for the computer program. Additional lime is not required when using cement based SiC briquettes, but may be needed to offset the SiO<sub>2</sub> produced when using the 96% Lump material. SiC can be used for chemical heating in the BOF, where hot metal is short or where there is an economic advantage to using a higher percentage of scrap.

SiC is added to the foundry cupola charge as cement bonded bricks typically containing 36% SiC with 20 - 30% free carbon, to 75% SiC with almost no free carbon. Si recovery is usually 70 - 85%. In induction melting, 90% metallurgical grain is added for Si and C pickup and to deoxidize the bath. In heel melt applications, SiC is added before the charge metal. In batch melt furnaces, SiC is added after, between 1/4 and 1/2 the charge is in. Sprue is added first when batch melting and steel added first in heel melt operations.

## **ROLLING/FORGING**

Silicon strengthens ferrite and, to a lesser degree, austenite by solid solution hardening. Mill loads will therefore increase nominally with increasing silicon content. Strengthening is accompanied by a reduction in ductility, although this has little effect on workability at the silicon levels found in ordinary alloy steels. High silicon steels such as the electrical grades (see below) are quite brittle and require special care during cold rolling to the extent that hand mills are still sometimes used on special high-quality grades.

Silicon steels have a reduced tendency to scale at elevated temperatures, but such scale as does form will be more difficult to remove during pickling.

Silicon has a mild hardenability effect. Its multiplying factor is between that of chromium (higher) and nickel (lower). Silicon is therefore not added to steels for deep hardening, its function in heat treated steels being primarily to strengthen the ferrite in which carbides appear. Silicon is a graphitizer and, like nickel, has limited application in tool steels. It is used, however, in a class of oil hardening graphitic tool steels, AISI 06, as well as an air hardening graphitic tool steel, AISI A10, and two shock resisting tool steels, AISI S2 and S5.

Silicon lowers the eutectoid carbon content but raises the eutectoid temperature. It is a ferrite former and when present in sufficient concentration, closes the g-loop completely. The effect is strongly dependent on carbon content: 2.25% Si will close the g-loop at <0.02% C, but some austenite will remain when carbon increases beyond 0.05%. Silicon may increase the tendency to 260 C (500 F) embrittlement and will have a slight, though detrimental, effect on temper embrittlement. It raises the impact transition temperature (ITT) but does contribute to solid solution strengthening.

## APPLICATIONS

The solid solution strengthening properties of silicon are exploited in several classes of steels including HSLA grades and such ultrahigh strength steels as 300-M (1.6% Si). Silicon is present in AISI/SAE heat treatable alloy steels because these products are always produced in the fully killed condition. Additionally, however, silicon confers a modest resistance to tempering (it does not produce secondary hardening).

Silicon improves high temperature oxidation resistance and is therefore intentionally added to heat resisting Cr-Mo and Cr-Mo-V steels. It is also present in high temperature valve and spring steels for automotive engine applications. Both ferritic and austenitic stainless steels will contain about 1% silicon for oxidation resistance: Type 314 contains 2% silicon for this purpose.

Silicon is the principal alloying element in a unique class of electrical steels used in transformers, electric motor laminations, generators and relays. Silicon confers a relatively high permeability, raises electrical resistivity and lowers hysteresis (core) loss, all beneficial trends in these materials. Generally, core losses decrease (quality is raised) as silicon level increases. Electrical steels will contain between 0.5 and 5.0% silicon, but there are two overlapping classifications: oriented sheet is heat treated to produce a particularly favorable crystallographic texture for ease of magnetization: non-oriented sheet has a random texture but may contain as much or more silicon. Electrical steels must be very clean (free from inclusions) and often require such special processing as pack rolling, frequent intermediate anneals plus, in the case of oriented grades, a final recrystallization anneal in dry hydrogen.

# **Manganese**

Atomic number : 25  
Density, 20° C : 7.44 g/cm<sup>3</sup>  
Atomic weight : 54.93  
Melting point : 1244° C (2271° F)  
Boiling point : 2095° C (3803° F)

## **GENERAL**

Manganese is intentionally present in most grades of steel and is a residual constituent of virtually all others. Aside from its historic importance as a desulfurizer and deoxidizer, manganese is undoubtedly the most prevalent alloying agent in steels, after carbon. Understandably, therefore, ferromanganese is the most widely used ferroalloy: average U.S. annual consumption should exceed 14 lbs. of manganese per ton of steel.

Standard ferromanganese is produced in blast furnaces and, more often, in submerged-arc electric furnaces. In addition, the high-manganese slags resulting from the EF process can be used to make silicomanganese.

The U.S. has considerable manganese ore reserves, but since these are far leaner than those available around the world, they have not been commercially exploited. As a result, all steelmaking manganese products are imported - normally as ferro- and silicomanganese. The leading producers, sharing over 85% of world capacity, are the CIS, the Republic of South Africa, Brazil and China.

## **AVAILABLE FORMS**

Manganese is sold in an extensive variety of product forms. These can be classified into three major groups: ferromanganese, silicomanganese and manganese metal, with several standard or proprietary grades within each group.

Of the 15 steelmaking manganese products recognized in ASTM standards, the most important is high carbon (standard) ferromanganese. It is generally sold in two manganese concentrations: 74-76% and 78-82%, with the latter predominating. Carbon content will not exceed 7.5%, silicon will be less than 1.2% and sulfur and phosphorus, 0.050 and 0.35%, respectively. A low phosphorus variety is available as well. Medium carbon ferromanganese (80-85% Mn) is sold in several grades, varying broadly in silicon content. As usual, the product commands a higher price than the standard high carbon variety. More expensive still is low carbon ferromanganese containing 80-85% Mn or 85-90% Mn, depending on grade. Maximum silicon content here is usually less than 2%, but a product containing 5-7% Si has also been standardized. Low carbon ferromanganese is available with guaranteed maximum carbon contents of 0.070, 0.10, 0.15, 0.30, 0.50 or 0.75%.

Silicomanganese contains 65-68% Mn, <20% Si and 1.5, 2.0 or 3.0% C. Silicon and carbon contents are always inversely proportional. Silicomanganese has a higher deoxidizing power than ferromanganese.

Ferromanganese-silicon (63-66% Mn, 0.08% C, 28-32% Si) can be used as an alternative to low carbon ferromanganese, electrolytic manganese or ferrochrome-silicon (in stainless steel production) as part of the reducing mix. With the importance of ladle steelmaking nowadays, ferromanganese-silicon is used as a low carbon ladle addition, replacing more expensive low carbon ferromanganese and manganese metal. This is particularly the case in HSLA steel production provided, of course, that its relatively high silicon content can be tolerated.

Manganese metal addition agents can be subdivided into purity ranges: Electrolytic manganese (99.90% Mn, min.) is the purest commercial form and is usually reserved for stainless steels and nonferrous alloys. It is available in regular, intermediate and low H2 grades, as well as 4.5 and 6% N2 products.

A product often referred to as high density manganese contains 96 or 97% Mn, depending on grade. Iron, the principal impurity, varies accordingly. High density manganese is also sold in a nitrided form (5-8% N). Its composition and solubility make it a desirable addition agent for superalloys, stainless steel, non-ferrous alloys and low carbon, nitrogen strengthened HSLA steels.

Most manganese addition agents are sold in lump or crushed form in a series of size ranges from 8 in. x 4 in. to 20 mesh x D. Fines are sometimes briquetted or pelletized. The full series of available addition agents are tabulated in the appendix. Standard ferromanganese bears an ASTM friability rating of 4 (scale 1-6): there will be an "appreciable reduction in size of large pieces upon repeated handling", to quote the ASTM definition.

Manganese addition agents (except high-silicon products) also have a tendency to oxidize in air, forming a dark surface film. This MnO film is actually beneficial, however, since it provides a wetting action in liquid steel that enhances solubility. It also improves slag fluidity in the furnace and can therefore reduce fluorspar consumption. For this reason, manganese ores can be used as substitutes for fluorspar.

## ADDITION PRACTICE

Manganese addition agents can often be used interchangeably, depending on conditions. Because the situation will vary from practice to practice and even heat to heat, it is best to outline a few fundamentals:

Manganese is a mild deoxidizer and desulfurizer. Its major uses in steelmaking over the past century relied heavily on these properties, and still do to a large extent. With the advent of hot-metal desulfurization (where called for in the product) and ladle deoxidation (to reduce expensive furnace time, among other reasons) these traditional uses for manganese have declined. They have, incidentally, been supplanted by increased manganese consumption as a true alloying constituent, mainly in HSLA steels. Nonetheless, the efficiency of any manganese addition - no matter when or why added - will depend on the steel's oxygen and sulfur contents. Bath temperature is important not only as it affects the carbon/oxygen balance, but also in relation to chill factors, especially when large manganese additions must be made.

Processing factors are also important: long tap times or extended holding in the furnace or ladle may provide opportunity for reoxidation, for example. Slag composition and the type and condition of refractories must also be considered. The addition of stronger deoxidizers than manganese (e.g. aluminum or silicon) can cause reversion of Mn from slag to metal, just as they do for phosphorus. Finally, cost and availability of addition agents must be weighed against all of the above factors as they apply to the heat process. A fast response chemical analysis system coupled to a computer is obviously helpful, especially given increasingly more stringent quality and productivity requirements, but it must be noted that the skill and experience of individual operators enabled them to solve these complex problems intuitively for many decades.

All other factors considered, however, manganese addition agents are generally chosen on the basis of carbon content. Inexpensive standard ferromanganese is used when the steel is well oxidized (low in carbon) or when higher residual carbon contents are allowable. As maximum steel carbons become more restricted it is necessary to switch to the more costly low-or medium carbon ferroalloys. The final aim chemistry will determine which addition agents can or cannot be used. Silicon content is often a second deciding factor.

In basic electric furnace practice, furnace addition of ferromanganese is usually not needed, assuming sulfur has been adequately controlled by proper charge selection or other means. Silicomanganese can be a cheap and useful reducing agent, but some steels require that aluminum or ferroaluminum be used instead.

Ladle additions will consist of one or more of the standard products depending on the factors listed above. Sizes on the order of 5 in. x 2 in. or 4 in. x 1/2 in. are preferred for their higher solution rates and relative absence of fines. Timing of the additions depends on their function. Deoxidation additions are made early, sometimes along with ferrosilicon. Trim or alloying additions must come later, and standard, medium- or low carbon products may be used. Metallic manganese addition agents are used for premium grades such as stainless steels, specialty alloy and interstitial-free (IF) steels. They are used exclusively as alloying additions since they are too expensive to use as deoxidizers. High density manganese is added to the ladle, the AOD or the degasser. Electrolytic manganese has a tendency to ball up and form floaters when added to the ladle and is therefore better applied as an induction furnace addition during the production of specialty alloys. It can also be added to the AOD or the degasser and, if done in such a way that dissolution proceeds uniformly, floaters will be avoided.

## ROLLING/FORGING

Manganese improves hot workability by preventing the formation of low-melting iron sulfide, FeS. Steels with a Mn/S ratio of at least 8/1 will not exhibit hot shortness. MnS, which forms preferentially to FeS, has a high melting point and appears in ingots as discrete and randomly distributed globules. (However, see Sulfur for a discussion of segregation.) Although solid at hot working temperatures, the MnS inclusions are soft enough to deform into elongated stringers during rolling or forging. Their presence may be harmful, beneficial or benign, depending on the product form and its application. Manganese sulfides are necessary in any steel that must be machined since they are effective chip breakers. On the other hand, long manganese sulfide stringers are detrimental to the transverse and through-thickness ductility and impact properties of flat-rolled products. Where these properties are not critical, MnS is essentially harmless.

Manganese may be present in other inclusions, as well. It forms complex and sometimes mutually soluble oxides,

sulfides, oxysulfides and silicates with a number of elements. The more important of these are the ones used for inclusion shape control, i.e., calcium, titanium, zirconium and the rare earth metals.

Manganese has a negligible solid solution strengthening effect in austenite and only a moderate effect in ferrite. Mn increases strength and toughness after rolling by lowering the austenite decomposition temperature during cooling to give ferritic grain refinement and a reduction in grain size. Manganese increases the work hardening rate in austenite and actually reduces work hardening (through enhancement of dislocation cross slip) in ferrite, at least at ordinary concentrations. Since manganese increases a steel's resistance to deformation, manganese steels will be stiffer during rolling or forging.

## HEAT TREATMENT

Manganese very strongly retards the transformation of austenite and therefore promotes deep hardening in heat treatable steels. Manganese also lowers the transformation temperature and the eutectoid carbon content. These properties - especially the first two - account for the wide use of manganese in steels in which transformation must be controlled.

Because it is the most cost-effective hardenability intensifier (hardenability factor divided by cost), manganese is present in all standard AISI/SAE heat treatable steels. Up to about 1% Mn is specified in these steels. However, manganese is also important in flat-rolled steels. The lower transformation temperature produced by manganese addition promotes finer grain sizes, either as-rolled or normalized. As grain size is reduced (either ferrite, bainite or pearlite) yield strength increases and impact properties improve. As an added benefit, pearlite content increases with increasing manganese concentration for a given carbon content. This raises strength, without sacrificing weldability. Depending on which carbon equivalent formula is applicable for the steel in question, manganese is only 1/6 to 1/20 as detrimental to weldability as carbon itself.

Very high manganese contents suppress the  $\gamma$  -  $\alpha$  transformation entirely, and such steels (see below) will be fully austenitic at room temperature. In all cases, manganese lowers the  $M_s$  temperature, and high manganese steels will tend to contain residual austenite.

Although it forms a carbide that is similar to cementite, manganese produces no secondary hardening during tempering. Manganese does enhance susceptibility to temper embrittlement when present in excess of 0.30% and care should be taken to avoid the critical temperature range (375-575 C, 700-1070 F) during tempering. Heavy sections should be quenched from the tempering temperature, if it is above this range.

## APPLICATIONS

Besides the heat treatable steels already mentioned, manganese is present in a wide variety of steels, for an equally wide variety of reasons. Flat rolled carbon and HSLA steels contain up to 2% Mn for microstructural refinement and resulting improved mechanical properties. Solid solution strengthening is also important here. These steels may contain Mn-V-C, Mn-V-N, Mn-Mo-Cb or other combinations of elements, depending on grade, product form and application.

Manganese may be substituted for part of the nickel content in austenitic stainless steels (200 series). Such steels gained importance during times of critical nickel shortage, such as World War II. They will contain between 5.5 and 10% Mn. One of the earliest, and most interesting, types of alloy steels contains 10 to 14% Mn and 1.0 to 1.4% C. These are the so-called Hadfield steels, which were originally developed before the 1900's. When quenched from above 1000 C (1832 F), they remain fully austenitic at room temperature. Their utility is based on their extremely high work hardening rate, which makes them useful as, for example, railroad frogs and earthmoving and mining equipment components. When the surface of a Hadfield's steel is deformed it becomes very hard, resisting further deformation. The underlying metal, however, remains soft and ductile.

Carburizing steels of the AISI/SAE family contain up to about 1.0% Mn, but considerably less may be present in certain grades. Nitriding steels contain typically 0.55% Mn, but the range within the several commercial grades extends from residual traces to almost 1.0% Mn. Manganese does form a nitride, but its use in these steels is mainly based on heat treatment (hardenability) effects.

Similarly, tool and die steels rely on manganese for deep hardening. This is important when high concentrations of strong carbide formers are present, as these can withdraw carbon from solid solution, thereby reducing hardenability.

# Chromium

Atomic number	: 24
Density, 20° C	: 7.1 g/cm <sup>3</sup>
Atomic weight	:52.01
Melting point	:1850° C (3362° F)
Boiling point	:2680° C (4856° F)

## GENERAL

Chromium is one of the most versatile and widely used alloying elements in steel. It imparts corrosion and oxidation resistance, is a mild hardenability agent, improves wear resistance and promotes the retention of useful strength levels at elevated temperatures. Chromium is an irreplaceable constituent in all stainless steels; in fact, over 70% of all chromium used in steelmaking is found in the many stainless grades. Next in tonnage consumption of chromium are the constructional alloy steels, most of which contain well less than 3% Cr. Tool steels, superalloys and other specialty metals, though often high in chromium content, are produced in smaller quantities and therefore rank lower in over-all chromium application.

Having almost no chromium ore deposits of its own, the U.S. is completely dependent on foreign sources for chromium materials. The Republic of South Africa holds more than 70% of the world's known deposits and is one of the leading suppliers. Zimbabwe, with 25% of the known reserves, is also a major source. Kazakhstan has moderate reserves but a high chromium production rate. Turkey, Finland and Brazil supply significant tonnages as well.

Chromium is relatively abundant in the Earth's crust but, on occasion, political and economic factors have created an artificial shortage. As a result, chromium conservation has been the subject of intensive study. While such programs may have limited effectiveness, the unique properties of chromium as an alloying element, such as in the stainless steels, will doubtless keep demand high.

## AVAILABLE FORMS & ADDITION PRACTICE

About half of the chromium used in steelmaking is derived from scrap. The remaining chromium is most commonly supplied as ferrochrome, of which several grades are commercially available.

The principal impurities in ferrochrome are carbon and silicon. As is often the case, carbon level is most important in determining the price differential between the various ferrochrome grades. The widespread shift toward duplex refining practices such as the AOD, CLU, etc., has led to greatly increased use of high-carbon ferrochrome. Low carbon ferrochrome, once quite common, is now added mostly for final chemistry adjustments in the production of stainless steel. Another low carbon ferrochrome alloy once widely used is ferrochrome silicon. It is used in the EAF to maintain silicon levels in the bath to prevent chromium oxidation and for final chromium adjustments.

High carbon ferrochrome, or at least the grades commonly designated charge chrome, remains the most widely used chromium addition for the production of stainless and alloy steels. High carbon ferrochrome, 6-8% C grade, 65-70% chromium, for many years remained the standard of the industry. The reduced availability of the high Cr:Fe ores made the lower cost, low Cr:Fe ratio ores from South Africa more attractive and forced the steel industry to make the change to the widespread use of charge chrome. Charge grade ferrochrome is generally available in two chromium ranges: 63-67% and 50-55%. Carbon content is typically about 5-1/2% for the 63% chromium grade and a maximum of 8% in the 56% chromium grade. Silicon will normally run between 2 and 4% in charge chrome, depending upon carbon content. Carbon and silicon have an inverse relationship in smelting ferrochrome, i.e., high carbon with lower silicon, and the reverse.

The industry has developed a large number of specialty compositions to serve the needs of a variety of applications. As an example, low carbon ferrochrome can be supplied in a range of carbon grades from 0.010% maximum to 0.25% maximum. Induction furnace production of ELC stainless would be a typical application, whereas the intermediate grades of 0.015% and 0.05% carbon types of low carbon ferrochrome might be applied to the production of vacuum melted superalloys, regular low carbon stainless, high chrome stainless, heat

resistant alloys, as well as in the production of both low and high alloy steel, including heat resistant and corrosion resistant stainless grades. Other applications for special composition low carbon ferrochromes are the low carbon, low nitrogen ferrochrome and the low carbon, low nitrogen, low silicon ferrochrome. These latter two low carbon ferrochromes have frequently been used as a substitute for chromium metal in the production of certain high temperature or nickel-base specialty alloys. Reactor grade ferrochrome is a low carbon ferrochrome with a very low cobalt content. It can be used as a substitute for chromium metal in the production of nuclear equipment components. Refined high carbon ferrochrome provides a ferrochrome with both low silicon and titanium contents. High carbon ferrochrome, 8-10% carbon grade, is used in the production of abrasion-and heat-resistant alloys since it alloys simultaneous addition of both chromium and carbon. A low phosphorus grade of charge chrome is available to control phosphorus levels in stainless and high alloy steels, when needed.

Ferrochrome silicon was originally developed as a process ferrochrome to be used in the production of low carbon ferrochrome. It was subsequently introduced to wrought stainless steel producers in the 1950s as a lower cost form of low carbon ferrochrome. Two grades are available: 40/43 and 36/40. The use of these alloys has also declined in direct relationship to the growth of AOD refining.

Nitrogen-bearing low carbon ferrochrome provides a simple means of making a nitrogen addition to chromium bearing steels, particularly conventionally melted stainless grades. These grades of stainless can also be produced economically with elemental N<sub>2</sub> in the AOD.

Pure metallic chromium metal is produced both aluminothermically and electrolytically. The vacuum grade of electrolytic chromium requires a second stage of carbon reduction refining which is not required for the vacuum grade of aluminothermic chromium.

Chromium metal is used primarily in superalloy, high temperature and other alloys in which tight restrictions on residual elements found in ferrochrome prevent its use, i.e., C, Si, Co, Fe, O, N, P, S, etc.

Other binary aluminothermic chromium alloys available for special alloying requirements are high carbon chromium and chromium molybdenum.

Iron foundries occasionally use chromium briquettes in cupola melting; however, lower cost crushed charge chrome as a ladle addition has largely replaced this practice.

Standard sizes of ferrochrome range from 8 in. x 4 in. lump to 20 mesh X D. Bulk delivery is most common although smaller packaging in super sacks or drums is available, especially for higher unit cost grades.

Chromium-containing HSLA steels, ferritic stainless grades and even some tool steels may be produced in the BOF using a charge of hot metal, scrap and alloy addition agents, including charge chrome. Chromium recoveries should be 90% or greater. In all practices, however, proper selection of charge materials, careful process control - particularly with regard to slag chemistry - and precise analytical techniques will result in maximum chromium recovery.

## **ROLLING/FORGING**

Special care must be taken in rolling or hot forging high chromium and/or chromium-nickel stainless steels as their behavior is quite different from plain carbon or low chromium alloy steels. Thorough surface conditioning is important. Heating for hot working must be performed slowly since stainless steels have considerably lower thermal conductivity than plain carbon steels. Rapid heating can lead to surface burning. Soaking should generally be performed above 1150 C (2100 F) but specific ranges vary with the grade in question. Overheating should be avoided at all costs since excessive grain coarsening (to which the stainless steels are particularly sensitive) can lead to difficulties in rolling or forging.

Ferritic and martensitic stainless grades (400 series) hot roll and forge quite easily. Austenitic grades (300 series), on the other hand, are stiffer at high temperatures than carbon or alloy steels and will exert greater roll stresses for equivalent reductions.

Austenitic stainless steels may be rolled at normal rates after hot working: the air hardening martensitic grades should be cooled slowly to avoid the likelihood of thermal cracking during subsequent conditioning, where applicable. All stainless steels are annealed prior to cold working.

## **HEAT TREATMENT**

Chromium itself is not as strong a hardenability agent as, for example, manganese or molybdenum. However, it is highly cost effective (degree of hardenability increase/relative alloy cost) and is a constituent of almost all of the AISI/SAE alloy steels. Further, chromium has a strong tendency to form hard and stable carbides. This property gives chromium steels the ability to resist softening during tempering and makes the resulting products hard and wear resistant. However, it also means that for a given hardness level, chromium steels will require somewhat higher tempering temperatures, or longer tempering times, than their plain carbon counterparts. This effect increases with increasing chromium content.

Tool steels, and alloy steels containing significant quantities of carbide-forming elements such as chromium, require higher austenitizing temperatures in order to dissolve the carbides completely. As in the case of stainless steels, chromium has a tendency to promote grain growth, therefore careful control of austenitizing temperatures is important in chromium alloy and tool steels. (Some chromium steels contain vanadium to counteract this phenomenon.)

Chromium and nickel-chromium alloy steels are particularly susceptible to several heat treatment-related embrittlement mechanisms. These should be understood and care taken to avoid them.

Temper embrittlement is the loss of ductility (or increase in ductile-to-brittle transition temperatures) after tempering in the range of 375-575 C (700-1070 F) or slow cooling through this range. It is now known to be related to impurities such as phosphorus, tin, arsenic and particularly antimony. Unless special care is taken, these impurities are invariably present in sufficient concentrations to cause damage. The presence of more than 0.5% molybdenum retards but does not eliminate the embrittlement. Unless otherwise impossible, as in the slow cooling of large forgings or castings, care should be taken to avoid the dangerous temperature range.

350 C (500 F) embrittlement is the loss of room temperature impact toughness after tempering to high strength levels, i.e., in the range 200-370 C (400-700 F). Aluminum tends to reduce this problem, but 0.10% Al is required to eliminate it completely. In martensitic stainless steels, the critical temperature for embrittlement is raised to about 480 C (900 F).

500 C (932 F) embrittlement is found in high chromium ferritic stainless steels that have been held in the damaging temperature range, 400-500 C (750-932 F), for very long periods of time. The problem does not exist in steels containing less than 15% Cr. It can be cured by heating to temperatures above the embrittlement range for several hours.

Sigma phase embrittlement results from the precipitation of the iron-chromium compound FeCr after holding austenitic or ferritic stainless steels for long periods of time in the range 560-980 C (1050-1800 F). Slow cooling from the range 1040-1150 C (1900-1200 F) produces the same effect, as does quenching from this range followed by subsequent heating in the range 560-980 C (850-1560 F).

## APPLICATIONS

Steels containing a minimum of about 12% chromium are considered stainless, i.e., resistant to oxidation and corrosion due to the existence of a thin but tightly adherent protective oxide layer on the steel's surface. The most widely used stainless steel, Type 304, contains approximately 18% chromium and 8% nickel. It is found in chemical, food processing, architectural, automotive and other decorative and functional applications. Like the remainder of the 300 series, it is austenitic in structure and does not transform to martensite on cooling from elevated temperatures. Most other 300 series stainless steels can be looked upon as modifications of this basic 18/8 type, with compositional changes specifically tailored for particular metallurgical or corrosive/oxidation resistance reasons. Thus, Type 304L has carbon restricted to 0.03% maximum to avoid intergranular corrosion; Types 321 and 347 contain small additions of titanium and columbium, respectively, for the same reason; Type 316 and its low carbon variant; 316L, are slightly richer in chromium and nickel and contain 2-3% molybdenum for increased pitting corrosion resistance. Type 310, with nominally 25% chromium, 20% nickel, has very high resistance to oxidation and may be used in such applications as combustion chambers and high temperature heat exchangers. Many stainless grades, 300 series and others, may be modified with additions of sulfur or selenium for improved machinability.

Type 409 is the most popular of the ferritic stainless steels, and has been widely used in automotive exhaust systems and fuel tanks. Lacking nickel, it is less expensive than the austenitic grades. Type 410, a martensitic grade, and its lower silicon modification, Type 403, are extensively used for steam turbine blading and for such

mechanical uses as valve parts, pump components, shafts and screens. Cutlery is manufactured from Type 440C, a martensitic stainless high in both chromium and carbon.

Up to about 1% chromium is found in most standard AISI/SAE alloy steels, including those of the 41XX, 50XX, 51XX, 61XX, 86XX and 94XX series. Chromium imparts hardenability, wear resistance and a measure of corrosion resistance. Bearing steels, such as AISI 52100, contain up to 1.5% chromium for just these reasons. Carburizing and nitriding steels contain chromium (as in the Nitralloy series) since chromium has a strong affinity for both carbon and nitrogen. Here, chromium is usually used in combination with other strong carbide or nitride formers such as vanadium, aluminum and molybdenum to form thin but extremely hard nitrided cases.

Chromium improves the resistance of steels to hydrogen attack. Chromium and chromium-molybdenum steels have long been standard materials in applications where hydrogen-bearing atmospheres are present: petrochemical plants, petroleum refineries, power boiler tubing, etc. It is believed that chromium carbide, being stable at elevated temperatures, resists the strong reducing power of hydrogen present in these environments.

The presence of chromium carbide also gives structural steels the ability to resist softening at elevated temperatures. This leads to greater creep and stress-rupture resistance. Steels selected for elevated temperature service will contain increasing amounts of chromium and molybdenum depending on the expected service temperature. Chromium contents may range from a minimum of 1.25% to the maximum values found in austenitic stainless steels and high temperature/corrosion resistant alloys.

Chromium is the most important element in tool steels, after carbon. Besides imparting hardenability, chromium forms a variety of carbides (depending on composition and heat treatment). These carbides, along with those of vanadium, molybdenum and other constituents, provide the necessary wear and abrasion resistance. As mentioned above, chromium does have a tendency to promote grain growth, and since most tool steels require high austenitizing temperatures, vanadium is frequently added as well.

# **Carbon**

Atomic number : 6  
Density, 20° C : 2.3 g/cm<sup>3</sup>  
Atomic weight : 12.01  
Melting point : >3550° C (6422° F)  
Boiling point : 4827° C (8721° F)

## **GENERAL**

Carbon is the most important alloying constituent in steel and cast iron and is chiefly responsible for the broad range of mechanical properties attainable in both wrought and cast products. When an iron based alloy contains more than 2.0% C (except in the case of ferroalloys), it is classified as cast iron. Plain carbon steels are metallurgically subdivided into hypo- and hypereutectoid grades, depending on whether their carbon content is less or more than 0.80%. Additional alloying elements (manganese, silicon, nickel, etc.) change the carbon content of this, the eutectoid point, and may even eliminate it entirely. Limitations of carbon led to the development of microalloyed steels (with low carbon content). However, this chapter will consider only those steels and irons in which carbon is the principal alloying element, ignoring the unavoidable presence of other elements remaining after deoxidation or necessary for the control of sulfur.

## **AVAILABLE FORMS**

Carbon is, of course, present in almost all steel from the onset of the steelmaking process. Steelmaking begins with raw materials (hot metal, pig iron, scrap, ferroalloys, etc.) normally containing more carbon than is needed in the final product. Carbon is eliminated by oxidation during steelmaking and heats are tapped when the required carbon content is reached, or at slightly below that level if high-carbon ferroalloy additions are to be made in the ladle. It is common practice in BOF practice to "blow down" to below 0.10% C and recarburize the steel in the ladle. Carbon is injected into EAFs for foamy slag practice and carbon cored wire is fed in ladle refining stations for precise control of carbon content.

When used, high carbon ferroalloys become, as well, the carbon "addition agent". When carbon levels are too low for compensation by the required amount of ferroalloy, carbon addition may take the form of graphite, coke, petroleum coke, anthracite coal or, very seldom, high-carbon scrap such as cast iron or cold pig iron. Cast iron used for carbon correction has the danger of exceeding the phosphorus specification. Similarly, coke used for recarburizing should be as low in sulfur and volatile components as possible.

The electric furnace production of cast iron often requires a recarburizing step because the process relies on inexpensive, relatively low carbon scrap as a starting material. High carbon scrap, high carbon ferroalloys or even pig iron are used as sources of carbon but when practice, specifications or economics dictate, specific recarburizers are needed. These usually take the form of graphite or coke.

Graphite may be natural or synthetic. The former is used more often in North America than elsewhere since a major source is located in Mexico. The natural product has less carbon (70-85%) and more impurities than either synthetic graphite or coke, and this restricts its usefulness. Synthetic graphite for iron foundries is a scrap product, often derived from the production of electric arc furnace electrodes. All graphites are crystalline, and this can influence the structure of the cast iron, as explained below.

Metallurgical coke is an inexpensive and widely available recarburizer, but its high ash content (~9%) may make it unsuitable for many applications. Calcined petroleum coke is a higher purity product (~99%) but may contain more than 1% S. Both forms of coke are amorphous.

## **ADDITION PRACTICE**

When carbon is added in the form of a high-carbon ferroalloy, addition may be made in the furnace, just before tap, or in the ladle. The common practice is to decarburize the heat slightly more than necessary in the furnace, using the ferroalloy to make up the specified carbon range. The carbon-oxygen-temperature balance at the time of tap is the governing factor, but the situation is somewhat at the discretion of the individual operator. Since furnace time is expensive, the tendency is to tap the heat "open" and deoxidize as necessary and make chemistry adjustments in the ladle. It should be emphasized that using cast iron to correct carbon levels can introduce too much sulfur and/or phosphorus. Unless the heat is already very low in these elements, or the amounts added

can be tolerated in the final composition, the hot metal should be as low in phosphorus and sulfur as possible.

The carbon recarburizers (graphite, coke, and anthracite) are quite light and will easily float on the slag, where they can burn wastefully. They should therefore be added very early in the tap, or placed in the ladle before the steel is introduced. The tap should have enough turbulence to provide rapid carbon dissolution.

In foundry practice, recarburizers are added in the ladle, observing the same precautions as described above. The type of recarburizer chosen depends on the cast iron being produced. Crystalline recarburizers, i.e., graphites, have an inoculating effect in iron, especially if the base sulfur content exceeds 0.04%. If the tap sulfur content is below this value, it may be more efficient to perform primary recarburization with (high sulfur) petroleum coke and trim with graphite just before casting. When inoculation is to be avoided, as in white irons, coke is the preferred addition agent. The higher nitrogen content of petroleum coke (~1%) can be used to increase strength through the formation of a fully pearlitic matrix and a compacted eutectic graphite. However, if nitrogen is known to produce porosity defects, it can either be avoided by using graphite or a low-nitrogen coke or controlled through the addition of titanium, zirconium or similar stabilizing elements.

It should be noted that in adding carbon, a reduction in temperature of 2.98 C (5.36 F) is produced for each pound of graphite per net ton of steel treated.

## ROLLING/FORGING

The carbon content of steel influences deformation processes in several ways. In general, such processes become more difficult as carbon content increases. The effect of carbon is first felt in the soaking pit or re-heat furnace. High carbon steels are more sensitive to thermal shock and must be heated slowly to avoid cracking. Step heating - allowing the ingot to equalize in temperature at several plateaus before the rolling or forging temperature is reached - may be necessary, especially for large cross sections. Steels with more than 0.30% C are also more susceptible to "burning", or deep surface oxidation. This leads to cracking or, at best, unacceptable surface conditions in the final product and almost always requires that the burned ingot be reverted to scrap. High carbon steels should therefore be heated slowly and evenly, avoiding hot spots due to direct flame impingement.

Both hot- and cold-rolling forces increase with carbon content. In hot rolling, the effect becomes more pronounced as the finishing temperature is approached. An additional 0.15% C in a plain carbon steel produces as much as a 20% increase in power consumption at 870 C (1600 F), for example. The energy required for cold working is strongly dependent on carbon content, a consequence of the proportion of pearlite in the microstructure. The need for intermediate anneals therefore increases with carbon content, all other factors being equal.

It should be noted that the carbon has a relatively strong tendency to segregate in thick sections (e.g. ingots), and will be enriched (along with manganese, phosphorus and sulfur) in the last metal to solidify. This can lead to nonuniform carbon distribution in the final product, such as the familiar "banding" (caused by phosphorus segregation: high P areas rejecting C) seen in hot rolled sheet and plate. This is not necessarily detrimental, however.

For steels utilizing microalloying additions, the ratio of atomic percent microalloying element (MAE) to carbon percent determines the amount of MAE precipitate formed at a given low temperature. Here, both cold rolled and annealed sheet steels rely on carbon content being under 0.01%.

Carbon increases the strength of hot rolled steels but decreases the notch toughness, ductility and weldability. Reference Vanadium, Columbium, and Titanium for details on carbon's use in continuously cast and hot rolled steels.

## HEAT TREATMENT

The interaction between carbon and iron is the basis for all common heat treating reactions. (Essentially carbon-free steels such as the maraging grades are heat treated as well, but these are special cases, which will not be considered here.) Unless added for specific reasons, e.g., corrosion resistance, alloying elements normally serve to modify the iron-carbon reactions - or combine with carbon themselves - to enhance mechanical properties.

Carbon dissolves in iron, but the solubility limits depend on crystal structure. High temperature  $\delta$ -ferrite can contain up to 0.10% C at 1492 C (2718 F); austenite ( $\gamma$ ) will dissolve up to 2.0% at 1130 C (2066 F), but lesser amounts are soluble at lower and higher temperatures; carbon is only sparingly soluble in low temperature  $\alpha$ -

ferrite, the maximum being about 0.025% at 723 C (1333 F). Less than 0.008% C is soluble in ferrite at room temperature.

The iron-carbon equilibrium diagram (Fig. 1) shows three reactions and indicates the formation of cementite, Fe<sub>3</sub>C, at 6.67% C. At 1492 C (2718 F), δ-ferrite containing more than 0.10% C reacts peritectically with liquid to form austenite. Iron containing more than 2.0% C undergoes an eutectic reaction at 1130 C (2066 F) forming ledeburite, a rod-like dispersion of cementite in austenite. At 723 C (1333 F), austenite decomposes eutectoidally into the lamellar composite, pearlite.

Carbon lowers the allotropic γ - α transformation temperatures from 910 C (1670 F) for pure iron to the eutectoid temperature at 0.80% C. Below the eutectoid (723 C, 1333 F), carbon has a strong influence on the kinetics (rate) of pearlite formation and reacts with iron to form the nonequilibrium phases bainite and martensite. Pearlite forms at higher temperatures, between about 550 C (1020 F) and the eutectoid temperature, becoming increasingly finer in structure as the transformation temperature is lowered. Between roughly 220 C (425 F) and the lower limit of the pearlite formation range, austenite transforms to bainite, of which there are two main types: Upper bainite is formed at higher temperatures. It has an acicular structure containing cementite particles oriented along the boundaries of the ferrite regions. Lower bainite is also acicular, though much finer in structure. In it, the carbide particles are oriented across the ferrite regions, a fact that contributes to its higher toughness. The temperature dividing upper and lower bainite is a function of composition, especially carbon content. Both bainites grow at rates determined largely by the diffusion of carbon in iron.

The diffusionless, or shear, transformation of austenite to martensite at temperatures below about 220 C (425 F) is the most important reaction in commercial heat treating. The martensite start, or M<sub>s</sub> as the eutectoid composition is approached.

If the product application requires a hard, wear resistant surface but a tougher, more ductile core, the steel may be carburized. In this process, carbon is intentionally diffused into the surface layer of a low carbon steel, normally to a depth not exceeding a few thousandths of an inch. Carburizing is carried out at about 925 C (1700 F), and it is important that the steel's composition allows it to remain fine grained at this temperature. After carburizing, the steel will be heat treated as usual.

## APPLICATIONS

Carbon steels constitute by far the largest tonnages of all steels sold. A full listing of their applications is obviously impossible. Carbon steels are used as castings and forgings, pipe and tubes, sheet and plate, wire, rod, rails and structural shapes. Carbon steels are, of course, the least expensive ferrous alloys and designers will endeavor to specify them unless specific properties necessitate the use of more expensive alloy grades.

Carbon steels may be classified in several ways. Composition is the most obvious, and this is usually done through the use of established standards, such as those published by the Society of Automotive Engineers (SAE) and the American Iron and Steel Institute (AISI). The American Society for Testing and Materials (ASTM) and the American Society of Mechanical Engineers (ASME) specify steel properties, regarding the compositions only as incidental. Many of these standards identify the same steels by their own individual specifications. The individual user may choose to add such requirements to any general specification to suit his needs. Many large users, such as automotive and construction equipment manufacturers, prefer to establish their own standards, which may be more restrictive than those published by national organizations.

Sheet steels tend to have the lowest carbon levels (under 0.10% C). In general, ultra-low carbon steels include high formability sheet steels with carbon under 0.02%. Low carbon steels include most hot rolled strip, plate and pipe with 0.05-0.20% C. Medium carbon steels include the forging grades with 0.25-0.55% C. The high carbon steels include rail steels with over 0.6% C

# **Nickel**

Atomic number	: 28
Density, 20° C	: 8.902 g/cm <sup>3</sup>
Atomic weight	: 58.69
Melting point	: 1455° C (2651° F)
Boiling point	: 2910° C (5270° F)

## **GENERAL**

An important and widely used constituent of alloy steels, nickel is best known as a solid solution strengthener, a mild hardenability agent and, most important, as a means of promoting high toughness, especially at low temperatures. Nickel was probably the first of the modern alloying agents; some nickel steels were commercially produced around the beginning of the 20th century.

Upwards of 8% nickel is used to produce the austenitic structure in 300-series stainless steels. This important application accounts for roughly three quarters of U.S. nickel consumption for stainless steelmaking. Wrought steels, including stainless, consume the majority of world production. In the concentrations found in low alloy steels, nickel has a modest but beneficial effect on atmospheric corrosion resistance. At the other end of the spectrum, nickel forms the basis for an extensive and important family of superalloys and heat-, oxidation- and corrosion-resistant materials.

Nickel ranks 24th (0.01%) in abundance in the Earth's crust. Its availability to steelmakers has fluctuated between severe shortage and occasional oversupply. Political crises such as World War II curtailed supplies and contributed to the development of replacement alloys as, for example, the National Emergency (N.E.) Steels and the 200-series (Cr, Mn, Ni) austenitic stainless grades. In recent years, labor difficulties have had their effect on nickel supplies. With the exception of a modest deposit in Oregon, the U.S. has traditionally been dependent on such leading producers as Canada and New Caledonia, Australia and Russia. Future prospects for adequate supplies are bright, however, since enormous reserves have been identified around the world. Cuba also has very large nickel deposits.

## **AVAILABLE FORMS**

Nickel-bearing addition agents are grouped in two general purity ranges: Class I agents are essentially pure metallic nickel; Class II agents include the less pure metallic forms, oxide, and the ferroalloys.

The very purest nickel available is produced by a carbonyl reduction process and contains less than 1 ppm (0.0001%) cobalt. It is used in superalloys and steels for nuclear applications where cobalt content and levels of the tramp elements lead, bismuth, tin and antimony are especially important. Carbonyl nickel is sold in powder form and as pellets.

Next in order of purity is electrolytic or cathode nickel. Also a Class I addition agent, the product normally contains no less than 99.9% Ni. It is sold as sheared cathodes or electrodeposited rounds. Electrolytic nickel has adequate purity for all but the most demanding applications.

Metallic nickel addition agents produced from nickel oxide by any of several reduction processes may contain from approximately 96 to 99.9% Ni. Utility nickel, for example, contains 96% Ni, 1% Co (max.), 1% Cu (max.), bal. Fe and C. Depending on purity, these products may be used for specialty or general steelmaking purposes. Many product forms are sold: briquettes, pellets, corrugates and ingots are most common.

Nickel oxide (NiO) itself is widely used as an addition agent. Standard oxide sinter will contain about 75% Ni, with major impurities being approximately 1.0% Co, 0.75% Cu, 0.30% Fe and 0.006% S, all maxima. NiO is granular and may be sold in bulk or in a variety of drum sizes, the most common containing 22.5 kg (50 lbs.) of nickel.

Ferronickel is used for general alloy and stainless steel production. Depending on grade, it may contain from 8 to 72% Ni. Nickel-chromium is also available and is often used for stainless steel production. Both products are sold as lump, pig, ingot or shot.

The choice of nickel addition agent used depends on product quality requirements, degree of refining possible in the steelmaking practice, individual steelmakers' preference and experience, and availability. It should be noted

that during times of nickel shortage (especially if nickel-containing scrap is also scarce) even highest purity nickel addition agents have been used for routine steelmaking operations.

## **ADDITION PRACTICE**

Nickel oxide is easily reduced under normal steelmaking conditions. This has two important implications: first, that NiO addition agents can be used (over-all purity requirements permitting) and second, that nickel recoveries will be quite high. With allowances for uncertainties in analysis, recovery should be over 95 per cent.

In the electric furnace, common practice is to add nickel, ferronickel or nickel-chromium to the charge. Oxide is often used in the furnace in conjunction with reducing slags or high-silicon charge chromes. Shot and utility nickel are often used for corrective (ladle) additions.

## **ROLLING/FORGING**

Nickel has little effect on hot working characteristics when present in small amounts. At the higher concentrations found in austenitic stainless steels (see also, Chromium), increased roll pressures may be experienced and drafting may have to be reduced accordingly.

Nickel steels are susceptible to attack by sulfide atmospheres at elevated temperatures. Furnace gases containing, for example, H<sub>2</sub>S can cause the formation of nickel sulfide on grain boundaries and should be avoided. The problem, when it exists, is marked by a tendency for the steel to crack or tear during hot working. On the other hand, nickel is invariably added to steels containing copper as it effectively prevents the hot shortness resulting from internal oxidation in these materials.

Nickel-bearing austenitic stainless steels can partially transform to martensite ("deformation martensite") during cold working. While this effect contributes to the high work hardening rate and increased rolling or drawing loads in these alloys, it also helps them attain extremely high strengths in the cold worked condition.

## **HEAT TREATMENT**

Nickel is a weak hardenability agent and is rarely if ever used alone in conventional heat treatable alloy steels. However, it is often used in combination with other alloying elements such as chromium and vanadium or molybdenum to improve toughness. Nickel also does have profound effects on transformation characteristics when present in higher concentrations and these effects provide the basis for a number of interesting alloys. In any event, nickel is an austenite stabilizer, as is manganese, and it tends to expand the gamma loop in the iron-carbon phase diagram. At very high concentrations (>30% Ni), no ferrite will be present at all. At lower nickel levels, the A<sub>3</sub> temperature will be depressed and, in the presence of carbon, the A<sub>1</sub> temperature, as well. Nickel reduces the eutectoid carbon content, therefore a nickel steel will contain proportionately more pearlite in its microstructure than a nickel-free steel of the same carbon content.

**Conventional Alloy Steels.** While its effects are not strong, nickel does have some influence on heat treating transformations. It retards both the pearlite and (more so) the bainite reactions. It has no effect on tempering as such, but care must be taken when tempering nickel steels at high temperatures for extended times. Under these conditions and because of the changes in transformation temperatures noted above, it may be possible to exceed the (lowered) A<sub>c1</sub> temperature and inadvertently reaustenitize the steel. The difference between the expected and actual A<sub>c1</sub> may be as much as 45 C (80 F). By the same token, nickel steels can often make do with a lower austenitizing temperature, the beneficial effects of which are a reduced tendency for distortion and/or cracking during quenching.

**High nickel steels.** The heat treatment of high nickel alloy steels can be quite different from that of conventional steels, but while detailed heat treatment parameters are best found in standard reference texts, a few notable examples can be mentioned here.

Cryogenic steels containing up to 9% nickel are used either in the quenched and tempered or double normalized and tempered condition. In the first case, they should be water quenched from 800 C (1475 F), tempered at 565 C (1050 F) and either air or water cooled. Double normalizing is carried out at 900 C (1650 F) and 790 C (1450 F), respectively, air cooling after each step. Again, tempering is at 565 C (1050 F).

The 9% Ni-4% Co ultrahigh strength steels are hardened from 830-860 C (1525-1575 F) by water or oil quenching.

A refrigeration treatment at -87 to -60 C (-125 to -75 F) is necessary in order to transform any residual austenite - a microstructural phenomenon to which nickel steels are especially prone. Double tempering at 200-600 C (400-1100 F) and at 540-565 C (1000-1075 F), depending on strength level needed, is recommended.

Despite the fact that they are microstructurally quite sophisticated and resemble superalloys in some respects, the ultrahigh strength 18% nickel maraging steels are simple to heat treat. Austenitizing is performed at about 820 C (1500 F) and may be followed by any reasonable cooling rate. Aging for 3-6 hours at 480 C (900 F) completes the treatment. Distortion is so slight that most parts can be heat treated in the finish machined condition.

## APPLICATIONS

Nickel alloy steels may contain as little as fractions of a percent to almost 30% Ni. As might be expected, properties of these alloys range from strengths similar to plain carbon steel to some of the strongest metallic materials known.

At the low end of the nickel scale are alloy and HSLA structural products. Hot rolled steels with yield strengths of 345 MPa (50 ksi) may contain 0.50-2.00% Ni for toughness and added corrosion resistance. Age hardening plate and strip steels contain 1.3-1.5% Ni plus copper and columbium. Quenched and tempered or normalized and tempered structural steels will contain nickel up to 2.25%, as well as a variety of other constituents including chromium, molybdenum or boron.

Nickel is noted for its ability to confer high toughness, especially at low temperatures. This property has led to the development of a well-known series of cryogenic steels having important applications in the transportation and storage of liquefied gases. In general, the lower the service temperature a structural steel of this type must withstand without risk of brittle fracture, the more nickel it will contain. Thus, a low carbon 2-1/2% nickel steel can be used down to -60 C (-75 F); 3-1/2% nickel lowers the allowable temperature to -100C (-150 F) while 9% nickel steels are useable to -196 C (-320 F).

Among the AISI/SAE standard alloy steels, those containing nickel alone as the principal alloying constituent (23XX series) are no longer listed. Instead, nickel is used in combination with other alloying elements to produce steels with excellent combinations of strength and toughness in the quenched and tempered condition. Examples include 43XX, 81XX, 86XX and 94XX series, among others. Most of these contain about 0.5% Ni, although over 3% nickel is found in some grades. Nickel is used in carburizing and nitriding steels where it benefits both case and core properties.

A variation of Hadfield steel containing 0.95-1.1% C, 1% Si, 13-18% Mn and 7-11% Ni has been used where extreme toughness as well as high wear resistance is important.

The nickel in 300-series stainless steels is needed to produce the austenitic structure. As little as eight percent is sufficient, but greater concentrations may be added when fully stabilized austenite is required. Type 310 contains approximately 20% Ni, while the sulfuric acid resistant Alloy 20 contains 29% Ni, 20% Cr and lesser amounts of Mn, Si, Mo and Cu. The precipitation hardening stainless steels are essentially unbalanced austenitic grades (similar to Type 301) containing such hardeners as Cu, Mo, Ti, Al, Cb, Ta or V. Nickel is also used in martensitic stainless grades such as Types 414 and 431 where the presence of up to 2.5% Ni prevents the formation of  $\delta$  - ferrite.

The use of nickel in ultrahigh strength steels was described above for the 9% Ni - 4% Co and 18% Ni maraging alloys. It should be noted that some variants of the latter steels can be treated to yield strengths of 3450 MPa (500 ksi). Other ultrahigh strength steels such as AISI/SAE 4340, D-6a and 300M will contain lower amounts of nickel, generally not exceeding two percent.

Nickel is rarely used in tool steels as its presence promotes graphitization in these high carbon alloys (inhibits through hardening). However, some grades contain minor amounts of nickel for toughness, grain refinement and ease of heat treatment.

Mention should be made of the nickel-bearing superalloys since these account for a significant fraction of nickel used. Based on nickel, these alloys will also contain chromium for oxidation resistance plus precipitation hardeners such as aluminum and titanium. They are among the most carefully made alloys, and may be vacuum induction melted, electroslag remelted or vacuum arc remelted. Only high purity metal and ferroalloys are used as melting stock. Nickel is also used in iron- and cobalt-based superalloys and corrosion-resistant materials, and in electrical resistance alloys.

# Vanadium

Atomic number	: 23
Density, 20° C	: 6.14 g/cm <sup>3</sup>
Atomic weight	: 50.94
Melting point	: 1890° C (3434° F)
Boiling point	: 3350° C (6060° F)

## GENERAL

Vanadium is traditionally known for its ability to retard grain growth at elevated temperatures and for its beneficial affinity for carbon and nitrogen. Vanadium promotes fine grain size, increases hardenability and improves wear resistance through the precipitation of its carbides and nitrides. Use is made of these effects in a large variety of steels, including the constructional alloy grades, carburizing steels, rail steels, heat-resisting tool and die steels and the so-called super-12% stainless steels. However, by far the largest tonnage application of vanadium is as a potent microalloying strengthener in high strength low alloy (HSLA) steels. Vanadium usage continues to grow with the rapidly expanding application of HSLA steels, both as flat-rolled products and in new classes of forging and cold heading grades. Vanadium usage is growing along with the emphasis on minimill steel production and thin slab casting.

Although quite abundant in both the Earth's crust and its oil deposits, vanadium is usually found in concentrations that would be uneconomical to mine or process for vanadium content alone. Consequently, it is most often produced as a by-product of other mineral operations e.g. from iron, titanium, non-ferrous metal deposits and, increasingly, oil by-products. Because of the costly extraction techniques needed for its production, vanadium is more expensive than such alloying elements as manganese or silicon. However, it is not considered a strategically critical element since adequate supplies are available from producers throughout the world. The Republic of South Africa, the United States, Russia, Australia, China, Mexico and Venezuela hold major reserves. The vanadium supply/demand situation has occasionally been out of balance, leading to episodes of price instability. This situation is unlikely to continue as new production far exceeds expected demand for a number of years.

## AVAILABLE FORMS

The common vanadium addition agents include a 42-48% vanadium product, an 80% vanadium grade and several proprietary vanadium-carbon and vanadium-nitrogen compounds. Product is delivered in bags or cans containing 10 or 25 pounds of vanadium or in larger bulk containers. Ferrovandium products are typically sized to 2 in. x D, although several specially screened size distributions are available.

The steelmaker's choice among these forms can depend on the product mix, the equipment available, operator/metallurgist skill, and residuals, which include elements such as carbon, aluminum, silicon, chromium, manganese or nitrogen. An additive high in carbon may be unsuitable for very low carbon steels. High aluminum contents are undesirable for continuous casters (nozzles).

## ADDITION PRACTICE

The deoxidation power of vanadium is much lower than that of aluminum or silicon, and vanadium may therefore be safely used in the semi-killed steels if normal precautions are observed. (Even so, recovery of vanadium from scrap melted in an oxidizing atmosphere will only range between 10 and 20 percent.) Addition is usually made to the ladle after deoxidation is as complete as called for, and should be completed between the time the ladle is 1/4 to 3/4 full. Standard ferrovanadium addition agents have sufficient density to allow good immersion in liquid steel, and recovery will be very high using normal addition practices. Vanadium carbide/nitride agents have lower densities and must be added very early in the tap, and with adequate protection, in order to reduce oxidation losses. Best practice is to add some manganese and silicon, then the vanadium carbide/nitride, followed by the balance of additions. Recovery may be somewhat lower than that experienced with standard ferrovanadium, which should give over 85% in semi-killed grades and as much as 95% in fully killed steels, especially after vacuum degassing.

For semi-killed, low-carbon HSLA steels and SBQ forging grades, the preferred addition agent in U.S. practice is the 42-48% vanadium grade (nominally 45% V, with 1% C and up to 5% Mn, 3% Ni, and 6% Cr). Its silicon content is designed to protect the vanadium; this has obvious advantages in high strength hot-rolled grades, which usually

contain less than about 0.15% V. There is no concern over residual phosphorous, sulfur and silicon from the ferroalloy addition since the addition's residuals are too low to present problems in microalloyed steels. The product can be added during primary melting, during secondary refining or in ladle stations. Other vanadium-nitrogen and vanadium-carbide addition agents have proven to be beneficial in steels that take advantage of vanadium carbonitride strengthening. Such products are best added as trim additions to the ladle, but they obviously must be used with care in steels with low or restricted carbon and nitrogen levels. And the nitrogen content inherent in EAF steels is plentiful to naturally combine with any vanadium addition agent.

The densities of low-carbon 80% V ferrovandium as well as 42-48% Ferovan® will range between 6.4 and 6.5 g/cm<sup>3</sup> at steelmaking temperatures (the density of liquid steel is generally taken as 7.15 g/cm<sup>3</sup>). Therefore, lumps of these addition agents will float with over 90% of their surface immersed in the bath. This reduces oxidation losses and leads to more rapid dissolution. Recoveries will be at least 85% in semi-killed grades and as high as 95% in fully killed steels, especially when vacuum degassed. The densities of vanadium carbide/nitride agents are lower, about 4.0 g/cm<sup>3</sup>. These products also typically have very high melting ranges. Although the carbide/nitride products are quite soluble in liquid steel, their densities and melting range factors indicate that greater care may be required in their use in order to maintain economical and consistent recoveries. Additions should be made early in the tap, for example, with adequate protection against oxidation.

Vanadium is occasionally added directly to the EAF just before tap. In such cases, double slag practice must be followed, rabbling the vanadium through the slag if necessary. Additions can be in the form of carbide/nitride or tech oxide under suitably reducing conditions. Final chemistry adjustments are always made in the ladle. Adequate superheat must be considered if major vanadium additions are made in the ladle, because vanadium addition agents are endothermic. A 0.10% (2 lb./ton, 1 kg/ton) addition of 80% ferrovandium will chill the bath about 2 °F (1.2 °C) at 2902 °F (1600 °C). The same quantity of 43% Ferovan( will chill the heat about 1.2 °F (0.6 °C), while 84% V, 13% C vanadium carbide will cause a chill of about 5.6 °F (3.2 °C). See Table 2 for more chill factor information.

## ROLLING/FORGING

Vanadium is one of the well-known microalloying elements, which also include titanium, columbium, zirconium and boron. These elements are characterized by their disproportionately strong effect on the structure and properties of steel when present in minute quantities, generally well less than 0.15%. The microalloying elements produce their effects, increasing strength and improving toughness, primarily through a combination of grain refinement and precipitation strengthening, both of which depend on the formation of carbide and nitride (or carbonitride) particles. By forming very fine precipitates during hot rolling, the microalloying elements retard the recovery and recrystallization of austenite. Depending on composition, this phenomenon continues (and can be exploited) during cooling on the run-out table and in the coil. The combined rolling/cooling effects have become known as controlled thermomechanical processing, and are widely used in the production of HSLA steels. The effectiveness of the various microalloying elements is governed by the solubilities of their carbides or nitrides and the way these solubilities change over the relevant temperature range. Effects of microalloying elements on transformation temperature are seen in the microstructure (generally with regard to pearlite content and bainite morphology), dislocation density and to some extent, grain size, as well.

Vanadium (i.e. as a carbide, nitride or carbonitride) is the most soluble of the microalloying elements, therefore its effects on austenite recrystallization are weak at high and intermediate rolling temperatures, where the carbonitrides revert to solid solution, but are more pronounced at lower temperatures, where the carbonitrides precipitate. For example, at typical vanadium (<0.10% v) and nitrogen (<0.02% n) contents in low-carbon steels, vanadium carbonitride is completely dissolved above about 1040 c (1900 f) and soaking at higher temperatures produces no added benefit with respect to subsequent vanadium precipitation behavior. also, because of its high solubility, vanadium does not contribute to "controlled rolling" (taking large reductions at low finishing temperatures) in the same sense as columbium or titanium. on the other hand, because vanadium does not lead to the formation of highly dislocated austenite it also does not produce the high rolling forces characteristic of columbium and titanium microalloyed steels. vanadium's strengthening effects become pronounced toward the end of and after hot rolling, at temperatures approaching 700 c (1300 f), when precipitation of vanadium carbonitride begins, continuing well into the ferrite region in low-carbon steels. precipitation strengthening has a harmful effect on toughness but this can be overcome at least in part through grain refinement achieved by accelerated cooling after finishing (depressing the ar3 refines transformation products) followed by coiling at a temperature high enough to optimize (V,C,N) precipitation.

Vanadium presents no special problems in the forging of low or medium alloy steels. Vanadium-rich steels, when low in carbon, will contain appreciable amounts of pearlite and will forge very much like ferritic steels. High alloy

grades, such as the high-speed tool steels, require over 90% hot deformation to break up as-cast segregation. Final forging should be performed at about 1180 C (2150 F).

Development of a new class of medium-carbon microalloyed forging steels began in the early 1970s. These steels have become widely accepted for automotive components in Europe, Japan and South America and are finding markets in North America as research to improve their impact properties progresses. Advantages of the steels, most of which contain vanadium, include a very low (micro-) alloy content compared with conventional constructional alloy grades and the ability to achieve, in the as-forged condition, mechanical properties comparable with quenched and tempered steels. Typical properties include yield strengths ranging from about 620 to 690 MPa (90 to 100 ksi) and ultimate strengths between 1000 and 1200 MPa (145 and 175 ksi). The steels' fine ferrite-pearlite or, in some compositions, bainitic microstructures are developed either by air-cooling or direct quenching from the forging operation. Low-temperature aging may be used to give additional strength. Vanadium plays a key role in these steels, providing the carbonitrides responsible for fine grain size and precipitation hardening. The kinetics of vanadium carbonitride formation are particularly favorable to forge shop practices.

## HEAT TREATMENT

Vanadium, due to its strong affinity for carbon, is very important in heat treatable (quenched and tempered) steels because of its ability to retard grain growth during austenitizing, an effect brought about by the presence of vanadium carbonitride precipitate particles. The action of vanadium is actually somewhat complex in these steels, since fine grain size detracts from hardenability. However, that vanadium which remains in solution acts as a very potent hardenability agent. Therefore, the heat treatment of vanadium steels always involves a balance between keeping enough carbides precipitated to prevent grain growth and driving enough into solution to promote hardenability. In general, vanadium steels require somewhat higher austenitizing temperatures than non-vanadium steels. The extremely hard (2400 Knoop) vanadium carbide can also precipitate during tempering generating a secondary hardening peak that retards softening at elevated temperatures.

Quenching low-carbon vanadium-nitrogen steels from the intercritical region produces the so-called "dual phase" structure, consisting of martensite islands in a ferrite matrix. Flat-rolled vanadium dual-phase steels have excellent formability yet, because they also have a very high work hardening index, they are capable of developing considerable strength during cold forming.

## APPLICATIONS

Vanadium-containing normalized steels have found wide acceptance in offshore- and pressure vessel construction and, along with quenched and tempered plate steels, are extensively utilized in heavy industrial equipment, architecture and off-highway vehicles. Weldable microalloyed strip and plate steels containing vanadium alone, but more often in combination with, columbium, titanium, aluminum and molybdenum, found their first important commercial applications as high-strength linepipe materials, many thousands of miles of which are now in service. Vanadium dual-phase steels have established their weight-saving advantages in automotive and truck applications primarily for heavy stampings such as bumpers and frame members. Vanadium-microalloyed forging steels, which need no heat treatment, are now commonplace in Europe, Japan and South America, and are used for such traditionally quenched and tempered products as connecting rods, axles, and steering- and suspension system components. Microalloying principles, i.e., eliminating heat treatment and reducing alloy content, are also being applied in a growing series of steels for high-strength fasteners and cold headed products.

Normalized and controlled cooled HSLA grades will contain about 0.05 to 0.15% V and up to about 0.02% N, and yield strengths of 550 MPa (80 ksi) are typical for this class of materials. Quenched and tempered high strength plate may also contain up to 0.15% V in combination with many other alloying agents, including boron. Strength and toughness are very high. Controlled rolled plate steels contain vanadium in concentrations around 0.10%, usually in combination with columbium. Thicker plates, in which controlled rolling is less effective or impractical because of rolling mill limitations, benefit from the additional precipitation strengthening V(C, N) provides.

The tool and die steels are second only to the HSLA grades in terms of vanadium consumption, and the amount of vanadium they contain typically depends on the intended service conditions: the more severe the service, the more vanadium. Tool and die steels may contain as little as 0.30% (principally for grain size control during austenitizing) or more than 4% vanadium (for wear resistance through vanadium carbide formation). Respective examples include the common hot work die steel H11 (0.4% V) and the high-duty grade, H13 (1% V). Similarly, the widely used air-hardening grade D2 contains 1% vanadium but more abrasive conditions call for D7, in which the vanadium content is raised to 4%. All high-speed steels, including both the M (molybdenum) and T (tungsten)

types, contain vanadium in concentrations ranging between 1 and 5% for grain size control and added wear resistance at high service temperatures. Grain size control is especially important in these steels, where austenitizing temperatures exceed 1200 C - 1300 C (2200 F to 2375 F). Vanadium also contributes to the "red hardness" the high speed steels are known for.

The quenched and tempered AISI/SAE steels also contain vanadium for grain size control during heat treatment. This is particularly important in carburizing grades. The wear resistance of rail steels is improved considerably by the addition of 0.08-0.12% vanadium. Wear resistant rails of this type are used in curves, switches and other points known to experience severe service. Vanadium also finds use in a wide variety of structural, heat treatable and special quality steels. The AISI/SAE 6100 series, for example, contain a minimum of 0.15% V for grain size control, especially during carburizing. Among the ASTM pressure vessel steels are the Mn-V grades containing up to 0.20% V under ASTM A225, several quenched and tempered grades under ASTM A517 (V=0.03-0.08%) and the HSLA pressure vessel grades designated under ASTM A737 and A634. Likewise, vanadium is a common constituent of many aircraft, military and specialty steels covered by AMS specifications. Concentrations range from 0.07% in 330M (AMS 6419) to the levels found in tool steels. Ordnance steels contain up to 0.20% V, while lesser amounts are found in the ultrahigh strength (1900 MPa, 280 ksi) bainitic 9% Ni-4% Co, and martensitic D6 alloys. Bolts, shafts and non-pressure retaining components for high temperature service are made from steels containing vanadium in addition to chromium and molybdenum. Generally, the higher the vanadium contents of these AISI 600-Series steels, the better their elevated temperature properties. Vanadium contents range from 0.25 to 0.80%.

Vanadium is also used for grain size control and improved high temperature properties in AISI Type 422 and Type 440C stainless steels-both martensitic types. Type 422 is one of the so-called "Super 12% Cr" steels, which attain strengths up to 1400 MPa (200 ksi), have useable hot strengths up to 650 C (1200 F), and are widely used in steam turbines. When produced under AMS 5655A (ASTM A565 Grade 616) or SAE J467, Type 422 contains up to 0.30% vanadium. Up to 0.5% vanadium is called for in MIL-S-861A (SHIPS), Class 422. Type 440C and its modifications contain 0.15% V. Both steels rely on vanadium for increased hot hardness and wear resistance, as do the special stainless alloys Lescalloy BG 42 (1.20% V) and 15Cr-4Mo-Co, containing 2.5-3.0% V.

# Titanium

Atomic number	: 22
Density, 20° C	: 4.54 g/cm <sup>3</sup>
Atomic weight	: 47.90
Melting point	: 1660° C (3020° F)
Boiling point	: 3287° C (5949° F)

## GENERAL

Titanium is a highly active element, which at room temperature normally forms a stable oxide coating on its surface, which limits further oxidation. At steelmaking temperatures, it forms stable compounds with oxygen, carbon, nitrogen and sulfur. Because of this property, it is often used in steelmaking to fix these elements, so lessening their harmful effects. Titanium also acts as a grain refiner in many steels, and in many respects it has a similar function to the addition of both aluminum and columbium (niobium). Titanium is more expensive than aluminum, so its use as a deoxidizer has diminished considerably.

The reactivity of titanium is such that, like magnesium, thin ribbons such as machine turnings, or powder, can quite easily be set on fire, e.g. by welding sparks or by addition to the surface of a steel melt without plunging. Titanium burns with a very bright white flame, which can be harmful to look at. A titanium powder fire is doubly dangerous, because the convective current caused by the fire can cause the unburned powder to become airborne, with the risk of explosion. Ferrotitanium powder is also flammable, with the finest sizes and highest Ti content being the most hazardous.

As the ninth most abundant element in the earth's crust (0.6%), titanium does not suffer from the availability problems which affect some other alloying constituents. However, the variable demands for titanium alloys from the aerospace industry makes the price of scrap fluctuate widely. Large quantities of titanium ores, principally ilmenite (FeO•TiO<sub>2</sub>) and rutile (TiO<sub>2</sub>) are mined throughout the world. About 95% of titania feedstocks are used to make titania pigments; the more pure, and relatively scarcer rutile is preferred for metal production. The conversion of rutile into titanium is generally by the Kroll process. Chlorine gas is passed over a mixture of rutile and coke at 800 C (1472 F) to produce chloride:



The TiCl<sub>4</sub> is then passed over molten magnesium, forming magnesium chloride and titanium sponge, which is then compressed and remelted into ingots under vacuum.

## AVAILABLE FORMS

Titanium addition agents generally fall into three general categories: metal scrap, ferroalloys and master alloys. These are considered separately below:

Titanium scrap may be of commercial purity (CP) titanium, or one of the many titanium-rich alloys. The most common of these is 6%Al-4%V (6-4), followed by 6%Al-2%Sn-4%Zr-2%Mo. Scrap is generally available in the form of solid scrap, turnings or sponge. Solid scrap is generally clean, but turnings must be degreased before use. Sponge is often from the Kroll process (above), and may occasionally be contaminated with MgCl<sub>2</sub>, which reacts with water vapor, making some sponge potentially dangerous to melt. Titanium turnings may be contaminated with lead or bismuth, which are in the brazing alloy that is often used to fix a boss onto a piece of titanium prior to machining it.

It should be noted that the melting point of titanium is higher than that of the bath to which it is generally being added. This means that titanium added as metal generally enters the steel by dissolution, rather than melting. The low density of titanium means that it has to be plunged into the melt; otherwise, oxidation can cause very low recovery into the melt.

Ferrotitanium is available in many grades, but by far the most common contains approximately 70% Ti. The use of 90-6-4 scrap makes a ferroalloy with approximately 4.5% Al and 3% V, which is the basis of many specifications. CP grades of scrap can be used to make alloys with <1% Al, but generally at a significant price premium. Tin is generally unwanted in most steels, so the tin bearing grades of scrap are used in the lower grades of ferrotitanium.

Ferrotitanium is now almost invariably made in an electric induction furnace by melting scrap titanium with iron units. Previously, the alloy was produced by aluminothermic reduction of ilmenite, using a variation of the Thermite process. This produced an alloy with about 40% Ti and 8% Al, balance Fe. This was used in the formulation of many welding rods, and such an alloy remains available today, although it is mostly used for welding and similar operations.

Since the main use of titanium is as a scavenger for carbon, nitrogen and oxygen, the steelmaker naturally prefers to buy ferrotitanium that has the lowest possible content of these elements. This is especially true as the alloy is generally priced on the titanium content, and 1% N can combine with over 3.4% Ti. To minimize the content of carbon, oxygen and nitrogen, the titanium scrap must be carefully selected, and extra measures are taken during the ferrotitanium production process, causing a slight increase in its price.

Other impurity elements in ferrotitanium may be picked up from the titanium scrap that is used in its manufacture. These can include Cr, Ni (from stainless steel which may get mixed into the titanium scrap before it reaches the ferroalloy manufacturer), Zr and Cu.

Proprietary alloys will contain titanium plus additional elements such as aluminum, zirconium, silicon or chromium. They are not commonly used as titanium additions per se, but rather for a combination effect, such as sulfide shape control or increased yield strength. In some cases, they are added simply as a protection mechanism for boron, which would otherwise be lost from the steel melt by its reaction with nitrogen or oxygen (see Boron).

Ferrosilicon-titanium alloys permit the simultaneous addition of silicon and titanium. They usually contain roughly equal amounts of silicon and titanium; 20%-20%, 30%-30% and 45%-45% being the most common grades.

Ferrotitanium alloys are normally supplied in crushed and sieved form, often as 50 mm x down (2 in. by down). Many customers apply a minimum size limit, such as 5 mm (1/4 in.), in order to minimize the amount of fine material, which can give poor recoveries in less well-controlled melting practices. Packing is normally loose in 250 kg or 500 lb. drums, alternatively pre-packed in plastic or paper sacks of up to 20 kg or 50 lb. each. Ferrotitanium is also supplied in supersacks.

There has been a trend towards the use of cored wire for the addition of ferrotitanium at the steelworks. Ferrotitanium (70% Ti) of size 2 mm (0.08 in.) or finer is encapsulated inside a sheath of mild steel, wound onto a coil. By this technique, the ferrotitanium can be added continuously to a bath, launder or tundish of steel. The steel sheath protects the ferroalloy from oxidation. The fine size of the ferroalloy ensures quick and high recovery of titanium into the melt.

An alloy of 70% titanium 30% iron falls at the eutectic point of the system, with a melting point of 1085 C (1985 F), and so is known as eutectic ferrotitanium. As this is well below steelmaking temperatures, the ferroalloy melts, which is far quicker than the dissolution required for metallic titanium to enter the steel. It is for this reason that eutectic ferrotitanium is the preferred analysis for use in steelmaking.

## **ADDITION PRACTICE**

Because titanium is so easily oxidizable, great care must be taken when adding either the metal or its ferroalloys to steel. Failure to do so will drastically reduce alloy recoveries. All efforts should therefore be made to avoid contact between the titanium addition and air or oxidizing slags.

Titanium additions are typically made in the ladle as scrap or lump during tapping, as cored wire into the ladle, or as lump in ladle degassers or CAS-OB processes. The steel should be thoroughly deoxidized first, usually with a prior addition of aluminum. Most steelmakers prefer to add the titanium late in the tap, when the ladle is 1/2 to 3/4 full, and after all other additions, except boron. The object is to leave as little time as possible for reoxidation of the steel to occur, since the titanium will take up any available oxygen, thereby reducing its effectiveness. Contact with oxidizing slags should likewise be avoided, since (a) slag/metal reactions will be detrimental to recovery and (b) the coating action of the slag will impede the otherwise rapid melting and dispersion of the ferroalloy in the melt.

When furnace additions are necessary, titanium should be added only after thorough deoxidation and just before the tap. A thin layer of reducing slag will help prevent reoxidation and will act as a nitrogen barrier as well.

Titanium recoveries are invariably lower than those for most other additives. Recovery can vary between about 50% and 90% depending on the level of care taken by the steelmaker, the steelmaking practice and the type of additive used. Because of their higher density (less likely to float on the melt surface and oxidize) and their lower melting temperature, ferrotitanium alloys generally give higher recoveries than scrap. They are therefore the preferred addition agents for most products.

## ROLLING/FORGING

The processing of titanium-bearing steels on the hot strip mill is fairly straightforward and follows, in general, the pattern established for other controlled rolled products (cf., for example, Columbium). Titanium nitride, formed while the steel is still liquid, will be carried over into the slab: thus, changes in soaking temperature will have little effect unless columbium is present as well. Most of the strengthening imparted by titanium derives from the precipitation of titanium carbonitrides; a lesser amount comes from grain refinement. Thus, titanium steels will have poorer impact resistance than other microalloyed grades unless extra precautions are taken to insure the finest possible grain size in the finished product. Lowering the finishing temperature to about 840 C (1550 F) has a beneficial effect on impact transition temperature. For higher strength products (Y.S. above 550 MPa, 80 ksi), coiling temperatures should be kept below 650 C (1200 F).

One of the more important uses for titanium in steel is the control of sulfide morphology. Without titanium (or zirconium or the rare earths), sulfides tend to become elongated during hot rolling. This leads to poor impact properties and reduced ductility in the through thickness dimension, and can be particularly harmful in welded structures. Titanium hardens the sulfides and allows them to retain a less harmful globular shape throughout the hot rolling process (see Cerium & Rare Earths).

## HEAT TREATMENT

The effects of titanium on heat treatment and microstructure are directly related to the element's reactivity, particularly that with carbon. Thus, pearlitic titanium-bearing steels will contain less cementite (less pearlite) since any titanium not already combined with carbon or nitrogen will form the highly stable carbide, TiC. Carbon scavenged in this manner will be about one quarter the weight percent of the available titanium. Said another way, pearlite will be completely absent in steels containing titanium equal to more than four times the carbon content. There are no double carbides of iron and titanium. Titanium raises the grain coarsening temperature. It is much more effective than aluminum when concentrations of either element exceed 0.035%. However, a steel containing 0.03% Al and 0.005% Ti will have a grain coarsening temperature elevated by about 30 C (50 F).

The effect of titanium on hardenability is complex. As titanium concentration increases, hardenability generally decreases unless austenitizing temperatures are raised. Reason: the formation of TiC (see above) lowers the carbon concentration in austenite. Further, titanium refines the grain size, and this decreases hardenability all the more. If only acid soluble (uncombined) titanium is considered, its hardenability factor is about the same as that for molybdenum.

Titanium steels do exhibit secondary hardening upon tempering due to the precipitation of TiC. The effect is increased when austenitizing temperatures are above 980 C (1800 F).

## APPLICATIONS

Titanium is valuable as a carbide stabilizer in stainless steels. Type 321, an austenitic grade, contains titanium equal to at least five times the carbon content in order to prevent the precipitation of chromium carbides on grain boundaries during extended holding at elevated temperatures. Without the presence of Ti, the chromium would be depleted at grain boundaries, leading to intergranular corrosion (see Chromium).

The carbide fixing properties of titanium are also valuable in Type 409 stainless steel, a ferritic grade widely used in the manufacture of automotive catalytic converters and other exhaust components. Low strength, highly formable steels are required for auto body pressings of complex geometry, and for tinplate beverage cans. Vacuum degassed, interstitial free steels are used here. Ti is added at typically ten times the (low) carbon content of the steel, to form TiC and TiN, so freeing the steel of dissolved carbon and nitrogen. The resulting steel can have carbon levels <30 ppm and nitrogen <40 ppm, giving a low yield strength and good formability.

High strength low alloy (HSLA) steels rely on a combination of precipitation of carbides and nitrides, and grain refining for their strengthening mechanism. Columbium (niobium) and vanadium are the principal elements for this, but titanium is also used, especially for the precipitation of TiCN, following controlled rolling and rapid

cooling. TiCN is the only micro-alloy carbo-nitride that is stable at the high temperatures attained in the HAZ during welding, where it reduces grain growth and increases toughness. Ti also forms its nitride at very high temperatures and is therefore used to reduce grain growth of austenite during hot rolling of plates.

Titanium is used to protect boron in hardenability steels. The titanium is added before the boron, to tie up any oxygen and nitrogen, so improving the effectiveness of the boron addition (see Boron).

In low alloy steels that have been grain refined with aluminum, AlN can cause intergranular fracture, known as "panel cracking". An addition of Ti causes TiN to be precipitated uniformly in the matrix and increases ductility. A Ti content of 0.05% would be typical for this application.

The precipitation of titanium intermetallic compounds is one of the principal strengthening mechanisms in maraging steels, which may attain yield strengths in excess of 3450 MPa (500 ksi).

Enameling steels require an addition of typically 0.15% Ti to control the surface roughness, to allow a good, even coating with the enamel.

Titanium is occasionally used in tool steels, which it can make less susceptible to quench cracking. Because of their reduced air-hardening tendencies, such steels will develop tougher core structures.

# **Boron**

Atomic number : 5  
Density, 20° C : 2.34 g/cm<sup>3</sup>  
Atomic weight : 10.81  
Melting point : 2079° C (3774° F)  
Boiling point (sublimes) 2550° C (4620° F)

## **GENERAL**

Boron is added to steels for its unique ability to increase hardenability when present in concentrations of around 0.0015% to 0.0030%. It has long been used as a replacement for other alloying elements in heat treatable steels, especially when these constituents were in short supply. Boron is also used in austenitic stainless steels to control hot shortness, or to improve their creep properties. Boron is added to some steels for the nuclear industry, where neutron absorption is required. It is also used in deep drawing steels, where it removes interstitial nitrogen and allows lower hot rolling temperatures.

Boron is also a key component in FeNdB magnets, which are among the most powerful permanent magnets known.

Boron reacts readily with oxygen and nitrogen and is, unfortunately, completely useless in steel when in combined forms. Great care must therefore be taken during steelmaking to ensure that boron is adequately protected. Failure to recognize this requirement can lead to erratic heat treatment response.

## **AVAILABLE FORMS**

Boron is supplied to steelmakers as ferroboron or as one of several proprietary alloys. Choice of addition depends, as always, on steelmaking practice, product mix and volume, individual operators' experience and preference, and price. A steelmaker should choose that addition agent giving the highest and most reliable recovery consistent with his overall melt shop economics.

Ferroboron is the lowest cost addition agent. Boron content is relatively high: standard grades are sold with incremental boron levels between 12 and 24% B. Major impurities are carbon (0.10-1.5%), silicon (0.30-4.0%) and aluminum (0.5-8.0%). A typical analysis will include 18.0% B, 0.50% C, 0.50% Si, 0.2% Al, 0.03% P, 0.01% S. All except boron are maximum values. Product is supplied in lump form, 2 in. or 1 in. x down, packaged in 250 kg or 500 lb steel drums, or supersacks (bulk bags) of up to 3000 lb (1360 kg) capacity. Many customers apply a minimum size limit, such as 5mm (0.2 in.), in order to minimize the amount of fine material, which can give poor recoveries in less well-controlled melting practices. Ferroboron is also available as cored wire.

Because ferroboron does not contain appreciable concentrations of protective elements, it requires greater care than the proprietary alloys in order to give adequate and consistent results. It is normally added after other oxygen/nitrogen scavengers, such as ferrotitanium.

The proprietary boron addition agents are more expensive than ferroboron on an initial cost basis but are often preferred for their greater efficiency, ease of application and more consistent results. All will contain varying proportions of oxygen and/or nitrogen scavengers such as titanium, aluminum, silicon and zirconium. These elements generally have an even greater affinity for oxygen and nitrogen than does boron.

The most common proprietary addition agent typically contains 2.0% B, 15% Al, 30% Ti, 10% Si, bal. Fe. This product's high scavenger/boron ratio ensures its effectiveness for all boron steels, provided they have been adequately deoxidized first.

A variety of other composition proprietary boron addition alloys are available, with boron contents varying between 0.5% and 4%. Generally, the higher the ratio of boron to scavenger elements, the greater the care required to ensure adequate recovery of the boron in the steel.

Proprietary boron addition agents are sold in lump form 1-1/4 in. and 2 in. x down, packaged in bags, cans or large drums.

## **ADDITION PRACTICE**

Boron combines aggressively with oxygen and nitrogen dissolved in steel; great care must be taken in steelmaking and addition practices, to prevent these reactions from occurring or the boron's effectiveness will be irretrievably lost. Steels should be fully killed before boron is added: aluminum killing provides additional protection against nitrogen but steelmakers with continuous casters prefer to keep aluminum levels as low as possible to forestall nozzle blockage problems. Vacuum carbon deoxidation or AOD processing, where possible, reduce oxygen levels without the need for large scavenger additions.

Standard practice is to add boron to the ladle after all other alloying additions have been made and between the time the ladle is 1/4 to 3/4 full. Precautions against reoxidation of the heat through the use of inert gas shrouded nozzles, synthetic slags, etc., are highly recommended. Boron 'fade' (loss of effectiveness in the last alloy cast) can be prevented by using slightly higher aluminum and/or titanium contents.

Mold additions of boron were made successfully for many years, but general experience has been that these give less uniform results than carefully controlled ladle additions.

Cored wire additions can be made at the ladle furnace, ladle stir station or degasser.

## ROLLING/FORGING

In their zeal to make sure enough boron went into solution, steelmakers used to add much more than the minute amounts required. The result was a hot-short steel that would break up in the roughing stands or during hot forging. Even if successfully hot worked, such steel often had poor room temperature impact properties.

It is now recognized that these problems stem from the formation of a low melting point B-C-Fe eutectic (Fe<sub>2</sub>B/Fe<sub>3</sub>C/Fe), which forms when the boron content exceeds about 0.007%. Only soluble boron is effective for hardenability, so the normal aim composition is 0.0015% to 0.0030% B. Boron does segregate, and dangerously high concentrations can form even when average boron contents are within specification.

Other than that, boron steels will roll and forge just about the same as their plain carbon or alloy counterparts. There is a slightly greater danger of overheating, though. Boron's diffusivity in steel is about the same as carbon's, and it is possible to deboronize steels in high temperature oxidizing atmospheres. Likewise, furnace atmospheres should be kept low in nitrogen to prevent the formation of boron nitrides.

The scale formed on boron steels is not so tightly adhering as that on other alloy steels; this property is claimed to improve die life.

## HEAT TREATMENT

Boron suppresses the nucleation (but not growth) of proeutectoid ferrite on austenitic grain boundaries. Various theories have been advanced to explain this: most propose that the presence of boron on or near these boundaries reduces strain- or interfacial energies, so lowering the driving force for ferrite nucleation. The result, however, is that the TTT curve for a steel containing as little as 0.0005% B will be markedly shifted to the right compared to a similar, but boron-free, carbon or alloy steel.

Boron's effectiveness increases linearly up to about 0.002% B, then levels off. Upper limits are set by the hot working and embrittlement considerations described above. Most specifications for boron steels now define the allowable limits as 0.0005-0.007%.

Carbon content has a strong effect on boron's hardenability factor, FB where

$$FB = \frac{\text{hardenability of (base steel + boron)}}{\text{hardenability of base steel}}$$

The empirical formula given is  $FB = 1 \pm 1.5(0.9 - \%C)$ . Thus, boron will be much more effective at low carbon levels, its contribution falling to zero as the eutectoid carbon content is approached. An interesting sidelight on this phenomenon is that carburized boron steels are marked by a high core hardenability but a low case hardenability.

Boron is unique among alloying elements in that its hardenability factor increases with the amount of martensite

chosen as the standard. Boron will have a relatively greater effect on a section that can be fully hardened than on one which quenches only to, say, 50% martensite. As a practical matter, the effect of boron on hardenability is often denoted by the 'Boron Factor', the ratio of the ideal diameters of a boron steel to the same steel with no boron. Medium carbon steels should have boron factors in the range 2.0-2.5. Lower values indicate a loss of boron effectiveness through poor steelmaking practice or improper heat treatment.

Boron has no significant effect on either the  $A_e$ , or  $A_{e3}$  temperatures. The  $A_{r1}$  is similarly unaffected although the  $A_{r3}$  is lowered somewhat. Thus, boron steels should be heat treated the same as comparable boron-free steels. Overheating should be avoided. Boron is a grain coarsener and hardenability will not improve with increasing grain size; exactly the opposite is true here. However, hardenability lost through overheating can be regained by slow cooling and reheating to the proper quench temperature. Oxidizing and nitriding atmospheres should be avoided; boron steels should not be carbonitrided.

Boron neither raises nor lowers the  $M_S$  temperature and has no effect on retained austenite. It will not change the fineness of pearlite, nor will it produce any solid solution strengthening in ferrite. It shows no effect on tempering response except a slight but tolerable increase in susceptibility to temper embrittlement. The magnitude of this susceptibility is such that, if a boron steel is used to replace a molybdenum grade, the danger of embrittlement will be greater; if a Cr-Mn steel is replaced, it will be reduced.

## APPLICATIONS

Carbon-manganese-boron steels are generally specified as replacements for alloy steels for reasons of cost: C-Mn-B steels are far less expensive than alloy steels of equivalent hardenability. Applications for these steels include earth scraper segments, track links, rollers, drive sprockets, axle components and crankshafts.

Boron alloy steels are specified when the base composition meets mechanical property requirements (toughness, wear resistance, etc.), but hardenability is insufficient for the intended section size. Rather than call for a more highly alloyed (therefore more expensive) steel, a user may simply specify the corresponding boron grade, thereby ensuring suitable hardenability.

An expanding area of boron usage is the field of high strength low alloy and other structural steels. These may be supplied as hot rolled or as quenched and tempered (for boron grades, the latter are more common). Boron assures adequate hardenability in heavier plate sections.

Boron is sometimes used in non-heat treated steels. Ferroboration may be added as an intentional nitrogen scavenger in carbon steels for automotive strip stock. By avoiding interstitial nitrogen, boron makes the steel more formable. Aluminum is sometimes used for a similar duty, but AlN is slower to precipitate, so requiring higher annealing temperatures. Boron addition makes the steel more formable and eliminates the need for strain age suppressing anneals.

Boron has a high neutron absorption capability. For this reason, it is added to certain types of stainless steel for use in the nuclear industry. Levels of 4% boron or more have been used, but the lack of hot ductility and weldability mean that boron contents of 0.5 to 1.0% are more common for neutron absorption application. Nonetheless, even at these boron contents, the ferroboration has to be of the highest purity.

# **Sulfur**

Atomic number	: 16
Density, 20° C	: 2.05 g/cm <sup>3</sup>
Atomic weight	: 32.066
Melting point	: 119° C (300° F)
Boiling point	: 444.6° C (832.3° F)

## **GENERAL**

Sulfur is often regarded as an impurity in steel, to be reduced to the limits of practicality. Nonetheless, steels that are to be machined require a certain minimum sulfur content for proper chip formation. Where machining constitutes a major fraction of the end products cost, many types of steel (carbon, alloy, and less often stainless) are intentionally resulfurized for just this reason.

## **DESULFURIZATION**

Except in those cases where it is added for machinability, or where residual sulfur contents of approximately 0.040% max. are tolerable, the usual aim of iron- and steelmaking is to reduce sulfur to low levels, consistent with mechanical property requirements. For high strength plate and extra quality bar products, this may mean removing sulfur to less than 0.005%. There are several commercial means now available and widely used to achieve this degree of cleanliness, as will be discussed. First, it should be noted that the efficient removal of sulfur from liquid steel or iron depends on specific metallurgical, i.e., thermodynamic, conditions. Although conditions vary with the type of sulfur removal system, most require that reducing conditions (low FeO presence) be maintained. Also, it is important that slag, and therefore refractory, conditions be basic (high V or V<sup>A</sup>I ratio) and that the temperature preferably be high; the latter due to the fact that sulfur removal is usually endothermic. While sulfur can be removed anywhere between the blast furnace and the ladle, it is now generally accepted that greatest cost benefits are obtained when desulfurization is performed early, at the hot metal stage.

The insatiable need of the BOF or Q-BOP for hot metal encouraged the use of less stone in the BF, thereby increasing capacity, but also raising hot metal sulfur contents accordingly. Removal of this excess sulfur in the BOF/Q-BOP was time-consuming, often requiring an afterblow that was not very reliable. Of course, the EF can easily remove sulfur by trapping it in a removable slag, but few EFs take hot metal in the charge. LMFs have helped solve that problem. At any rate, thermodynamic and economic conditions together gave the go-ahead to the development (actually redevelopment, since the principles and some practices were well known as early as the 1950s) of the hot metal desulfurization techniques now employed at all major steelworks.

All of these processes rely on contact between sulfur in the iron and a desulfurizing agent able to form a nonsoluble sulfide, which could rise to the slag. Of all desulfurizing agents in use, most contain one or more of the alkali metals, usually calcium or magnesium. They are relatively cheap, widely available, and highly reactive. Actually, they are often too reactive and must be diluted or dispersed in order to prevent violent boiling in the vessel. In all cases, it is important that the desulfurizer remain in intimate contact with the hot metal for as long as possible, and that all the metal be contacted during the process. To accomplish this, pneumatic injection is employed.

Calcium carbide and some form of magnesium are frequently injected. It is important that the carbide be finely divided since it is not volatile and reaction with sulfur occurs only at the particles' surfaces. Thus, fine sizes maximize the reaction area. Magnesium, on the other hand, does volatilize quite violently, so much so that it can lead to spillage and safety hazards. It is therefore diluted with either lime, dolomite, or alloyed with aluminum. Typical mixtures, for various processes, run 10 to 20% magnesium powder, the balance lime. These mixtures are injected into the vessel (hot metal transfer ladle, mixer, submarine ladle, etc.) by means of a refractory lance, using argon or nitrogen as a carrier gas. The gas, in addition to acting as a propellant, gives additional stirring action to disperse the reactant. There is little nitrogen pickup, even when pure N<sub>2</sub> is used as a carrier. The choice of using magnesium or calcium carbide usually rests on which is cheaper or more available at the time, although magnesium is thermodynamically the more active agent. Many processes are so designed that they can take either or both reactants.

It should be noted that desulfurizers also lend themselves to injection in pneumatic steelmaking processes, the BOF and Q-BOP. Lime or burned dolomite is used in this fashion. The latter has the added advantage of protecting the (normally 100%) magnesia linings of the Q-BOP vessel.

Treated hot metal will contain less than - sometimes very much less than - 0.010% S after desulfurization. With injection of lime or burned dolomite in the basic oxygen steelmaking furnaces, this can be reduced still further. In the electric furnace, sulfur can enter through the scrap (which should be carefully segregated if a low sulfur heat is to be made). Ladle desulfurization, more properly sulfur control, is another process that has come into widespread use. Again, it may take the form of simple addition of bagged material to the ladle or pneumatic injection. Calcium compounds, normally either  $\text{CaC}_2$  or calcium-silicon alloys are injected using argon as a carrier gas. Nitrogen can also be used, but only if the residual amounts remaining can be tolerated in the final product, or if nitrogen-fixing elements such as aluminum or titanium are present in sufficient quantity. For a discussion of ladle injection, see Calcium. Synthetic slag practices, including additions of relatively high alumina slag from ferrovanadium producers, for example, help also as modern ladle furnace steelmaking practices have been developed employing synthetic slags for efficient sulfur removal prior to casting.

The function of these additions is either to remove sulfur in excess to that specified or to control the shape of the remaining sulfide inclusions, rather than remove them completely. It is simply a question of practicality and economics: It is cheaper and easier (besides increasing BF capacity, as explained above) to remove the sulfur at the hot metal stage. Nonetheless, a considerable amount of sulfur can be removed in the ladle.

## AVAILABLE FORMS

Cored wire, flowers of sulfur, stick sulfur and iron sulfide (or pyrite,  $\text{FeS}$ ) are the most common resulfurizing agents. Manganese sulfide ( $\text{MnS}$ ) and sodium sulfide ( $\text{Na}_2\text{S}$ ) or sulfate ( $\text{Na}_2\text{SO}_4$ ) are also used, but much less frequently.

All of the above products are relatively free from impurities and may be used without danger of contaminating otherwise clean steel.

## ADDITION PRACTICE

Resulfurization is normally performed in the ladle. If added to the furnace, sulfur tends to suppress the evolution of CO since it is also a fairly strong deoxidizer. This thermodynamic property can be beneficial in that MnS containing steels will not require so much aluminum for deoxidation, (silicon containing alloy additions are avoided in free machining steels since silicate inclusions are detrimental to machinability), thereby reducing cost.

Sulfur additions are normally in the form of cored wire, which is typically added to the ladle furnace. It can also be added to the tapping stream. All addition agents have low density and will float at the slag/metal interface, so addition should be made with adequate mixing in the ladle to insure rapid dissolution. Manganese sulfide is used in free machining stainless steels because it gives more consistent recoveries than pure sulfur and better morphology and distribution to the sulfides. Pure sulfur boils well below steelmaking temperatures. It also oxidizes readily in air. Basic slags react with sulfur, tending to remove it from solution; slags should therefore be held back or decanted in a heat to be resulfurized. Despite the potential for loss, sulfur recoveries will normally be quite high, 85-90%. It should be remembered that sulfur is a relatively low cost addition; it is certainly the cheapest free machining addition agent.

## ROLLING/FORGING

In the absence of manganese, sulfur readily combines with iron to form low-melting iron sulfide, a grain boundary phase that causes severe hot shortness during rolling or forging (see Manganese). In normal steels, even those which have been resulfurized, manganese contents are high enough ( $\text{Mn/S}=8/1$  min.) to prevent this problem. Thus, sulfur appears in the microstructure as MnS inclusions: if the steel has been hot worked, the inclusions will be deformed accordingly. Their shape and orientation, along with that of other nonmetallic inclusions, gives the steel a characteristic texture, which is reflected in directional ductility and impact properties. In high strength flat rolled products, where directional isotropy is important, this texture is definitely detrimental. Preventing it has been the basis for the development of modern, extremely low sulfur steels and the technology of inclusion shape control.

## HEAT TREATMENT

Sulfur is only sparingly soluble in steel (about 0.003%) and takes no part in normal heat treating reactions.

## APPLICATIONS

Steel that must be machined may contain sulfur to break up chips and reduce tool wear. The exceptions are aircraft quality steels that, despite reduced machinability, will have reduced sulfur contents for the sake of improved mechanical properties. Common alloy steels will contain no more than 0.04% S. Free machining resulfurized carbon steels in the AISI/SAE 11XX series contain 0.08-0.13% S, but the AISI/SAE 12XX series carries up to 0.24-0.33% S (and 0.04-0.09% P). Resulfurized stainless steels, such as types 303 and 416, contain up to 0.35% S.

The directional ductility and impact properties of plate steels are reduced by the presence of elongated manganese sulfides and other inclusions. For this reason, sulfur may be kept as low as 0.005% or less in these products, particularly when they are used for such critical applications as arctic grade line pipe and ship plate. Mention should be made, however, of what has been called the "sulfur paradox" in HSLA steels. Increasing the sulfur content from a nominal, say 0.008% to 0.060% lowers the Charpy upper shelf level, thereby raising the transition temperature as fixed by a given impact energy. However, when transition energy is defined at, for example, 85% shear area in a Battelle Drop-Weight Tear Test (BDWTT), the trend is exactly the opposite. Sulfur content specified for a given steel must therefore be predicated on the stated design parameters.

Other considerations are also important, however. High sulfur contents are known to increase corrosion rates in certain environments. They promote stress corrosion cracking and hydrogen induced cracking, possibly, through electrochemical or "poisoning" effects (see Hydrogen).

# **Phosphorus**

Atomic number : 15  
Density, 20° C : 1.82 g/cm<sup>3</sup>  
Atomic weight : 30.974  
Melting point : 44.1° C (111.4° F)  
Boiling point : 280° C (536° F)

## **GENERAL**

Phosphorus is normally considered an impurity in steel. It is present in varying concentrations in iron ore, is retained in hot metal, but is eliminated early in the steelmaking process. Phosphorus oxidizes readily and is removed from steel as P<sub>2</sub>O<sub>5</sub>, which is taken up by the oxidizing slag, before the oxidation of carbon takes place. Carryover of any P<sub>2</sub>O<sub>5</sub> containing oxidizing slag can result in phosphorus reversion to the steel in subsequent steelmaking operations.

In normal commercial steels, residual phosphorus contents will run less than 0.040%, but concentrations as low as 0.005% are not unusual. Phosphorus is readily removed only in basic steelmaking processes; acid processes must therefore begin with low phosphorus raw materials. It was the ability to remove this element that led to the widespread adoption of the basic open hearth and basic electric furnace processes, and to the use of the basic Bessemer, or Thomas-Gilchrist, converter and subsequently BOF's in Europe and the United Kingdom.

Phosphorus is sometimes intentionally added to steel to improve strength, machinability and atmospheric corrosion resistance. These uses are described below.

## **AVAILABLE FORMS**

Phosphorus is added to steel in the form of ferrophosphorus, containing 23-26% P. Ferrophosphorus is a lump alloy, available in sizes from 8 in. x 3 in. to 1/2 in. x D. It is normally shipped in bulk although pallet boxes or drums can be specified.

Ferrophosphorus fines are usually briquetted, after using a binder that is capable of oxidizing the residual silicon to silica, thus enabling it to float out to the ladle slag. The intent is to reduce the concentration of residual siliceous inclusions, which are detrimental to machinability.

Ferrophosphorus is normally added to the ladle after the steel has been thoroughly deoxidized. Recovery should be approximately 90 to 95%.

## **HEAT TREATMENT**

Although an iron phosphide, Fe<sub>3</sub>P, is known to exist, it is never present at the phosphorus contents encountered in commercial steels, but common in irons as an Fe/Fe<sub>3</sub>P eutectic, steadite. In steels, the element exists exclusively as a solid solution in ferrite. It is the most potent ferrite strengthener after carbon. Phosphorus coarsens the grain size and tends to produce massive, undesirable segregates. Aside from its grain coarsening property, phosphorus has an intrinsically positive effect on hardenability, but this feature cannot be exploited at the low concentrations present even in rephosphorized steels. In certain high carbon steels such as spring steel, the limits on phosphorus must be adhered to in order to prevent the formation of high concentrations of martensite.

## **APPLICATIONS**

Phosphorus is added along with sulfur to enhance machineability. Such steels are identified by the AISI/SAE 12XX designation. Limits on phosphorus content are 0.07-0.12% unless the steels are also leaded, in which case only 0.04-0.09% P will be present. The latter phosphorus content also applies when carbon is held below 0.10%.

Up to 0.15% P can be present in some HSLA steels for increased strength. Whereas phosphorus is normally considered to be an embrittling element in steel, substantial amounts can be tolerated when carbon is less than 0.15%. Phosphorus also improves atmospheric corrosion resistance in mild and low alloy steels, especially when copper is also present.

# Molybdenum

Atomic number	: 42
Density, 20° C	: 10.22 g/cm <sup>3</sup>
Atomic weight	: 95.95
Melting point	: 2610° C (4730° F)
Boiling point	: 5560° C (10,040° F)

## GENERAL

Molybdenum (often referred to as "moly") has many important uses in alloy and stainless steels, alloy cast irons and superalloys. Molybdenum is a potent hardenability agent and is a constituent of many heat treatable alloy steels. It retards softening at elevated temperatures and is therefore used in boiler and pressure vessel steels, as well as several grades of high speed and other tool steels. Molybdenum improves the corrosion resistance of stainless steels. In HSLA steels, it produces acicular ferrite structures. Molybdenum is the basis for several of the as-rolled dual phase steels used in automotive applications. While molybdenum may frequently be used interchangeably with chromium and vanadium, in many instances the properties it imparts are unique. As a result, its use has expanded considerably over the past several decades, with demand often outreaching supply.

Molybdenum is one of the few metals in which the U.S. can be completely self-sufficient. America supplies over half of the free world's needs. This number is down as, in more recent years, Chile and China have gained in prominence.

Molybdenite (MoS<sub>2</sub>) is derived from two sources: as primary ore (e.g. Colorado, Canada) or as a by-product from other metal production, usually copper (e.g. Arizona, Chile). In recent years, production has kept pace with world demand for molybdenum, with no shortages of molybdenum expected for steelmakers.

## AVAILABLE FORMS

Molybdenum is supplied as ferromolybdenum and as molybdic oxide, MoO<sub>3</sub>. In the U.S., the trend has been overwhelmingly toward the use of oxide, although the ferroalloy continues to have important applications in tool steel production and in iron and steel foundries.

Technical molybdic oxide (57% Mo, min.) is delivered in cans containing fixed amounts of molybdenum. SiO<sub>2</sub> is the major impurity, but the product may also contain small amounts of copper, sulfur and phosphorus. Molybdic oxide is also supplied as briquettes. This product form is suitable for use in small acid or basic electric furnaces where heat times are short and may not be adequate for complete reduction and homogenization. MoO<sub>3</sub> briquettes normally contain some carbon; its presence reduces the possibility of bath oxidation and can decrease slag volumes accordingly. The major remaining impurity is also silica.

Ferromolybdenum contains a minimum of 60% Mo. Up to 1% each of silicon and copper may be present. Product is supplied as lump, 2 in. x D, or in granular forms as fine as 8 mesh x D. Being a relatively expensive and sparingly used alloy addition, ferromolybdenum is packaged in cans or bags to prevent handling losses.

It should be mentioned that considerable quantities of molybdenum are recovered from alloy scrap and that the use of addition agents, as described below, is strongly governed by the quantity and molybdenum content of the scrap available. The scrap must be well segregated, both to recover its alloy content and to avoid contamination with Mo of steels in which its presence is undesirable.

## ADDITION PRACTICE

Molybdic oxide is easily reduced to metal in electric furnace, AOD and basic oxygen practice provided enough carbon or other reducing agents are present at the time of the addition. It is not suitable for use in induction melting furnaces, vacuum practices, or as a ladle addition. Well over 90% of "new" molybdenum used in U.S. steelmaking practice is now in the form of oxide. Ferromolybdenum is used as a ladle addition for final chemistry adjustment, in high speed steel production and in ferrous foundries.

In the EF production of alloy steel, heat resisting and HSLA grades (Mo content usually less than 1%), tech oxide is added to the bath after meltdown is complete and after a preliminary chemical analysis has been taken. This allows for normal uncertainties in scrap composition and permits closer control of final molybdenum content.

Adding fluorspar may help reduce slag foaming. Molybdenum recovery will usually be 95% or higher since molybdenum oxide is easily reduced in the bath. When needed, compensation for inaccuracies in the preliminary analysis can be made by adding ferromolybdenum in the ladle.

If the composition of the scrap is reasonably well known it may be more convenient to add oxide directly with the charge, leaving an allowance for final ladle trimming with ferromolybdenum, as appropriate. This is the normal practice in EAF and BOF steelmaking.

Molybdic oxide, usually in the form of briquettes, may also be used for the production of such moly-rich grades as high speed tool steels. In AOD stainless steel production, molybdenum oxide is normally added during the initial blow and ferromolybdenum is added in the final additions. Molybdenum oxide briquette recovery levels can be lower if they are added during the initial blow (87% compared with 95% when added to the vessel in the non-blow position). Electric furnace use of oxide requires some care to minimize losses due to volatilization and other causes. Nonetheless, some EF producers make as much as 70% of their molybdenum additions as oxide, with recoveries of up to 93%. The balance of the Mo addition comes from selected scrap and/or ferromolybdenum.

## ROLLING/FORGING

Careful adherence to well designed hot working procedures is necessary in order to take maximum advantage of the effects molybdenum produces in steel. This is especially important in the case of "as-rolled" HSLA plate and strip, and for moly high speed tool steels. Molybdenum slows ferrite separation from austenite to greatly enhance bainitic hardenability (helpful in HSLA steels utilizing acicular-ferrite).

For HSLA grades containing molybdenum, manganese and columbium, roughing should begin near 1205 C (2200 F). This provides the finest austenite grain size going into the finishing train.

Finish rolling may begin at controlled temperatures below 980 C (1800 F) although the Mn-Mo-Cb steels are not controlled rolled in the same sense as the Mn-V-Cb grades. Controlled cooling, using lamellar flow water and/or high pressure sprays, may be used to provide a strip temperature of 550-575 C (1020-1070 F) at the coiler. This prevents the formation of harmful coarse ferrite grains.

Molybdenum (as-rolled) dual phase steels do not require the post-rolling intercritical heat treatments needed for vanadium types, and can develop the dual phase (ferrite + martensite) structure directly off the hotmill. Close control of rolling variables is important but can be somewhat relaxed if silicon contents are high enough (~1.3%) and manganese is reduced to 0.7-0.8%. Then, slab reheat temperatures in the wide range 1150-1315 C (2100-2400 F) are acceptable. Finish rolling temperatures may be in the range 840-925 C (1550-1770 F), and coiling temperatures may vary from 450-620 C (850-1150 F) although optimum results are obtained when coiling at 565 C (1050 F).

Moly high speed steels, like other highly alloyed products, require a significant amount of hot working to break up segregated as-cast structures. Reductions in cross sectional area of 90% or more are considered mandatory. Final hot forging is performed at around 1180 C (2150 F). Powder metallurgy has gained popularity in the production of larger section high speed tool steel mill products because it reduces the amount of hot deformation needed.

## HEAT TREATMENT

Most alloy steels require higher austenitizing temperatures, high tempering temperatures and/or longer tempering times than carbon steels, and moly grades are no exception. Molybdenum steels have a tendency toward surface decarburization and protective measures such as controlled atmospheres, salt baths, borax coatings and even vacuum processes are advisable.

Both molybdenum and tungsten high speed steels require special care in heat treatment. After rough machining, parts should be given a subcritical anneal at 680-700 C (1255-1290 F) and slowly cooled to relieve machining stresses. This also improves dimensional stability during hardening. Heating for austenitizing should be performed slowly: both a preheat at 500 C (930 F) and a dwell in the range 820-840 C (1510-1545 F) are recommended. Another dwell at 1100 C (2010 F) is helpful. Thereafter, heating to the austenitizing range, 1170-1240 C (2140-2265 F) - depending on grade - should be rapid to minimize grain growth. Overheating (incipient fusion, or "burning") must be avoided, and the above precautions regarding surface protection are essential. Quenching may be direct or interrupted and should be followed by stabilization, preferably in liquid nitrogen, to help transform residual austenite. Double, or even triple, tempering in the range 510-610 C (950-1130 F) follows,

but the specific temperatures chosen depends on the composition involved.

## APPLICATIONS

The molybdenum content of alloy steels ranges from well less than 1% in HSLA and constructional alloy grades to as much as 9% in high speed tool steels.

Moly is used in many hot rolled (0.15-0.50% Mo), hot rolled and aged (1.30-1.50% Mo) and quenched and tempered high strength steels. The yield strengths of these materials range from 350-550 MPa (50-80 ksi) for HSLA grades to as high as 960 MPa (140 ksi) in the more highly alloyed varieties. Such steels are widely used in construction, earthmoving, automotive and oil country applications. HSLA pipeline grades take advantage of the changes moly produces in a steel's stress-strain behavior, i.e., giving a continuous yield range rather than a sharply defined yield point. Whereas U-O-E pipe fabrication decreases the yield strength of conventional C-Mn-V-Cb steels by up to 70 MPa (10 ksi) due to the Bauschinger effect, acicular ferrite moly grades actually gain as much as 140 MPa (20 ksi) during the same operations. In automotive HSLA steels, moly can be used to produce the highly formable dual phase structure directly off the hot strip mill without the need for subsequent heat treatment.

Molybdenum is a strong hardenability agent and is therefore found in many AISI/SAE constructional alloy steels. Because of its potency (and relatively high cost) molybdenum content will generally be held to 0.5% or less. Heat treatable alloy steels, particularly those containing chromium, are susceptible to temper embrittlement (see Chromium), but molybdenum can reduce or even eliminate this tendency. Thus heavy section forgings, which could be vulnerable to embrittlement because they can cool slowly through the known embrittling temperature range, will be made from molybdenum-containing steel.

Molybdenum is a strong carbide former and moly steels can exhibit a secondary hardening peak. This fact, plus molybdenum's ability to strengthen ferrite even at elevated temperatures, has led to the development of a series of heat-resisting steels the best known of which are the familiar 1-1/4 Cr-1/2 Mo and 2-1/4 Cr-1 Mo grades. In addition to elevated temperature stability, these steels are resistant to hydrogen blistering. This has made them standard choices for many power boiler and heat exchanger components, and for reactors, pressure vessels and piping for the chemical and petroleum industries.

Molybdenum is added to austenitic stainless steels, e.g., Type 316, for increased corrosion resistance. Pitting and crevice corrosion resistance in marine atmospheres is especially improved, as is the ability to withstand dilute (to 20%) and concentrated (over 75%) sulfuric acid. Moly also improves the pitting resistance of martensitic stainless steels. Here, it also provides higher as-quenched hardness and better wear resistance; thus, it is found in cutlery grades such as Type 440C. The addition of molybdenum to ferritic stainless steels improves their resistance to marine atmospheres and to certain organic acids.

Molybdenum is found in a number of tool steels, where its chief function is to provide hardness (wear resistance) and strength at elevated temperatures. The most important use of moly in this field, however, is in the molybdenum or M-series high speed steels. These will contain, depending on grade, between 3.5 and 9.5% Mo, plus tungsten, chromium, vanadium and possibly cobalt.

# **Copper**

Atomic number : 29  
Density, 20° C : 8.96 g/cm<sup>3</sup>  
Atomic weight : 63.54  
Melting point : 1083° C (1981° F)  
Boiling point : 2570° C (4658° F)

## **GENERAL**

Copper is added to steel to increase corrosion resistance. It also increases strength through precipitation hardening if present in concentrations greater than 0.75%. Copper produces these beneficial effects even though copper and iron have only very limited mutual solubility in both liquid and solid states. Maximum solubility of copper in austenite is 2.3% at 850 C (1560 F), rising to about 10% at 1450 C (2650 F). In ferrite, copper exhibits retrograde solubility to about 0.35% at low temperatures: this, plus the sluggish precipitation kinetics of primary (copper-rich) e - phase, makes age hardening copper steels possible.

Copper does not interact with carbon: the two elements are essentially immiscible. Therefore, all copper in mild steels will be dissolved or precipitated in ferrite, resulting in a slight hardening effect.

## **AVAILABLE FORMS**

Copper is added to steel in the form of pigs, refined ingots or as copper and nonferrous alloy scrap. Any copper already present in the steel scrap charge will be carried over into the melt with little or no loss. Scrap electric motors containing usually 10-15% Cu are often used as a source of copper.

## **ADDITION PRACTICE**

Copper may be added to the furnace or ladle. Both techniques give very high recoveries. Losses, if any, will be due to mechanical causes. When addition is made to the furnace, it should be done before the end of decarburization. (The use of lead bronze scrap as a copper source is not recommended because of the toxic fumes it produces.)

## **ROLLING/FORGING**

The presence of more than 0.2% Cu in steel produces a characteristic checking on forging surfaces. The degree of this effect increases with copper and carbon content, and with increasing preheat time and temperature if heating is done in an oxidizing atmosphere. In this case, preferential oxidation of iron near the metal surface leaves a copper-enriched zone containing the low-melting e phase on grain boundaries. In severe cases, the steel will be hot short and unworkable. Three solutions to this well-known problem are: (1) preheat only in protective or nonoxidizing atmospheres; (2) hot work only below 1090C (2000 F), the melting point of the copper-rich phase; (3) add nickel or cobalt in amounts equal to about 1/3 to 1/2 the copper content as these metals raise the melting point of the copper phase. The third solution is most common, and high copper steels will usually contain some nickel. As nickel content rises, so does the allowable forging/rolling temperature, although a practical limit in nickel content is signaled by the formation of a protective glaze at temperatures above 1280 C (2150 F).

In this same context, it should be noted that copper steels should never be welded with an oxidizing oxyacetylene flame. This can also cause preferential oxidation of iron, copper enrichment, and hot tearing. If oxidizing conditions are avoided, copper steels give excellent results will all welding processes.

## **HEAT TREATMENT**

Copper has a mild effect on hardenability, about equal to that of nickel. However, it is never added to heat treatable steels for the sake of deeper hardening. Rather, amounts in excess of 0.75% Cu are added to produce age hardening for substantial increases in mechanical properties.

Copper dissolved in steel at high, e.g., normalizing, temperatures can be retained in solution by fairly mild cooling rates. Air cooling is sufficiently rapid for moderate section sizes. Subsequent aging above 400 C (750 F) - typical treatment: 4 hours at 480-540 C (900-1000 F) - precipitates a fine dispersion of spherical e phase particles.

Overaging changes these particles to a rod-like morphology and again lowers the strength to the solution annealed state.

Aging raises the yield strength, tensile strength, and YS/TS ratio, but reduces ductility and impact resistance. Age hardening copper steels will therefore contain other elements to raise the over-all toughness of the steel to acceptable levels. Typical mechanical property changes in a normalized and aged 2% Cu-0.3% C cast steel are as follows: YS raised by 290 MPa (42 ksi), TS raised by 180 MPa (26 ksi), elongation decreased by 10% to a final value of about 20%.

Precipitation hardening can be used for additional strength in quench and tempered steels if tempering temperatures coincide with optimum aging conditions. Aging/tempering at 650 C (1200 F) will nearly double the tensile strength otherwise possible in a 1.5% Cu-C-Mo steel. In terms of equivalent strengthening, it is possible to replace approximately 0.1-0.15% C with 1% Cu.

In annealed steels, copper effects are limited to solution strengthening and improvements in mechanical properties are correspondingly lower. Two percent copper added to a 0.3% C steel raises the yield strength by 130 MPa (19 ksi) and the tensile strength by 90 MPa (13 ksi). Ductility remains practically unchanged.

## APPLICATIONS

The amount of copper added to steel depends on the desired effect and the end product use. Often, however, combinations of improved properties are possible if sufficient copper is present.

Copper contents from 0.15-1.5% will increase hardenability slightly, but heat treatable cast steels rely on copper more for its ability to improve fluidity and, as above, for age hardening.

Mild steels specifying 0.15-0.25% Cu do so mainly for improved atmospheric corrosion resistance. This improvement is especially notable in industrial atmospheres where corrosion rates may be two to four times less than for comparable carbon steels. Paint adhesion is improved as well, so copper steels will require less maintenance. The atmospheric corrosion resistance of copper steels is further increased if phosphorus is also present. Advantage is taken of this fact in the so-called "weathering" steels, the most notable example of which contains 0.12% max. C, 0.20-0.50% Mn, 0.07-0.15% P, 0.05% max. S, 0.25-0.75% Si, 0.25-0.55% Ni, 0.65% max. Ni and 0.30-1.25% Cr. Here, the improvement in corrosion resistance imparted by copper and phosphorus is greater than that for either element alone.

Copper also improves the corrosion resistance of stainless steels. An alloy containing 20% Cr and 1% Cu has good resistance to nitrosulfuric acid and has therefore been used in the manufacture of explosives. Steel containing 16-20% Cr, 1.0-3.0% Si and 1.0-2.0% Cu is resistant to sulfites and is used in the pulp and paper industries. Copper improves the resistance of austenitic stainless steels to sulfuric acid: an alloy designated "Stainless 20" containing 20% Cr, 27% Ni, 3% Mo, 2% Cu, bal. Fe was specifically designed for this type of service.

Large tonnages of copper-bearing HSLA steels, including weathering grades, have been produced for many years. Aging grades will typically contain 1-2% Cu; less will be specified for corrosion resistance and a little solid solution strengthening. HSLA copper steels are contained in ASTM specifications A242, A440, A441, A572 and A588, among others. Guaranteed minimum yield strengths range from 290 MPa (42 ksi) to 550 MPa (80 ksi). Age hardening copper-nickel-columbium steels with even higher strengths have been produced but have found only limited acceptance.

The slightly increased hardness caused by the presence of copper in amounts that enhance atmospheric corrosion resistance may make the steel unsuitable for deep drawing applications.

# **Lead**

Atomic number : 82  
Density, 20° C : 11.3 g/cm<sup>3</sup>  
Atomic weight : 207.21  
Melting point : 327.3° C (621.1° F)  
Boiling point : 1740° C (3164° F)

## **GENERAL**

Lead is only slightly soluble in liquid or solid steel and, when added, some will be present as a dispersion of discrete but preferably submicroscopic metallic lead inclusions. Its sole function is to improve machinability, which it does without serious degradation to mechanical properties.

Lead used for steelmaking consumes an insignificant fraction of the normal supply; adequate quantities have usually been available since the U.S. is self sufficient in the metal. A sizeable secondary lead industry exists as well, based largely on the reclamation of automobile batteries and cable sheathing.

## **AVAILABLE FORMS**

Elemental lead is supplied as cored wire (lead micro-shot), pellets and fine shot suitable for addition in the tundish, LMF, degasser or trumpet of bottom poured molds. Master alloys containing bismuth are also available.

Additions are carefully controlled to insure an even dispersion of lead in the solidifying steel. Segregation can be a problem. This can lead to cold working and machining difficulties, therefore products are normally checked for segregation. The slice is "sweated" at 700 C (1290 F) and examined for uniform lead distribution.

Although lead's boiling point is above normal tap temperatures, the metal does have a high vapor pressure and addition will be accompanied by considerable fuming. These vapors are toxic and must be vented to keep atmospheric concentrations below the permissible TLV-TWA limit of 50µg/m<sup>3</sup> of air. Residual blood lead levels of workers should be checked periodically to keep them within the OSHA recommended maximum value of 40µg/100 g.

## **ROLLING/FORGING**

When present in concentrations sufficient to produce the desired free-machining properties (0.15-0.35%), lead has no detrimental effect on hot working. Larger amounts can cause hot shortness but this problem can be readily detected beforehand by the sweat test outlined above.

## **HEAT TREATMENT**

Lead has no intrinsic influence on heat treatment reactions. Leaded steels form a slightly more adherent scale, the insulating quality of which can reduce cooling rates during quenching. Thus, leaded steels require a somewhat more severe quench for equivalent depth of hardening. This may be the reason why leaded steels are reported to be more susceptible to quench cracking.

## **APPLICATIONS**

Lead is only added to steels for improving machinability. Any steel may be leaded, and leaded free-machining versions of many carbon and alloy steels are widely available. The letter "L" in their AISI/SAE designations, e.g., 10LXX, denotes such steels. A number of proprietary free-cutting leaded steels are also marketed under company trade names. Usually, lead content is held to about 0.2%, but it may be augmented by the addition of other free-machining agents (see Bismuth).

Leaded steels are more costly to produce than free-machining grades containing added phosphorus or sulfur. However, their price is justified by their much improved machinability and the fact that they do not suffer from the embrittlement these other elements invariably cause. Lead does cause some changes in mechanical properties, but they are slight and usually considered tolerable; transverse ductility can be reduced in annealed steels; high temperature (345-425 C, 650-800 F) impact strength is impaired, and fatigue life suffers as the tensile strength of the steel increases. Current efforts may supplant lead's use (see tin).

# Calcium

Atomic number	: 20
Density, 20° C	: 1.53 g/cm <sup>3</sup>
Atomic weight	: 40.08
Melting point	: 848° C (1558° F)
Boiling point	: 1484° C (2703° F)

## GENERAL

Calcium, as limestone, has always been a basic ingredient in iron and steelmaking. Its uses as a fluxing agent are well known and need not be described in detail here. Rather, discussion will be limited to the use of calcium additions for refining, deoxidation, desulfurization and inclusion control beyond those generally considered part of traditional ferrous metallurgy.

Calcium cannot be thought of as a true alloying constituent since its solubility in steel is extremely low. Moreover, calcium has such a high vapor pressure (its boiling point is several hundred degrees below steelmaking temperatures) and reactivity that special techniques have had to be devised to introduce and properly retain even a few parts per million in the melt.

Nevertheless, treatment of liquid steel with calcium has become an important means of deoxidation and, more importantly, desulfurization to very low levels. Equally significant is the now routine use of calcium to control the shape, size and distribution of oxide and sulfide inclusions. Benefits directly attributable to calcium treatment include greater fluidity, simplified continuous casting and improved cleanliness (incl. reduced nozzle blockage), machinability, ductility and impact strength in the final product.

## AVAILABLE FORMS

Calcium is added to steel in the somewhat stabilized forms of calcium silicon, calcium manganese silicon, calcium silicon barium and calcium silicon barium aluminum alloys or as calcium carbide, CaC<sub>2</sub>. All are widely available, relatively inexpensive and supplied in lump, crushed or powdered forms suitable for mechanical or injection charging techniques. Calcium and CaSi cored wire are available for addition via standard wire or submerged lance injection.

Calcium silicon, containing 28-35% Ca, 60-65% Si and 6% Fe, is the most commonly used addition agent. It may contain up to 1% C and 1.5% Al and has a melting range of 980-1260 C (1800-2300 F). Standard calcium manganese silicon contains 16-20% Ca, 14-18% Mn and 53-59% Si, balance Fe (<10%) plus other residuals as above. Its melting range, 980-1105 C (1800-2020 F) is slightly lower than that for CaSi: however, melting range is not an overriding factor in these alloys as calcium vaporizes so quickly that it can provide a beneficial agitation as it bubbles through the melt. Elemental calcium is difficult and dangerous to add to liquid steel.

Commercial calcium carbide is a gray black carbide rich slag, comprised principally of CaC<sub>2</sub> and CaO and is used primarily in the manufacture of acetylene gas. Designed as a flammable solid, the product must be kept in dry storage. It is usually available in 1, 10, 50, 100 and 600 lb drums and in bulk bags. U.S. sizes available are 1-1/4 in. x 3/8 in., 1/2 in. x 1/4 in., 1/4 in. x 1/(1/12) in., 14 x 40 mesh and as 200 mesh injectable powder. Purity of the commercial grade is normally 72 - 85% CaC<sub>2</sub>. It has a melting range of 1750-1900 C (3180-3450 F) depending on purity.

## ADDITION PRACTICE

Calcium alloys can be, and are, added during all steps of the iron and steelmaking process, from blast furnaces to ladle. The demand for steels with high toughness and ductility, especially in the transverse direction, has prompted steelmakers to (a) lower the sulfur content of their products and/or (b) modify the shape of sulfide inclusions so that they are less damaging. Calcium is beneficial in both respects, and one form of calcium treatment or another has been recognized and used since the 1930's.

Hot metal desulfurization using calcium is efficient since oxygen has a severe negative effect on the partition ratio of sulfur between slag and metal. Calcium carbide is used extensively in Europe, and in the US is co-injected with magnesium at several plants in the hot metal ladle. If oxygen activity is too high, some calcium reacts with oxygen

as opposed to sulfur. Deoxidizers, such as aluminum or magnesium, are necessary to obtain low sulfur contents.

In the ladle, the low density and high reactivity of most calcium addition agents make their efficient use difficult and have led to the development of special addition techniques. Unless the ferrostatic head is quite high (as at the bottom of a deep ladle) calcium can only exist as a vapor at steelmaking temperatures. This, plus the fact that it is scarcely soluble in steel at any temperature means that any reaction between calcium and the oxygen and sulfur it is intended to remove can only take place at the calcium vapor/liquid steel interface unless, of course, the calcium is present as a component of the slag. In any event, the aim is always to make the contact between calcium and steel as intimate as possible for as long as practical limits allow. Techniques used to achieve this end include lance and cored wire injection.

Calcium - in the form of silicides or carbide, if final carbon contents permit - is injected into the ladle by means of a refractory coated lance using argon as a carrier gas. The lance is plunged into the ladle to a depth of about 2.7 m (9 ft). It is important that the addition agent be finely ground, with particle sizes smaller than 1 mm (0.04 in): this provides a smooth, even flow of deoxidizer to the steel and prevents blockage of the immersion lance. Calcium vaporizes as it rises through the steel, reacting with residual oxygen and sulfur and forming compounds that rise to the purifying slag introduced beforehand. From a thermodynamic basis, CaO should form first, followed by oxysulfides and finally CaS. The situation is complicated, however, by kinetics, slag/metal and refractory/metal reactions, and by the fact that calcium and its compounds can combine with silica and alumina already present in the bath or the refractories. (It is not uncommon practice to perform a preliminary deoxidation with silicon and/or aluminum before adding calcium.) The argon carrier gas helps purge the steel of hydrogen.

Alloy design has also played a part in reducing calcium's reactivity. Calcium alloys tend to give inconsistent results because of high reactivity at steel melting temperatures. Calcium barium silicon aluminum alloys were developed because barium significantly lowers the vapor pressure of calcium by reducing its activity and silicon greatly increases the solubility of calcium in steel.

No matter what addition technique is used, however, calcium will have two beneficial effects: it will reduce the total number of inclusions remaining in the steel - sulfur, for example, can be brought down to 0.001-0.003% with a little extra care and down to 0.007% in routine practice - and it will modify the shape of the remaining inclusions into one that is less detrimental to mechanical properties in the final product. Thus, calcium breaks up interdendritic alumina galaxies into fine Type III inclusions. These minute particles will remain in the steel through solidification but, unlike the original galaxies, have no tendency to clog continuous caster nozzles. In addition, their globular shape is retained even during hot rolling and the resulting absence of stringered or pancaked inclusions gives the steel more uniform properties in all directions.

It is important that all efforts be made to prevent reoxidation of the heat after the calcium addition. Use of protective slag blankets, inert gas- or refractory- shrouded nozzles and even submerged nozzles (into and from the tundish) are virtually mandatory if calcium protection is to be maintained. There are two reasons for this precaution: (1) reoxidation of the heat can cause sulfur rejection from calcium sulfides (CaO is more stable than CaS) and proper conditions can even lead to the re-formation of manganese sulfide; (2) there are a number of thermodynamically possible calcium aluminates and excessive reoxidation favors the formation of species which are just as harmful, especially in terms of nozzle blockage, than the alumina/silica precipitates the calcium was intended to remove or modify in the first place.

## **ROLLING/FORGING**

Calcium improves the hot workability of steels. Even at low manganese levels, calcium treated steels will be essentially free from any trace of iron sulfide and will therefore not be subject to hot shortness. High alloy steels, particularly high nickel steels (in which calcium is somewhat more soluble), are much improved by calcium treatment.

As mentioned above, calcium modifies the composition, size, and structure of oxides, sulfides and silicates already present in the melt. The resulting calcium-bearing inclusions will retain their globular shape, even when large, throughout hot working operations. Thus, alumina and sulfide stringers are eliminated and directional anisotropy, particularly with regard to through-thickness ductility, is greatly reduced.

## **HEAT TREATMENT**

Calcium has no effect on the transformations occurring during heat treatment.

## **APPLICATIONS**

Calcium improves cleanliness, desulfurizes, and reduces directional anisotropy in steels. Calcium treatment may be applied wherever these properties are needed. The low finishing temperatures used to produce fine grain sizes in HSLA sheet and plate, for example, will be especially conducive to inclusion stringering unless some form of sulfide shape control is employed. High through-thickness ductility (as gained by calcium treatment) is important in heavy plate to prevent lamellar tearing during welding. The effectiveness of rare earth treatments is improved if the steel is first given a Ca-Si or Ca-Si-Ba deoxidation. The low sulfur levels brought about by calcium treatment improve corrosion resistance and reduce susceptibility to stress corrosion cracking in specific media.

Calcium alloys are used mainly in the ladle in steel making. Normal additions are two to four pounds per ton of steel. Additions of 1-2 lbs/ton of calcium (contained) are made to high alloy steels to increase fluidity, cleanliness and surface quality. Typical examples include AISI 52100, Type 430 stainless steel used for automotive trim and the titanium-modified Type 321 austenitic stainless used in welded or sensitization-prone structures.

Calcium alloys are used to improve the fluidity and cleanliness of cast irons. Calcium silicon, calcium manganese silicon, and calcium silicon barium alloys are added to cast steels as 2-4 lbs/ton calcium alloy plus 2-1/2 lbs/ton aluminum for the same reasons. The violent agitation that accompanies calcium addition to hot metal also reduces the metal's gas content. This leads to sounder, less porous cast structures.

# Nitrogen

Atomic number	: 7
Density, 0° C	: 1 atm 1.25 g/cm <sup>3</sup>
Atomic weight	: 14.008
Melting point	: -210° C (-345.8° F)
Boiling point	: -195.8° C (-320.4° F)

## GENERAL

Nitrogen has been described as an essential, important and inexpensive alloying addition to steels, which is fortunate in that all steels contain some nitrogen. The content varies from as little as 0.002% (20 ppm) in BOF steels to about 10 times that amount in some EF steels and 150 times that amount in certain stainless grades. Degassed steels can be below 10 ppm. Nitrogen exists in steel as an interstitial quite similar to, but much more soluble than, carbon and as nitrides of iron, aluminum, vanadium, columbium, titanium and a number of other alloying elements. Nitrogen can be either harmful or beneficial to the steel's properties, depending on the form in which it is found. However, enough is now known about nitrogen's behavior that the element's status has progressed from that of an occasional nuisance to a safely controlled, useful alloying addition. During steelmaking, nitrogen can be carried over from raw materials such as coke, it can enter as a constituent, intentional or otherwise, in alloying additives, and most obviously it can enter by ordinary solution through contact of the liquid steel with air. Nitrogen can also be diffused into the surface of steels to give an extremely hard case. This chapter will discuss both aspects of nitrogen: its intentional addition and, where necessary, its removal or control.

## AVAILABLE FORMS

Nitrogen is added to liquid steel in the form of nitrogen-bearing alloying additions and as gaseous nitrogen itself. Nitrogenous alloying agents include nitrated ferromanganese, nitrated ferrochrome, a vanadium-nitrogen compound, nitrated metallic manganese and, less frequently, calcium cyanamid and urea compounds (the latter two react violently with steel giving severe fuming and splashing). Nitrated ferromanganese contains nominally 4-6% nitrogen, 74% manganese, 1.5% silicon and up to 1.5% carbon. It is a briquetted product with a density approximately equal to that of liquid steel. Two grades of manganese metal containing, respectively, 4.5 and 6.0% nitrogen are covered by ASTM A601. Up to 6-8% nitrogen is contained in high-density manganese metal. These addition agents are used in the production of nitrogen-enriched stainless steels as well as for grain size control in high-chromium cast irons. Vanadium-nitrogen compounds are used in the production of HSLA steels and other vanadium-alloyed grades.

## ADDITION PRACTICES

Addition of nitrogen, beyond that already present from the steelmaking operation, is not normally necessary, but where additional nitrogen is required, it is normally based on a nitrogen bearing ferroalloy. Thus manganese or vanadium and nitrogen trim additions can be made in the ladle. Two important factors to consider are the temperature and the overall composition of the heat. Temperature is important since it determines the solubility of nitrogen in liquid steel; the higher the temperature the higher the solubility of the gas. Control of composition is important in that elements such as aluminum, titanium, zirconium and the rare earths form very stable nitrides and, while these may be useful, they can tie up nitrogen intended for other purposes. Titanium nitride, for example, is so stable that it begins to form before the steel solidifies. Titanium nitrides can be used to produce improved properties, but removal of nitrogen from solution before solidification reduces the amount of nitrogen available, for example, for solid solution strengthening or for formation of other nitrides or carbonitrides during controlled rolling. Vanadium nitride precipitates below the steel's melting point. This latter fact is thought to contribute to the sometimes erratic recoveries experienced when using a nitrated vanadium-type addition agent. The agent must first dissociate, giving up its nitrogen to the melt, only to reprecipitate VN during subsequent processing.

Nitrogen addition agents should be added in stages, with adequate stirring, to insure a uniform concentration throughout the ladle and avoid exceeding the steel's solubility for nitrogen in localized areas. The aim is to avoid supersaturating the steel in stagnant areas. If nitride-forming elements are to be added in excess of the stoichiometric amounts, they should be added before the nitrogen addition agent itself. This will increase the

solubility of the nitrogen addition and thereby improve its recovery. For example, required manganese and/or chromium additions should be made before adding nitrated ferromanganese or nitrochrome.

Nitrogen can also be added by bubbling the gas through liquid alloy steel prior to teeming but only if sufficient nitride formers or fixers are present. This is commonly done in the AOD. Nitrogen bubbling can only be performed successfully after oxidation is complete because the evolution of CO bubbles during oxidation will flush dissolved nitrogen out of the steel.

In some circumstances, it may be necessary to remove nitrogen from the steel. This can be achieved by regular degassing. High sulfur contents and heavy slags can make nitrogen removal difficult.

## ROLLING/FORGING

The rolling and forging of nitrogen-bearing steels is based on the complex solubility relationships of nitrogen and the many alloy nitrides. These relationships are analogous, but different from, the corresponding relationships for carbon and alloy carbides. The situation is made somewhat more complex by the fact that alloy carbides and nitrides are normally isomorphous with a high degree of mutual solubility for carbon and nitrogen, so that it is quite correct to speak of the various species as carbonitrides of variable composition, e.g., Cb(C,N). The three general relationships governing the behavior of nitrogen in steel with respect to that of carbon are: first, that nitrogen is much more soluble than carbon, as much as ten times higher in ferrite; second, that alloy nitrides are generally much less soluble than iron nitride, and finally that the nitrides are usually more stable than the corresponding carbides. The solubility regimes of nitrides and carbides overlap, however, and the ability to perform controlled thermomechanical processing successfully depends on the total composition of the steel and the solubility of nitride- and carbide-forming elements in the hot working temperature range and below. For example, vanadium nitrides (along with columbium and titanium carbides and nitrogen-rich vanadium carbonitrides) can precipitate during hot deformation and therefore help control austenite recrystallization - the basis for controlled rolling - whereas "pure" vanadium carbide, which is too soluble, does not. Titanium and zirconium nitrides are too insoluble, i.e., if present, they precipitate at temperatures above, or high in the hot working range, and are therefore also less useful in this regard. The highly stable nitrides do, however, help maintain finer austenite grain size during soaking, and this is beneficial to subsequent processing. The microalloying elements used with nitrogen are frequently used in combination to take advantage of their individual effects throughout the thermomechanical processing temperature range.

Aside from its effects in controlling austenite grain size during controlled rolling, nitrogen also contributes to precipitation strengthening in ferrite in low-carbon microalloyed steels, forming a nitride and/or carbonitride, depending on overall composition and processing history. It has been shown that this extra increment of nitrogen strengthening amounts to approximately 5-10 MPa (750-1500 psi)/0.001% N. Precipitation strengthening by nitrogen occurs over a wider range than that by carbides, and this is obviously beneficial to the conduct of processing operations. Optimum precipitation of vanadium nitride, for example, occurs at around 600 C (1112 F), which is therefore the preferred coiling temperature. Detriment to impact toughness caused by precipitation strengthening is mitigated by the fact that vanadium nitride apparently forms within ferrite grains rather than (as in the case of vanadium carbide) on grain boundaries. Also, the loss of toughness due to precipitation is balanced by an improvement in toughness brought about by the refined grain size.

Conversely, uncontrolled nitrogen can have several harmful effects in steels, typically lowering ductility and reducing formability (i.e. enhancing embrittlement, reducing notch impact strength). Re-nitrogenized stainless steels can be difficult to hot work, possibly because of a high, nitrogen-induced work hardening rate and possibly because of the deleterious formation of chromium nitride particles or clusters. High-nitrogen stainless steels can also present difficulties during cold forming due to strain aging. Likely the most important deleterious effects of nitrogen on forming properties occur in cold working. Nitrogen contributes strongly to strain aging in flat-rolled carbon steels, which is caused by the interaction between dissolved nitrogen and the dislocations, or crystal defects, which always exist in metals. Besides decreasing ductility, strain aging produces non-uniform deformation during yielding (yield point elongation), leading to unsightly "stretcher strains", roping, or Lüder's lines in deformed sheet steel. This is aggravated by any prolonged holding between final cold rolling and sheet forming. The effect can be prevented, as in the familiar non-aging steels, by fixing the otherwise dissolved nitrogen in the form of alloy nitrides (aluminum, boron, vanadium, titanium, etc.). In the case of unalloyed and therefore susceptible steels, strain aging can also be avoided by giving the steel a light rolling pass ("skin pass") shortly before forming. This temporarily locks the dissolved nitrogen to dislocations. Such nonaging steels have been available for many years; examples are the aluminum killed drawing quality, or AKDQ, grades. Addition of nitrogen (and carbon) fixing elements in sufficient (hyperstoichiometric) concentrations produces the so-called "interstitial free", or IF steels, known for their high formability and complete freedom from strain aging. Boron,

which has a strong affinity for nitrogen and forms a highly stable boron nitride, has been used very successfully in this fashion.

## HEAT TREATMENT

Similar to carbon, nitrogen forms an iron martensite, but this phenomenon has never been exploited commercially and there are no heat-treatable nitrogen steels as such. Nitrogen does, however, have some effects on the heat treatment of conventional structural alloy steels. It probably has a mild but positive effect on hardenability; it depresses the martensite-start ( $M_3$ ) temperature; it retards formation of proeutectoid ferrite and bainite (lowers  $B_3$  temperature); nitrogen also possibly contributes to secondary hardening in vanadium steels by affecting the precipitation of  $V(C,N)$  during tempering and, in Cr-V steels, by retaining a finer grain size during tempering due to the presence of alloy nitride particles.

Nitriding, the intentional diffusion of nitrogen into finish-machined surfaces to produce extremely hard cases, is an important commercial process. All steels can be nitrided but the process works best if at least one percent of alloy nitride formers, typically chromium and aluminum, are present to help produce a fine grain size. One of the benefits of nitriding is that it can be performed at relatively low temperatures, thereby minimizing distortion. When combined with carburizing the process is known as carbonitriding or nitrocarburizing, depending on whether it is performed above or below the eutectoid temperature, respectively.

## APPLICATIONS

As an interstitial solid solution strengthener, nitrogen provides an inexpensive means to increase strength in hot rolled steels for automotive applications. About 0.010-0.015% N raises the yield strength of mild steels to 276-345 MPa (40-50 ksi). Cold forming and intentional strain aging in paint curing oven temperatures, for example, can further raise strengths to 414-483 MPa (60-70 ksi). Nitrogen is most widely used as a microalloying element in high strength low alloy (HSLA) steels, where it contributes to grain refinement as well as precipitation hardening. Applications include sheet, strip and plate for structural applications as well as high strength, weldable reinforcing bars and some forging and coldheading grades (see Columbium, Vanadium for more about grain refinement and precipitation hardening). Nitrogen, by itself, is an interstitial solid solution strengthener. Nitrogen has a very positive influence on creep strength and it is therefore used in steels for applications such as steam and gas turbine components and boiler tubes. Nitrogen is also used to extend the passive range of austenitic stainless steels.

Certain grades of steel, such as the Nitralloy family, were specifically designed for surface hardening treatments. Many AISI/SAE alloy steels containing Cr, Mo, V, etc., as well as die steels contain nitrogen both for strengthening and because nitrogen is an austenite stabilizer. This permits the formulation of compositions with somewhat reduced nickel contents.

# Oxygen

Atomic number	: 8
Density, 20° C	: 1.13 g/cm <sup>3</sup>
Atomic weight	: 16
Melting point	: -218.4° C (-361.1° F)
Boiling point	: -182.96° C (-297.33° F)

## GENERAL

Steelmaking is a process of controlled oxidation. That is, the production of "pure" steel containing specified concentrations of carbon and other alloying elements proceeds by the selective oxidation and removal of excessive carbon, phosphorus, silicon and manganese from blast furnace iron (hot metal), scrap and pre-reduced pellets, the metallic raw materials from which steel is derived. The steelmaker's main dilemma is to effect the most complete and efficient removal of these impurities through oxidation, but to do so in such a way that the resulting oxides are slagged off as much as possible by the time the heat is cast or teemed. In general, the subject of oxygen may be divided into two broad areas of concern: the use of the gas in oxygen steelmaking and the efficient removal or control of residual oxides, once refining is completed.

## OXYGEN STEELMAKING

**History.** One of the most important technological advances in steelmaking to occur in this century is the use of essentially pure oxygen to refine blast furnace iron. This development began modestly enough in both the US and Europe with the oxygen enrichment of open hearth atmospheres, followed by crude lancing in the years following World War II. To be sure, the principles had been understood for decades, but the unavailability of sufficient quantities of the gas at reasonable costs precluded commercial exploitation. It was, after all, hard to beat the price or availability of air and iron oxide.

As soon as "tonnage oxygen" became a reality, however, developments followed in fairly rapid order. Blast enrichment, in the OH and BF, and in the Thomas-Gilchrist converters in Europe, were established as fairly common practices for increased production efficiencies. The 1950s saw the first rapid growth of oxygen steelmaking. In North America, it took the form of improved roof lancing techniques, mostly aimed at increasing the output of the OH, upon which steelmaking then relied. Oxygen lancing in the EF is also widely practiced, even though it is strictly speaking a spin-off of the original development.

Concurrent with the beginnings of oxygen usage here, developments in Europe took a different and far more important turn. Investigators in several countries recognized that pure oxygen could not only augment existing steelmaking practices, but also actually become a principal part of them. Following many experimental trials, the first "heat" of oxygen steel was made in Switzerland in 1948 and the first actual oxygen converter (called an L-D, originally for Linz, Austria, its location, and Prof. Durrer, the Swiss inventor) began production in 1952. The process is popularly known in Europe today as Linz-Donawitz, the site of another early converter. The process was originally intended for low-phosphorus Central European iron ores. Steelmakers using the more common European high-phos ores (as in the Thomas-Gilchrist process) soon developed lime injection techniques, without which the new converter was thermodynamically unworkable. North American mills were not faced with this problem.

The value of oxygen steelmaking was quickly recognized throughout the world and within a decade, many converters had been built with vessel capacities almost ten times that of the original Austrian unit. Today, the 350-ton range is seen in several installations, and oxygen steelmaking has become the leading refining process in the world. Several variants exist, but those found in North America take two forms: the top-blown converter, or BOF (BOP) which is quite similar to the original L-D, and the bottom-blown (Q-BOP) converter, which may be thought of as a descendent of the Thomas-Gilchrist, or basic Bessemer.

**Oxygen requirements.** As mentioned above, the BOF required the development of high-capacity oxygen plants before it could become a commercial reality. Such plants, which rely on air liquification and fractional distillation, are usually located "on site" or very near to it. Their product is 99.5% O<sub>2</sub>; the major impurity is argon. Some nitrogen may be present as well, but its concentration is so low as to contribute only trace amounts to the N content of the liquid steel.

Oxygen availability must be sufficient to deliver 48-57 m<sup>3</sup> (1700-2000 ft<sup>3</sup>) per ton of steel. Delivery rates are typically 565-710 m<sup>3</sup>/min (20,000-25,000 ft<sup>3</sup>/min) or more at pressure of 1.45 MPa (210 psig).

Steelmaking. In the BOF, oxygen is impinged on the surface of the liquid metal in the vessel through a water-cooled, multiported, retractable lance, creating a violent frothing action. Lance design is a critical factor for the success of the practice since it affects behavior of the metal in the vessel, yield and lining life. In the Q-BOP, oxygen is introduced through tuyeres in the vessel bottom, much as in a Bessemer converter. To protect the tuyere refractories from rapid wear, the incoming oxygen is shrouded by an annular flow of a protective gas such as methane (natural gas) or propane.

The charge to an oxygen converter consists of hot metal, scrap, lime and often some dolomitic burned lime, iron oxide (mill scale) and possibly limestone. Proportions will vary depending on the availability, temperature and composition of the hot metal, the price and availability of scrap and the operating parameters of the furnace. A typical hot metal/scrap ratio is around 72/28, but this can vary somewhat. More scrap will be charged during periods of limited hot metal availability (prevalent during early BOF operations and still felt today when, say, BOFs are down for relining) or when scrap prices are particularly favorable. When this occurs, it may become necessary to preheat the scrap, increase the temperature of the hot metal, or use auxiliary fuels. Solid fuels are added directly to the vessel and include calcium carbide, coke, silicon steel scrap, silicon carbide and ferrosilicon. The latter two are preferred for several reasons. Coke may make the production of low carbon heats difficult; calcium carbide presents awkward handling problems, etc. Alternatively, fuel may be mixed directly with the main oxygen source, as in the so-called oxy-fuel blowing technique. This does, however, require higher oxygen delivery rates.

Oxygen lancing, using a variety of lance techniques, is practiced in electric arc furnaces to speed up the process, reduce power consumption, and provide fast and efficient reductions in carbon level. Roof mounted lances are impractical to EAFs, so they are usually simply inserted through a port in the charging door or furnace wall. Oxy-fuel burners are becoming more prevalent to further shorten heat times.

## **DEOXIDATION**

Once a heat has been purified of the elements phosphorus, silicon and manganese it is quite saturated with oxygen, which exists as FeO dissolved in the bath. Typical oxygen contents at low carbon levels, below 0.10%, may run to 900-1000 ppm (0.09-0.10%) or a little more (Fig. 2).

However, from this point on until the addition of solid deoxidizers, the oxygen concentration will mainly be determined by the equilibrium between oxygen and carbon for the particular ambient temperature, with residual manganese having a strong effect below about 0.06% C. As temperature rises, the amount of oxygen in equilibrium with a particular deoxidizer (carbon or otherwise) increases. Thus, it is common practice to depict solubility isotherms for a range of temperatures of interest to steelmakers. Such curves are shown in Figs. 3 and 4. It should be noted that true thermodynamic equilibrium is probably never achieved in a process that proceeds as rapidly as steelmaking and, if it is achieved, it is certainly too complex to depict on any one diagram. However, the curves are very valuable in that they indicate the relative strengths of the deoxidizers, the changes in their rates of deoxidation with concentration, if any, and (as in Fig. 5) interactive effects. Most important, though, they depict the limit of oxygen possible for a given concentration of deoxidizer.

Fig. 6, for example, shows that aluminum and titanium are stronger deoxidizers than silicon, that carbon is stronger than silicon at high concentrations but not at low, and that both are stronger than vanadium, chromium or manganese. Note that this figure depicts the situation at 1600 C (2912 F) and at one atmosphere pressure. Under reduced pressure, as in a vacuum degasser, the partial pressure of CO above the melt is reduced and the deoxidizing power of carbon increases, surpassing that of silicon at all concentrations. The AOD works on the same principle, but uses argon gas instead of vacuum to reduce the CO partial pressure.

Low carbon steels, then, will have inherently higher oxygen content than high carbon steels at tap unless the gas is removed by other means. Aside from vacuum carbon deoxidation and the AOD, the "other means" are the solid deoxidizers. Aluminum, ferrosilicon, silicomanganese and calcium silicon are the most common. For a more thorough description of all the deoxidizers, see the appropriate chapters under their principal constituents.

One other aspect of the solution isotherms should be noted, as it has been put to important use in the past years. The development of so-called solid electrolytes (often solutions of oxides having the ability to transport ions such as O<sup>=</sup> and to convert this to a measurable EMF) has made possible the almost instantaneous determination of dissolved bath oxygen. This is the principle behind the oxygen probe. With a probe and a thermocouple to simultaneously record the bath temperature (they are customarily mounted in the same unit) plus a calibration against the applicable solubility isotherm, it becomes possible to determine (a) the carbon content via the oxygen value and (b) the amount of deoxidizer(s) required to complete the steelmaking process.

# Hydrogen

Atomic number	: 1
Density, 20° C	: 0.07 g/cm <sup>3</sup>
Atomic weight	: 1.008
Melting point	: -259.2° C (-434.6° F)
Boiling point	: -252.8° C (-423° F)

## GENERAL

Hydrogen is an inevitable impurity in steel and cast iron. It can be quite harmful in certain applications and, where necessary, should be avoided or removed as required.

## ENTRY

Hydrogen can enter steel by any of several routes. The first occurs during the steelmaking process itself where water, contained in the charge as damp scrap, fluxes and ferroalloys, in the furnace gases or in inadequately dried refractories, dissociates on contact with liquid steel and allows hydrogen to be absorbed by the bath. This hydrogen can be largely removed by the purging action of the carbon boil, but enough can remain to be troublesome later on. Contact between the liquid steel and moisture in ladle refractories and/or humid air is another common source of hydrogen. Since this hydrogen cannot be purged by furnace reactions, special techniques are required to remove it.

Water vapor contained in furnace gases is obviously more prevalent in practices utilizing the combustion of hydrocarbon fuels. However, the level of hydrogen in the steel at any instant is set by a balance between the competing reactions of entry (from the gases) and removal through the carbon boil and degassing. At low carbon levels, the rate of hydrogen absorption is greater than the rate of removal. Dissolved hydrogen content drops to its lowest level at the end of the boil but can increase again with additional alloy and synthetic slag additions. The hydrogen content of steel melted under an oxidizing acid slag is lower than that under a reducing slag. High frequency induction melting produces lower hydrogen contents than electric furnace practice. At tap from the EAF, the hydrogen content of the liquid steel will be between 1-10 ppm, with 4-6 ppm the most common. Once solidified, steel can absorb hydrogen through the action of electrochemical reactions taking place on the steel's surface. The most common of these are pickling, electroplating, cathodic protection and corrosion. Hydrogen, liberated during these reactions, is in part absorbed by the steel before it has the opportunity to recombine to harmless bubbles of H<sub>2</sub>. Absorption is favored by the presence in the electrolyte of certain "poisons", such as sulfides, arsenides, phosphides, and selenides, which inhibit the recombination reaction. Hydrogen can also enter steel through exposure to the gas at high temperatures and pressures, a condition not uncommon in chemical and petrochemical processing equipment. Water vapor and hydrocarbons are also harmful in this regard. In any event, hydrogen dissolves in steel interstitially as a monatomic species, but whether it does so as atoms or protons is not known.

## SOLUBILITY

The solubility of hydrogen in steel is strongly dependent on crystal structure, temperature and composition. Hydrogen is much more soluble in austenite than in ferrite, for example. In all cases, solubility increases with temperature, ranging from less than 1 ppm at room temperature to about 8 ppm at 704 C (1300F).

Mention should be made of the units used to express hydrogen content in steel. The most commonly encountered are parts per million (ppm) and millimeters or cubic centimeters of hydrogen, corrected to standard temperature and pressure, per 100 g of steel. The relationship between the two is 1 ppm = 1.11 ml/100 g.

Carbon generally increases the solubility of hydrogen, but the situation is made more complex at high temperatures by the formation of methane, CH<sub>4</sub>. Manganese also has a complex effect, which may be based on crystal structure. Silicon lowers hydrogen solubility, as may aluminum. Chromium contents up to 10% increase hydrogen solubility, but higher concentrations decrease it. The effect is explained in terms of crystal structure, since about 10% Cr closes the g-loop and higher concentrations cause the steel to be fully ferritic up to the melting point. Nickel increases hydrogen solubility, with solubility being proportional to nickel content. Molybdenum has no effect on solubility, while tungsten decreases it. Vanadium, titanium, columbium, zirconium and tantalum all increase hydrogen solubility, particularly at low and moderate temperatures.

Cold work has no effect on hydrogen solubility in pure iron, but the presence of carbides causes a marked increase. It is believed that hydrogen migrates to, and collects in, internal voids formed next to carbide and inclusion particles. Thus, when a cold worked steel is annealed, some, but not all, of the hydrogen is removed by diffusion.

## PERMEABILITY

Although the diffusivity of hydrogen is an important physical property, it is more common to speak in terms of the permeability, defined as the product of diffusivity and solubility,  $P=S \times D$ . In contrast to solubility, hydrogen permeability is higher in ferrite than in austenite. This is fortunate since it facilitates the removal of hydrogen from steel by heating, as described below.

Again, alloying elements display individual effects. Carbon decreases permeability, but hydrogen will decarburize Fe<sub>3</sub>C at high temperatures. Manganese is believed to play only a small role, and molybdenum has no effect at all. Silicon decreases permeability. Chromium has no great effect in austenite, but decreases hydrogen permeability in ferrite. Permeability increases with nickel content up to about 6% Ni, then decreases thereafter.

There are no known iron hydrides, although iron is an endothermic (negative heat of absorption) occluder. Hydrogen expands the ferrite lattice as it takes up interstitial positions, but the degree of lattice expansion is difficult to measure by X-ray diffraction techniques. Thin foils charged with hydrogen from one side only will bow visibly, and this effect can be used to estimate the degree of distortion caused by the dissolved atoms.

## EFFECTS

Hydrogen is generally harmful to steel, but can be tolerated in many instances and by most steels. Hard, high strength steels and those used under severe service conditions are more sensitive to hydrogen and here, steps must be taken to remove the impurity or add protective alloying elements.

Hydrogen remaining after steelmaking migrates to internal defects where it recombines to form gaseous H<sub>2</sub>. The pressures exerted by this precipitated hydrogen can be substantial. For example, if liquid steel contains 10 ppm hydrogen, pressures exceeding the yield strength will be generated before the steel has cooled to room temperature. This so-called hydrogen flaking is particularly damaging in heavy section forgings, and has led to many catastrophic failures in items such as large crankshafts and turbine rotors. Nickel steels are particularly susceptible to flaking, but in general hydrogen contents below 2.5 ml/100 g are considered safe.

The hydrogen that enters solid steel can also collect at internal voids. As pressures build up in these voids, the familiar hydrogen blistering occurs. Chromium-molybdenum steels are resistant to this form of attack (as well as to graphitization) at elevated temperatures and are therefore widely used where potential hydrogen hazards are known to exist.

Dissolved interstitial hydrogen is also very harmful, causing an increase in yield strength and a corresponding decrease in ductility and impact properties. This is one form of hydrogen embrittlement. More important, though, is the effect known as delayed failure or static fatigue. This occurs in high strength steels that have been cathodically or otherwise charged with hydrogen and loaded in tension to stresses below their yield strengths. After a period that may extend from minutes to several weeks, depending on hydrogen content, temperature and stress level, the steel fails in a completely brittle manner.

Finally, hydrogen is known to cause cracking in welds, especially in high strength steels with tensile strengths exceeding 1690 MPa (240 ksi). The mechanism is related to the delayed failure described above and is prevented through the use of low-hydrogen electrodes or a post-weld heat treatment.

## PREVENTION/CURE

Hydrogen content in liquid steel can be minimized by assuring that all charge materials, furnace and ladle additions and refractories are thoroughly dried. While contact with furnace gases or atmospheric moisture is more difficult to avoid, practices used to prevent reoxidation should also be helpful in keeping hydrogen from entering the steel.

Several techniques have been developed to remove hydrogen from liquid steel. These include argon bubbling, the AOD, and a number of vacuum processing operations. The latter two have been found to be most effective and are now widely used. The steel may be degassed in the ladle, the AOD, or as a stream of fine droplets passing from

the ladle to another held in a vacuum chamber. Alternatively, the steel may be cast into consumable electrodes that are subsequently arc remelted under vacuum. In all cases, the aim is to reduce the dissolved hydrogen content to below the harmful threshold of about 2.5 ml/100 g.

Hydrogen can be removed from solid steel by baking or annealing. The rate of removal depends on the temperature and the square of the diameter of the part being treated. Hydrogen removal is roughly 250-400 times faster at 205 C (400 F) than at room temperature, but annealing temperatures may not be too high as hydrogen solubility increases with temperature. Small parts such as plated screws can be baked at 190-205 C (375-400 F); higher temperatures may damage the plated surface or, in the case of cadmium, lead to liquid metal embrittlement. Baking times for small to moderate sections extend to about 24 hours.

Large forgings and slabs, which are susceptible to flaking, require more extensive treatment. Forging ingots should be slowly cooled to allow as much hydrogen as possible to diffuse out of the steel. Then, depending on residual hydrogen content and section size, the forging will be further degassed by soaking at 650 C (1200 F). Five-inch diameter billets containing 3 ml/100 g require 20 hours at this temperature to reduce hydrogen content to 2 ml/100 g; 30-in forgings containing 10 ml/100 g must be soaked for 880 hours to achieve the same effect.

# Columbium (Niobium)

Atomic number : 41  
Density, 20° C : 8.57 g/cm<sup>3</sup>  
Atomic weight : 92.91  
Melting point : 2467° C (4473° F)  
Boiling point : 4740° C (8564° F)

## GENERAL

Columbium was discovered in 1801 by Charles Hatchett, who named the element to signify the American origin (Connecticut) of his raw materials. Subsequent rediscovery and renaming in Europe led to the official adoption of the name niobium but the original designation is almost always used in the U.S. steel industry.

The U.S. is completely dependent on foreign sources for columbium ores since domestic resources (800 million lbs. identified) are uneconomic at current prices. Brazil is the world's leading supplier of columbium raw materials with 77% of the known ores and 80% of the productive capacity. The primary Brazilian ore is pyrochlore, richer and easier to refine than the columbite/tantalite ores that formed much of the basis for columbium production in earlier times. Canada and several African countries also hold significant columbium reserves, both as pyrochlore and columbite/tantalite, but Brazil has led the market since exploitation of its vast deposits began in the 1970s. There have been no serious shortages of columbium addition agents in recent decades.

The ability of columbium to maintain fine grain sizes in steels at elevated temperatures has been known since before World War II and steels that take advantage of this effect have been commercially produced for many years. In recent years, however, columbium has become better known as one of the most important of the "microalloying" elements (MAE), a group of additions so named because they promote significantly improved properties at very low concentrations. (See also: Vanadium, Titanium, Zirconium and Boron.) Microalloying, combined with controlled processing, has led to the development of perhaps a hundred or more varieties of high strength low alloy (HSLA) steels. The HSLA steels are grades generally defined as having a total alloy content less than two percent but having yield strengths, in the as-rolled or as-forged condition, greater than about 345 MPa (50 ksi), up to about 690 MPa (100 ksi). The important role columbium plays in these steels is described below. Columbium also has important applications in tool steels, wear- and abrasion-resistant steels, steels for elevated temperature service, stainless steels and superalloys. Many of these uses depend on columbium's strong affinity for carbon and/or nitrogen.

## AVAILABLE FORMS

Standard Grade Ferrocolumbium, the usual steelmaking addition, contains 60-70% Cb. The product can also contain aluminum (3.5% max.), silicon (3.00% max.) and titanium (2.00% max.). Carbon content is held to 0.30% while its tantalum content will be less than 0.50%. In the higher-purity "A" Grade Ferrocolumbium (60% Cb, min.) the aluminum content is reduced to 3.00%, silicon to 1.75%, titanium to 1.00%, carbon to 0.20% and tantalum to 0.30%, all maximum. High Purity Grade Ferrocolumbium (62-68% Cb) contains only 1.00% aluminum, 0.20% silicon, 0.10% carbon and 0.30% tantalum, but all are usually lower. Less than 0.50% manganese and chromium may be present, but potentially harmful impurities such as phosphorus, sulfur, tin and lead will be well below 0.02%. Tantalum was once an almost unavoidable impurity in columbium products but the gradual overshadowing of columbite/tantalite ores by pyrochlore has reduced the tantalum content of columbium products to negligible levels. Since the concentration of columbium in most low-alloy and HSLA steels is less than 0.1%, impurities in the ferroalloys are not considered a problem.

Columbium additions to superalloys and low-iron nickel-base alloys are made using nickel columbium or, for AOD processing, columbium pentoxide, Cb<sub>2</sub>O<sub>5</sub>. High Purity NiCb contains 60-68% columbium and 1.0% max. each of aluminum and iron with very low tramp impurities.

Columbium addition agents are supplied in standard crushed sizes of 2 in. x D, 1 in. x D, 1/2 in. x D or to customer specifications. Product is normally packed in 500-lb (227-kg) steel drums or 10- or 25-lb (4.5- or 11-kg) contained Cb bags or cans. Further data on columbium addition agents is given in Tables 1 and 2.

## ADDITION PRACTICE

Ferrocolumbium is added to the ladle after final deoxidation (after additions of silicon and/or aluminum), either

along with or just after manganese. Common practice is to begin the addition when the ladle is about one quarter full and complete the addition before the ladle is half full. Ferrocolumbium has a fairly high melting range (1580-1400 C, 2876-2552 F), therefore making the addition early in the tap helps to insure complete dissolution with adequate dispersion, both of which tend to improve recovery. Avoiding large lump product (over 2 in.) and using off-center pouring to provide a good stirring action in the ladle is also helpful. FeCb has a chill effect (decrease in bath temperature) of 0.7 ° C/kg/ton at 1600 C (1.2° F/lb/ton at 2902 F).

Columbium is not an exceptionally strong deoxidizer and alloy recoveries will generally be quite high, although recovery of Cb when remelting scrap in an oxidizing atmosphere will only be around 10-20%. Recoveries in fully killed steels should be at least 80% and can easily exceed 90% if conditions are carefully controlled. Ferrocolumbium is not an especially difficult addition agent to work with and if low recoveries are a recurring problem, the most likely causes are weak stirring action, insufficient solution time (addition made too late), use of oversized product or combinations of these factors.

Although it is a grain refiner, columbium does not (unlike aluminum) lead to nozzle blockage problems in the strand caster.

## **ROLLING/FORGING**

**Flat-rolled products.** Columbium produces significant strengthening in flat rolled products through the precipitation of a hard and stable carbide, nitride or carbonitride, CbC(N). (In relative terms, the carbide-forming tendency of columbium is stronger than that of vanadium while as a nitride former, columbium is weaker than titanium.) Unlike vanadium, however, the carbonitrides of columbium are stable at temperatures up to the lower ranges of slab reheating conditions. Their existence at those high temperatures, and their ability to precipitate throughout the hot rolling process, was the basis for what came to be called controlled rolling.

The beneficial effects of columbium cannot be separated from this controlled thermomechanical processing, rolling, and/or cooling. Many current controlled rolling schedules depend on the precipitation of CbC(N) during hot working. During hot rolling, the degree of deformation in and rate of cooling through specific temperature ranges is carefully adjusted to the chemical composition of the steel, particularly its MAE + carbon content. Controlled rolling usually also implies adjusting the rolling schedule to end at fairly low finishing temperatures, below about 850 C (1560 F). The object of thermomechanical processing is to produce the extremely fine grain sizes that give control-rolled steels their excellent properties.

The choice of the specific practice followed is based on steel composition, final product type (strip or plate) and thickness, tensile and impact property requirements and, importantly, equipment limitations. A detailed discussion of controlled rolling is beyond the scope of this volume, and many excellent books and technical papers exist on the subject. It should be noted, however, that all controlled rolling cycles rely on the control or retardation of recrystallization and grain growth in austenite as it is being deformed during hot rolling.

Hot rolling can therefore begin on a finer existing grain structure. As hot rolling proceeds, the continuing precipitation of CbC(N) retards the growth of deformed and recrystallized austenite grains. This is especially important during the "hold for cooling" included in many controlled rolling cycles. Upon eventual transformation, extremely fine-grained ferrite-pearlite or acicular structures (depending on steel composition) result.

In hot-rolled steels the beneficial effect of columbium begins during reheating, while the element is partially in high-temperature solid solution and partially still precipitated as fine carbonitrides. The residual precipitates help maintain a fine austenitic grain size before rolling. Slabs for plate steels, i.e., steels which have high toughness requirements and therefore must rely relatively more on grain refinement than precipitation strengthening to achieve their desired strength levels, should be reheated to about 1095-1150 C (2000-2100 F) to take advantage of this effect. Strip steels without stringent toughness requirements can take relatively greater advantage of precipitation strengthening. Strip steels should therefore be reheated to somewhat higher temperatures to dissolve all columbium carbonitrides before rolling begins in order to maximize the potential for precipitation strengthening later on. In both cases some ultrafine precipitates of columbium carbonitrides will form during hot rolling, especially during the later stages of deformation. These particles strongly retard the recovery and recrystallization of austenite during hot deformation and the "hold for cooling" needed in some controlled rolling schedules. Retarded austenite recrystallization leads to the formation of a fine, "pancaked" austenitic grain structure at the end of the hot deformation process. This structure in turn leads to an even finer ferrite/pearlite/bainite (depending on composition) grain size after transformation. By retarding the austenite recrystallization temperature, columbium in effect raises the finish-rolling temperature needed to produce the pancaked "control-rolled" structures necessary for high mechanical properties in the final product. Raising the finish-rolling temperature also permits controlled rolling to be performed on small mills and/or on somewhat

heavier product thicknesses than when columbium is absent. Columbium also depresses the  $\gamma$  -  $\delta$  transformation temperature, which contributes to the formation of extremely fine acicular ferrite or bainite grains with high dislocation densities. Such microstructures result in steels with high strength and good notch toughness. Because carbon contents can be quite low, weldability (freedom from weld cracking) is very high in these high strength steels. Finally, the ferrite in microalloyed steels can be further strengthened by precipitation of extremely small columbium carbonitride particles during transformation. In this regard, columbium and vanadium (another potent precipitation strengthening element) are often used together in HSLA steels, usually in heavier section sizes and in normalized steels. On the other hand, columbium-bearing strip steels benefit from the addition of titanium, which increases the precipitation strengthening effect of columbium by maximizing the formation of CbC.

Accelerated cooling (AC) following controlled rolling has become an increasingly important technique for raising strength and toughness properties while maintaining low carbon equivalent values (CEV) for good weldability. Yield strengths on the order of 87 ksi (600 MPa) can be achieved in the as-rolled and AC condition at a CEV < 0.35. Variations of AC have been used by some American steel mills since the 1960s but Japanese and some European steelmakers have been especially active adapting and/or developing new AC technology in recent years. Columbium is particularly beneficial to AC steels, it is now thought, by promoting the formation of fine-grained ferrite-bainite microstructures (i.e., improving bainite hardenability) despite the fact that it also produces fine-grained austenite.

Normalized and quenched and tempered plate steels utilize columbium's grain-growth-inhibiting effect during normalizing or austenitizing. The finer grains that result from columbium additions increase strength and toughness at constant CEV levels, or permit constant strength and toughness levels to be maintained at lower CEV levels. In sheet steels, other benefits to be gained from columbium additions include the development of favorable crystallographic textures and elimination of strain aging, with improved formability. This depends on the degree to which carbon and nitrogen are combined as columbium (and other such as titanium) carbonitrides. Exploitation by sufficient removal of carbon and nitrogen from solid solution in ferrite has resulted in the popular "interstitial-free" (IF) steels.

Forging grades. When present in appreciable quantities, Cb acts as a ferrite stabilizer, progressively closing the  $\gamma$  loop. As in long products, columbium's main function in microalloyed forging steels is to maintain a fine grain size. Fine grain size contributes to high toughness, an important consideration in safety-related applications such as steering- and suspension system components. Low-to-medium carbon columbium-vanadium steels utilize a combination of grain size and precipitation hardening to achieve high strength levels. Low carbon columbium-molybdenum microalloyed forging steels derive their mechanical properties from a fine-grained bainitic structure. Properties in this steel depend on cooling rate, and optimum strength and toughness are gained by quenching directly from the forging operation. In very large Cb-treated stainless steel ingots, CbC may segregate and cause a decrease in ductility in the center of large forgings.

## **HEAT TREATMENT**

Columbium has a negative effect on martensite hardenability because of its strong ability to remove carbon from solution. Columbium is therefore not a specified constituent of the heat treatable AISI/SAE constructional alloy steels. Some grades of structural, pressure vessel or abrasion-resistant steels do contain the element in combination with manganese, molybdenum, nickel, copper and chromium.

Direct quenching of microalloyed columbium forging steels is commercially practiced in numerous plants around the world, but the steels involved are largely proprietary and their heat treatments are not conventional; therefore, general rules cannot easily be given here. A number of columbium-bearing plate steels are roller-quenched and tempered; one heat treatable, low-carbon, microalloyed columbium forging steel recently developed by a U.S. mill requires controlled quenching after forging to produce an autotempered martensitic structure. Copper-nickel-columbium naval steels (see Copper) are heat treated by accelerated cooling and a simple aging treatment at 550 C (1022 F).

## **APPLICATIONS**

Because only about one-half the amount of columbium (0.012% Cb ( 0.025 % V) is needed to produce the same strength increase brought about by vanadium additions, columbium steels can have economic advantages for the steelmaker in some grades. Columbium is a constituent of many proprietary and a number of ASTM, ASME, API and SAE steels falling into the general category of HSLA steels. Widely used grades include ASTM A572, A735, A736 and A737. The latter three grades are included in specifications for pressure vessel quality steels. However since columbium's chief function is to increase yield strength while at the same time improving toughness, and since U.S. pressure vessel codes are essentially based on tensile strength, the use of columbium is pressure

vessel applications is somewhat restricted. The challenges on its wider use are very much the same, in this regard, as are those on vanadium.

Normalized and control-rolled plate steels used for heavy equipment and thick-walled structures, including offshore platforms, benefit from columbium's ability to maintain fine grain size and improve strength while retaining high toughness. Specifications for high-pressure oil and gas transmission lines, such as API 5LX, are yield strength based. API linepipe steels are the application in which control-rolled columbium and columbium-vanadium steels first came into their own and it is a market they still largely dominate. The trend in linepipe over the past 30 years has been toward higher yield strengths with lower carbon contents for improved weldability, plus better cleanliness (lower S and P) and inclusion shape control for better directional properties. Modern microalloyed linepipe steels meet X80 and X100 yield strength requirements (80 and 100 ksi, 550 and 690 MPa, respectively) through combinations of alloy content, controlled rolling and accelerated cooling. The technology to produce microalloyed steels for shapes and heavy structural sections is developing rapidly, and may eventually supplant traditional normalized grades. Weight reduction is the major driving force for these steels' development. Offshore platforms and mining support structures utilize control-rolled columbium and columbium-vanadium structural sections with minimum yield strengths in the 550 MPa (80ksi) range. Quenched and autotempered sections made from columbium-vanadium steels reach yield strengths of 700 MPa (110 ksi). Columbium steels are excellent candidates for arctic and other low temperature structural uses since their fine grain size gives them a very high resistance to brittle failure under these conditions.

Applying controlled thermomechanical processing to microalloyed bar steels produces high mechanical properties in the as-forged condition, thereby eliminating the need for heat treatment while reducing total alloy content substantially (the dual phase structure of ferrite + martensite has exceptional formability). Low-to-medium carbon microalloyed manganese-vanadium-columbium and manganese-vanadium-columbium-copper steels have so far enjoyed the greatest commercial success, mainly in the European and South American automotive industries. Tensile strengths typically range from 750 MPa (109 ksi) in as-forged low-carbon grades to 1100 MPa (160 ksi) in as-forged and aged medium carbon varieties. Still higher strengths can be achieved by cold reduction after forging and direct quenching from the forging operation. Microalloyed cold heading steels are another application in which microalloying with columbium can be used to circumvent the need for heat treatment. Bolts meeting classes 8-8 and 10-9 can be made in columbium-boron or columbium-boron-molybdenum steels without any heat treatment, including the costly patenting anneal. Both weldable and non-weldable high strength reinforcing bars are common applications for columbium steels. Here, columbium provides additional strengthening beyond that resulting from carbon and manganese through a combination of grain refinement and precipitation hardening. Some steel mills have in the past, however, experienced cooling bed problems with columbium rebar grades (cambering, warping), but these are not considered common. They are thought to result from nonuniformity in heating, cooling bed design or alloy chemistry.

Microalloying technology has successfully been applied to the development of high strength columbium-vanadium cast steels for applications ranging from offshore platform nodes to ingot tongs and slag pots. The low-carbon Mn-Si-Cr-Mo-Cb-V-Cu steels have yield strengths of 355 MPa (50 ksi) and tensile strengths of 500 MPa (73 ksi) with excellent toughness and weldability. Columbium is well known as a carbide stabilizer in austenitic stainless steels. Columbium-stabilized stainless steels, notably AISI Types 347 and 348 (nominally 18% Cr-8% Ni) are used for welded structures and where service-induced sensitization can occur. Columbium, in amounts at least ten times the carbon content (0.80% Cb max.), improves corrosion resistance by forming a highly stable columbium carbide. This prevents the formation of detrimental chromium carbides, whose presence can have a strong detrimental effect on resistance to intergranular corrosion (sensitization). Up to eight times the carbon content (0.75% Cb max.) is used in Alloy 20, a 29%-nickel, 20%-chromium, molybdenum-copper stainless steel designed for sulfuric acid service. Columbium is also used as a strengthener in precipitation hardening stainless steels (such as 15-5PH and 17-4PH, contain 0.25% Cb). While columbium-bearing ferritic and martensitic stainless steels exist, they are less common than the austenitic grades.

Columbium's use in superalloys is second only to that in HSLA steels. Alloys such as Inconels 625, 718 and X750, Hastelloys F and G, René 95, S-590, S816, 713C and others use columbium for solid solution strengthening and, more importantly, precipitation hardening. Columbium has beneficial effects on the formation and properties of  $\gamma'$  in nickel-base superalloys. In iron-nickel superalloys columbium forms  $\text{Ni}_3\text{Cb}$ , or  $\text{gll}$ , the principal strengthening phase. Columbium also forms MC-type carbides, which strengthen superalloys without detriment to ductility. Finally, columbium-based alloys are used in the aerospace, chemical, electroplating and nuclear industries in applications requiring high-temperature strength and corrosion resistance.

# **Tin**

Atomic number : 50  
Density, 20° C : 7.31 g/cm<sup>3</sup>  
Atomic weight : 118.7  
Melting point : 231.9° C (449.4° F)  
Boiling point : 2260° C (4100° F)

## **TIN IN STEEL**

While often applied to steel as a protective and/or decorative coating, or for ease of soldering, tin has never been intentionally added as an alloying agent. Even small amounts of tin are harmful to ductility and sheet formability and can cause hot shortness during forging or primary rolling. Tin is also one of the tramp elements (with phosphorus and arsenic) known to make steels susceptible to temper embrittlement, especially when chromium, nickel or manganese are also present (see Chromium). For these reasons, efforts are made to keep tin from entering the steel.

Tin is not often associated with raw materials entering the blast furnace, but any tin compounds present here will be reduced, allowing tin to dissolve in the iron. A more serious problem is the carryover of tin in the scrap charge in steelmaking furnaces. Solders and tinplate are the most common sources. Some tin may also be contained in galvanizing spelters, where it is used to control spangle appearance. All such tin will be retained in the melt throughout the steelmaking process, with the result that the buildup of residual tin levels was a matter of serious concern for a number of years. Fortunately, the use of tin in canning stocks has diminished due to the development and wide use of the so-called "tin free steels" (TFS). Also, the heavier tin coatings once produced by hot dip tinning have virtually disappeared since the replacement of this process by electrolytic tinning in the U.S. Nevertheless, steels for critical applications should still be made from selected scrap and other known low-tin raw materials.

Tin does have metallurgical uses in cast iron. It is a pearlite stabilizer and therefore increases strength and hardness. Unfortunately, tin-bearing irons are another source of the metal when used as scrap for steelmaking. A major exception to this discussion could be in the making of lead-free machining steels now appear to be possible due to a cost competitive tin addition, thanks to research by Drs. DeArdo and Garcia of the University of Pittsburgh. Tin has the same grain boundary properties as lead without the associated problems of stringers, inconsistency and toxicity.

## **Arsenic**

Atomic number	: 33
Density, 20° C	: 5.72 g/cm <sup>3</sup>
Atomic weight	: 74.92
Melting point	: (sublimes at 613° C - 1 atm) 814° C (1497° F)
Boiling point	: --° C (--° F)

### **GENERAL**

Arsenic is almost always present as a trace element in steel because of its natural occurrence in iron ores, coke, ferroalloys and nonferrous addition agents. Residual concentrations will be in the range of 0.005 to 0.030% for domestic steels and up to three times this amount in steels produced abroad. Although arsenic has a mildly beneficial effect on strength it is never intentionally added to steels, mainly because of its high toxicity. Also, even trace amounts are known to promote susceptibility to temper embrittlement, especially in chromium-nickel steels. Therefore, it is regarded as an unwanted "tramp" element.

### **APPLICATIONS**

Arsenic helps create a more uniform sphericity in the graphite nodules of ductile iron and is acknowledged as a potent pearlite stabilizer. However, commercial exploitation of these effects is very limited, and most metallurgical uses for the metal occur in nonferrous alloys.

# **Bismuth**

Atomic number : 83  
Density, 20° C : 9.747 g/cm<sup>3</sup>  
Atomic weight : 208.98  
Melting point : 271.3° C (530.3° F)  
Boiling point : 1560° C (2840° F)

## **GENERAL**

Bismuth is a relatively scarce element (abundance in the Earth's crust: 0.2 ppm, about the same as silver) with important, but limited applications in iron and steel. One quarter of the bismuth consumed in the U.S. is used metallurgically: some is added to leaded free-machining steels, but it is mostly used as a graphite suppressant in the production of malleable iron.

Bismuth is not mined for its own sake but is derived as a by-product in the refining of lead. It is also associated with some copper and molybdenum deposits.

## **AVAILABLE FORMS**

Metallic bismuth is supplied in the form of pellets or elongated shot suitable for pneumatic injection (air gun) techniques.

Lead-bismuth master alloys containing 67% Pb-33% Bi are a convenient additive form when both elements are to be used in combination. All bismuth addition agents are denser than liquid steel and gravitational segregation can be a problem. Bismuth alloys containing nickel, manganese or ferromanganese have been produced in Europe and are claimed to give improved recoveries, but they have not found widespread commercial acceptance in the U.S.

A 90% Bi-10% Te inoculant is frequently used in the manufacture of malleable iron. This additive is also sold in pellet and shot form.

## **ADDITION PRACTICE**

In steelmaking, bismuth and its alloys are added to the pouring stream during ingot teeming. Hand feeding or air gun injection is carefully controlled to give uniform distribution throughout the ingot. Bismuth has a tendency to sink and segregate at the bottom of the ingot, especially when larger amounts are added. Such segregation can be detected by an exudation, or "sweat" test, in which case the ingot bottoms can be cropped accordingly.

Bismuth's boiling point is just below the range of tap temperatures for low and medium carbon steels, and inoculation will therefore be accompanied by considerable fuming. This presents no toxicity problems unless a lead-bismuth alloy addition agent is used. However, all fumes should be vented to a bag-house filter. A burned dolomite refractory blanket will reduce vaporization losses, but recoveries will be only 40-50% unless a high melting alloy such as bismuth-nickel or bismuth-manganese is used, in which case recovery can exceed 95%.

Ingots should be removed from the molds only when completely solidified, and the segregated section cropped as necessary.

In malleable iron manufacture, bismuth is added to the pouring ladle shortly before casting. Addition should be made in small quantities to insure rapid dispersion and avoid gravity segregation.

## **ROLLING/FORGING**

Bismuth steels are treated the same way as normal leaded grades, and no special processing techniques are required. Bismuth is not, however, added to nickel-bearing austenitic stainless steels since it seriously impairs hot workability in these materials.

## **HEAT TREATMENT**

Bismuth has no effect on transformation or microstructure produced by heat treatment in steels. The element does have a chill stabilizing effect in cast irons, therefore considerable quantities are consumed in the production of malleable iron. Here, bismuth is frequently added in combination with tellurium, an even more potent carbide stabilizer. By adding the two inoculants together, it is easier to (a) insure thorough chilling action during solidification but (b) retain the ability to transform carbide to graphite during the normal graphitizing anneal.

## **APPLICATIONS**

In the U.S., bismuth is added to leaded free-machining steels in amounts equal to one-half the lead content, typically 0.1% Bi and 0.2% Pb. It has no strong effect on mechanical properties but produces substantial improvements in machinability. Bismuth, like lead, is thought to act as an internal lubricant, reducing the friction between tool and chip. All the bismuth in these steels will be dissolved in the lead inclusions, intensifying their effectiveness and providing up to 20-30% improvements in machinability.

Bismuth-treated steels are not listed separately in U.S. specifications, although many proprietary Bi/Pb variants of standard leaded steels (e.g., 10LXX) are sold under various trade names. Unleaded bismuth steels are not produced in the U.S., although some are made in Europe.

Bismuth-treated leaded steels are more expensive to manufacture than ordinary free machining types and are therefore only justifiable when large amounts of metal must be removed, as in automatic screw machine operations.

# **Cerium & Rare Earths**

Atomic number : 58  
Density, 20° C : 6.657 g/cm<sup>3</sup>  
Atomic weight : 140.12  
Melting point : 799° C (1470° F)  
Boiling point : 3426° C (6200° F)

## **GENERAL**

Cerium is the most common member of the rare earth, or lanthanide series of elements. In decreasing order or abundance, other important members of this series include lanthanum, neodymium, praseodymium and yttrium. While several rare earth metals (REM) have commercial applications in the electronics and glass industries, they are supplied to steelmakers cost effectively only in the form of mixtures of the metals or their compounds. The following discussions will therefore deal with the REMs as a group.

The REMs are, in fact, plentiful enough that several thousand tons of metal and compounds are used annually. Metallurgical applications account for 35% of the consumption. The leading supplier country today is China. Other countries include the USA, Brazil and India.

## **AVAILABLE FORMS**

Rare earth metals are sold in the form of mischmetal (German for mixed metal) or as REM silicides.

Mischmetal is an alloy of REMs with a composition corresponding roughly to rare earth concentrations in the ore, from which they are electrolytically extracted. Thus, the composition typically runs 45-51% Ce, 23-26% La, 15-19% Nd, 4-6% Pr, 1-2% remaining REMs plus 3% Fe, aluminum and other impurities. It is sold as precast canisters suitable for a plunging addition or as small piglets or pellets.

Rare earth silicide contains approximately equal portions of REMs, silicon and iron. It is less reactive than mischmetal, and is not intended for plunging additions. Silicide is sold in lump form, generally not finer than 1 in. x 1/2 in.

## **ADDITION PRACTICE**

It must be understood that, while the REMs are potent deoxidizers and desulfurizers, in practice they are never added for these purposes since alternative alloys are more economical. Rather, their function is to control the shape of inclusions remaining in a steel which has already been deoxidized and desulfurized, and their efficient use depends strongly on prior treatments the steel has received.

When REMs are added to steel, no matter in which form, they combine with oxygen and sulfur, and with oxides, sulfides and silicates already present, in many cases reducing them completely. For example, REMs will reduce SiO<sub>2</sub> and even Al<sub>2</sub>O<sub>3</sub> and for this reason, REM silicides will leave all their silicon dissolved in the steel, even though REM recovery itself may be quite low. The stable and most likely deoxidation products in an Al-deoxidized, REM-treated steel are REM oxysulfides.

Recommended practice for highest recovery of REM additions includes the following: (1) establishing a tap sulfur content in the range 0.010-0.020% S (though over-all optimum cost effectiveness is claimed to occur at 0.008% S) through suitable hot metal and steel treatment; (2) thorough deoxidation (0.04% min. Al residual); high ladle steel temperatures, > 1565 C (2850 F); (3) adequate basicity, as with a slag treatment of 6-10 lbs./ton pulverized burnt lime and, preferably, basic lined ladles. For a well deoxidized steel, REM additions should be calculated on the basis of 0.1 lbs/ton/0.001 % S. For oxide inclusion control, total oxygen must be considered. In practice, therefore, REM additions will range 0.75-2 lb./ton provided sulfur has been lowered to recommended levels.

REM silicides are added to the second pouring ladle when reladling a heat, or to the ingot mold. Addition is made to the pouring stream to insure adequate dispersion. Fines should be avoided as these have a tendency to clump. Addition will be made on the basis of sulfur content, as above, taking into account the fact that the silicides contain 33% REM. Tap silicon levels should not be near specified maximum values, due to the full recovery of silicon from this addition agent. REM recovery will be approximately 30-40%. REM oxide fumes are generally believed to be non-toxic.

Mischmetal additions are made by plunging precast canisters of the REM alloy into the ladle. Canisters of appropriate weight, depending on residual sulfur level, are attached to the end of a billet to provide deep immersion in the ladle. The above recommendations regarding desulfurization, deoxidation, slag treatment and ladle temperatures apply. Further precautions against reoxidation are strongly advised. The fact that some reoxidation will invariably occur reduces recovery from plunging below that obtainable with ingot mold practice. If reoxidation is severe enough, sulfur will revert to the melt from REM oxysulfides. The resulting formation of MnS then reduces the beneficial effects of the REM addition. Mischmetal additions may also be made to the molds, 1-2 lbs./ton; sulfide modification is obtained, but no desulfurization.

The REMs are known to cause severe nozzle blockage (even worse than aluminum) and their use with continuous casters is not recommended. Oxygen content can get too low, allowing calcium sulfides to form.

## **ROLLING/FORGING**

REM treatment improves the hot workability of steel. Sulfur is effectively controlled, even in low-Mn steels, and there is a greatly reduced danger of high temperature transverse cracking. Although REM treatment in the U.S. is reserved almost exclusively for carbon and HSLA flat-rolled products, foreign mills have added mischmetal to austenitic stainless steels, claiming the practice gives large reductions in mill loads. The hot workability of high chromium steels is also said to be improved by this treatment since the REMs refine the coarse grained structures these grades are known to exhibit.

## **HEAT TREATMENT**

The REMs do not take part in heat treating reactions. The existence of REM carbides has been reported but their stability should be low compared to such normal alloy carbides as chromium, vanadium, columbium, etc.

## **APPLICATIONS**

The sole reason for adding REMs to steel (in U.S. practice) is to modify the shape of nonmetallic inclusions into one that will not harm mechanical properties - so called "inclusion shape control". Sulfide, oxide and silicate inclusions can be soft enough at hot working temperatures to deform into long stringers oriented parallel to the hot rolling direction. Their presence is especially harmful to transverse ductility and impact strength since they act as infinitely sharp internal notches, or crack initiators. They can reduce formability and lead to edge splitting during press-brake bending of wide sheets. A more serious problem is the lamellar tearing (internal longitudinal splitting) that occurs when heavy plates containing inclusion stringers are welded.

The REM inclusions that form after rare earth treatment of a deoxidized, low sulfur steel are harder, and have a higher melting range, than the inclusions they replace. They do not deform during hot working but remain globular even through the unidirectional deformation seen in a hot strip mill. Without inclusion stringers, the steel will have transverse and through-thickness ductility and toughness essentially equal to the normally higher longitudinal properties. This lack of directionality is especially important in carbon and HSLA steels for automotive applications, and in the skelp and plate used to produce oil and gas transmission lines.

It has been known for some time that REMs can be used to modify graphite structures in cast iron. Original applications involved the use of REMs as nodularizing agents in hypereutectic irons, followed by claims they can improve the properties of grey iron by causing the formation of vermicular graphite.

# **Cobalt**

Atomic number : 27  
Density, 20° C : 8.7 g/cm<sup>3</sup>  
Atomic weight : 58.94  
Melting point : 1492° C (2718° F)  
Boiling point : 2900° C (5252° F)

## **GENERAL**

Cobalt has few, but highly specialized, uses in alloy steels. Its behavior is similar to nickel, in that it forms a complete series of solid solutions with iron at elevated temperatures and is also extremely soluble in ferrite. It is a potent ferrite strengthener; this solid solution strengthening persists to quite high temperatures, and cobalt is therefore found in several grades of high speed tool steels, among others. Like nickel, cobalt is ferromagnetic. This led to its use in a series of magnetic steels as well as the widely-used Alnico alloys. Cobalt is an important constituent of the 18% Ni maraging steels and several other ultrahigh strength steels and is added to one grade of austenitic stainless steel.

About one-quarter of the cobalt in the U.S. (depending on market conditions) forms the basis for a family of superalloys and corrosion and abrasion-resistant alloys. To a certain extent, it is interchangeable with nickel in this regard. Because of the high cleanliness standards imposed on these latter alloys, many of them are produced by specialty-alloy and stainless steel mills.

Although large reserves are known to exist around the world, cobalt has often been in short supply - occasionally to the point of allocation. Political unrest in Africa and labor disruption in affiliated nickel production (see Nickel) have been major contributors to the cyclic supply situation. The U.S. is not self-sufficient in cobalt.

## **AVAILABLE FORMS**

Cobalt metal is supplied to alloy and steel producers in the form of briquettes, granules, broken electrolytic cathodes, rondelles, fines and powders. Purity generally depends on the means of production, but grades in the range 98-99.9% Co are most commonly sold. A metallurgical grade "grey oxide" analyzing 76% Co is also available.

While not strictly an addition agent, scrap must be considered as an increasingly important source of cobalt. Unfortunately, superalloy scrap often contains high concentrations of nickel and is therefore not acceptable for tool steel production: however, maraging and ultrahigh strength steel producers can benefit from this additional source, as can suppliers of the superalloys themselves.

## **ADDITION PRACTICE**

The metallurgical behavior of cobalt is similar to that of its sister element, nickel, and it may be treated in much the same way in steel and alloy production. Cobalt oxide is readily reduced in all but the most oxidizing steel baths and may be added to the electric furnace or the AOD (see Nickel). More common practice in tool and alloy steel production, however, is to melt down a high scrap charge, adjusting final cobalt values with virgin metal.

Many cobalt-bearing alloys are subject to extremely high quality and cleanliness requirements, and appropriate metallurgical processes are used accordingly. Induction melting of magnetic alloys and some superalloys is commonly practiced. Vacuum melting is not necessary for cobalt alloys (because cobalt's affinity for oxygen is low), but may be required in cases where other, readily oxidizable, elements or gases are present as well. Also, products such as surgical implant alloys and certain aerospace materials require vacuum practice for reasons of surface quality or internal soundness.

## **ROLLING/FORGING**

Cobalt-base superalloys and cobalt-bearing magnetic alloys such as the Alnico series are notoriously difficult to hot work, being subject to high temperature cracking. As a result, they are normally cast to near finished dimensions. High speed tool steels containing cobalt are treated in much the same way as cobalt-free alloys (see

Molybdenum). Whereas the complex composition of these highly alloyed materials makes them very susceptible to segregation, they ordinarily require massive amounts of hot reduction to break up ingot structures. However, the development of powder processes in combination with hot isostatic pressing (HIP process) techniques has circumvented many of these problems.

## HEAT TREATMENT

Cobalt is unique among alloying constituents in steel in that it is the only element that decreases the hardenability of steel by accelerating the decomposition of austenite. It is never used in the standard AISI/SAE heat treatable steels. Cobalt is, however, a constituent of maraging and 9Ni-4Co ultrahigh strength steels but here, its presence is overcome—from a hardenability standpoint—by the remaining alloying constituents (see Nickel).

Cobalt raises the A3 temperature in tool steels, thus calling for somewhat higher austenitizing temperatures. This is beneficial in that it forces a greater degree of dissolution of the complex carbides these materials contain. Cobalt does form a carbide of the Fe<sub>3</sub>C type, but this compound does not contribute to secondary hardening.

## APPLICATIONS

In order of decreasing tonnage usage, cobalt's primary applications are in non-ferrous (super)alloys, magnets, high speed tool steels, ultrahigh strength alloy steels, abrasion-resistant cemented carbides for cutting tools and stainless steels.

Among the cobalt-based high temperature alloys, the oldest and best known (HS-21) contains 62% Co, 3% Ni, 27% Cr (for oxidation resistance) and 5% Mo. Other cobalt-based superalloys will typically contain 1-20% Ni, 0-6% Mo, 0-4% Cb, 10-28% Cr, plus varying concentrations of tungsten, titanium, aluminum, iron, vanadium and boron.

The cobalt-based superalloys are usually cast to near final shape by lost-wax or other precision processes. They are preferred for stator vanes and diaphragms in gas turbines because of their excellent thermal shock- and corrosion resistance.

Magnetic steels containing from 9 to 40% Co have been used for compass needles, hysteresis motors and electrical instrumentation.

The addition of 5 to 35% Co to Al-Ni-Fe magnetic materials gave rise to the well-known Alnico series of alloys. Cobalt makes these brittle alloys somewhat easier to treat and greatly increases their coercive force. It should be noted that cobalt has the highest Curie temperature (change from ferromagnetic to paramagnetic behavior) of any of the ferromagnetic elements. This property is carried over into cobalt-bearing magnetic alloys and allows them to be used, in some cases, at temperatures over 540 C (1000 F). Other cobalt-bearing magnetic alloys include the Remalloys (17-20% Mo, 12% Co, bal. Fe), which are similar to the cobalt magnet steels mentioned above, Vicalloys (10-13% V, 35-38% Fe, 52% Co) for instrumentation, and many ferrous and nonferrous compositions.

Cobalt is added to high speed steels to improve hot hardness. It is found in both molybdenum (M33) and tungsten (T15) grades.

Cobalt-bearing high speed steels have a somewhat greater tendency to decarburization and are more sensitive to checking and cracking when exposed to abrupt temperature changes. They are also somewhat more brittle than non-cobalt grades. However, their excellent "red hardness" is gaining them increasing popularity.

The addition of cobalt to cold work die steels (as in D3, with 3% Co) increases hardness and promotes greater wear resistance than grades such as D2, where it is not used.

Likewise, hot work die steels may contain about 0.5% Co for better wear resistance and higher hot hardness. The chromium-bearing Type H19 contains up to 4.25% Co for this reason.

Maraging steels (see Nickel) contain about 8% Co, and the 9Ni-4Co grades about one-half that amount. These ultrahigh strength alloy steels are commonly heat treated to yield strengths approaching 2070 MPa (300 ksi) and have excellent toughness as well. Their primary application is in aircraft and aerospace components.

The only use of cobalt in stainless steel occurs in Type 348, which contains 0.20% of the element.

Other uses of cobalt include the cemented carbide cutting materials, where cobalt acts as a binder. It is ideally

suited for this use because (1) it is liquid at a low enough temperature to penetrate all interstices between carbide particles, (2) it dissolves tungsten carbide and (3) wets it, thereby forming strong metallurgical bonds in the finished workpiece. Cobalt is also used in hardfacing alloys, where it is most effective above 650 C (1200 F) in retaining the hardness and wear resistance for which these alloys are known. Minor uses for cobalt-bearing alloys include metal-to-ceramic and metal-to-glass seals, watch springs, pen nibs and medical and dental alloys.

Due to the ability of cobalt to absorb neutrons, severe restrictions are placed on its concentration in steels destined for atomic energy applications. Levels of 0.01 and 0.005% Co maximum and lower are commonly listed by the N.R.C.

## **Magnesium**

Atomic number : 12  
Density, 20° C : 1.74 g/cm<sup>3</sup>  
Atomic weight : 24.32  
Melting point : 650° C (1202° F)  
Boiling point : 1105° C (2021° F)

### **GENERAL**

Magnesium is essentially insoluble in solid steel and is not used as an alloying constituent per se. However, like calcium, magnesium is very useful as a desulfurizer, and large quantities have been consumed in steelmaking for this purpose. (For a further discussion of this topic, see Sulfur.) Magnesium is a powerful inoculant in cast iron. When added in concentrations exceeding 0.04%, it produces a spheroidal form of graphite that improves the iron's strength and ductility.

Magnesium is an abundant metal with a price roughly comparable to that of aluminum, albeit usually higher. The US is a leading world supplier.

### **AVAILABLE FORMS**

Desulfurization. There are many, often proprietary, iron desulfurizers in which magnesium is the active ingredient. NiMg (foundry), MgFeSi, and Mg-Lime are examples.

Magnesium is highly reactive and volatilizes explosively at hot metal temperatures. These factors can combine to produce dangerous, if spectacular, pyrotechnics unless the magnesium can be released from the addition agent in a controlled manner. An American steel company has developed, and licenses, a process using lime and magnesium powders. Again, the function of the lime is primarily to control the violence of the magnesium addition, but it also increases the basicity of the resulting slag, a condition that further insures low residual sulfur levels in the hot metal. Another supplier offers a preblended mixture of powdered magnesium and lime. Its magnesium content (20%) is double that used in the foregoing process. Magnesium-dolomitic lime briquettes containing 60% Mg are also in use. It has been found that magnesium metal itself can be utilized for hot metal desulfurization if the metal is finely divided (powdered or granulated) and the particles appropriately coated to control release rate. Some coatings should remain shrouded in proprietary secrecy, but sodium chloride and silicones are known to have been used.

Inoculation. Magnesium is normally added to cast irons in the form of alloys for the same safety considerations given above. However, since the addition is typically made just before casting, the diluents must be compatible with the compositional and property requirements of the final product.

Ferrosilicon forms the basis of a number of magnesium cast iron inoculants. Known as magnesium-ferrosilicon, the products are available in several grades containing incremental concentrations of Mg between 5 and 10%. Cerium may also be present, since it insures complete nodularization even in the presence of such detrimental "poisons" as antimony, bismuth, lead and titanium. Calcium-silicon-magnesium (25-30% Ca, 50-55% Si, 10-15% Mg) is another effective inoculant; its high calcium content aids in deoxidation and desulfurization as well. Alternatively, magnesium may be added in the form of a nickel- or silicon-based alloy. The nickel-based alloys contain 15% Mg, and are available in grades with or without 30% Si. Silicon-based alloys contain approximately 18% Mg, 65% Si, 2% Ca and 0.6% Ce. Both nickel-and silicon-based materials are also sold in 30% Mg grades.

Note that Mg can also enter the bath via aluminum used for deoxidation and possibly from reduction of MgO from the slag or refractory.

### **ADDITION PRACTICE**

Desulfurizing agents are added either by plunging, pneumatic injection or mechanical stirring. Magnesium impregnated coke and briquetted products are normally plunged into hot metal under a refractory or graphite bell. Powders and granules are injected through a lance using argon or nitrogen as a carrier gas. Injection is also used

to desulfurize steel although it is more common practice (and more cost effective) to desulfurize the hot metal and reserve (steel) ladle treatments for inclusion shape control.

Cast iron inoculation additions are made to the casting ladle. Allowance must be made for the sulfur content of the iron and fading of magnesium effectiveness before solidification. Since magnesium is a strong desulfurizer, it will react with sulfur present in the liquid iron to form MgS. This floats out of the metal, removing some magnesium from the field of action. Extra magnesium must be added to compensate for this effect. Magnesium also has a very high vapor pressure at liquid iron temperatures (boils at 1105 C, 2021 F), and there can be some loss due to evaporation from the metal surface. This loss, or fade, increases with increasing temperature, magnesium concentration and ladle surface/volume ratio.

## **APPLICATIONS**

Magnesium desulfurized steels (and other low sulfur grades) are used in applications where ductility, formability and directional uniformity are especially important. Examples include linepipe and other oil country goods, high quality forging grades and heavy plates intended for welded construction.

Nodular, or spheroidal graphite, irons are essentially gray irons in which the graphite morphology has been altered from flake to globular form. Lacking the semicontinuous network or sharp internal notches inherent to ordinary gray irons, nodular irons have a much higher ductility, up to 25% elongation in some cases. In addition, magnesium's pearlite-stabilizing property leads to higher strength.

Note that magnesium aluminate spinels contribute to caster nozzle (well and gate areas) clogging, and these spinels must be avoided or minimized since they are more difficult to liquify than pure aluminates (with using calcium). Lowering slag basicity will lower the available Mg in steels.

# **Selenium**

Atomic number : 34  
Density, 20° C : 4.85 g/cm<sup>3</sup>  
Atomic weight : 78.96  
Melting point : 220° C (428° F)  
Boiling point : 695° C (1283° F)

## **GENERAL**

Selenium is recovered as a by-product during the refining of copper and lead. Its principal uses are in electronics and only 5% of total consumption is relegated to steel. Most of this goes into the production of free-machining grades.

## **AVAILABLE FORMS**

Selenium is sold as elemental metal and as ferro-, copper-, and nickel-selenium alloys. All are available in lump form; the metal may also be purchased as powder. Lump selenium metal is the preferred addition agent for carbon and low alloy steels, while the ferroalloy is normally added to stainless and high alloy grades.

Selenium is not recovered from alloy scrap in oxygen or electric furnace steelmaking practices. Induction melting, being less turbulent, will recycle between 30-40% of scrap selenium values.

## **ADDITION PRACTICE**

All selenium addition agents are lighter than liquid steel and will tend to float on the bath before being assimilated. Selenium metal is also very volatile, with a boiling point well below steelmaking temperatures. These factors combine to give relatively poor recoveries (around 60%) unless special techniques or ferroselenium is used, in which case recovery would be 80-85%.

For more even distribution, selenium additions to the ladle or ingot mold should begin early in the tap-teeming cycle and be completed before the receiving vessel is one-half full. Ladle additions give more uniform distributions but lower recoveries than ingot mold inoculation. Although metallic selenium is generally regarded as being physiologically inert, hydrogen selenide and selenium oxide are extremely toxic compounds, producing effects similar to arsenic when present in atmospheric concentrations as dilute as 1.5 ppm. Maximum time weighted average allowable concentration of selenium compounds in air has been fixed by OSHA at 0.2 mg/m<sup>3</sup> for any 8-hour shift in a 40-hr. workweek. Since selenium addition to liquid steel can produce copious fuming it is absolutely imperative that provision be made for adequate venting and removal of both gaseous and particulate emissions. To avoid contamination and reaction with moisture, addition agents should be kept dry in sealed containers and handled mechanically or with gloves.

## **ROLLING/FORGING**

Selenium does not produce the hot shortness effects common to its sister element, tellurium, and no special processing precautions need therefore be taken when processing selenium steels.

## **HEAT TREATMENT**

Selenium does not affect hardening or tempering reactions and is generally benign toward weldability and mechanical properties.

## **APPLICATIONS**

Selenium improves the machinability of steels. As little as 0.05-0.10% is effective in carbon and low alloy steels, but about 0.30% is needed in high alloy and stainless steels. The "internal lubricant" properties of selenium are retained in steels even when they are heat treated up to at least 1300 MPa (200 ksi). Selenium is, however, a relatively expensive free-machining additive and its use versus cheaper replacements such as sulfur or lead must

be weighed against added benefits gained.

Transverse ductility and toughness are improved when selenium is added in equal proportion to the steel's sulfur content (e.g. about 0.035%). Selenium alters the shape of sulfide inclusions, making them more globular, and is thus similar to calcium and the rare earth metals. Somewhat larger concentrations, 0.05%-0.10% Se, significantly reduce the rate of nitrogen absorption in liquid steel, and steels treated in this fashion will have better cold forming properties. High alloy steel castings inoculated with 0.02% Se will show less pinhole porosity, even at hydrogen concentrations of 8 to 11 ppm.

# Tellurium.

Atomic number : 52  
Density, 20° C : 6.24 g/cm<sup>3</sup>  
Atomic weight : 127.60  
Melting point : 450° C (840° F)  
Boiling point : 990° C (1815° F)

## GENERAL

Tellurium is recovered commercially from the anode muds produced during the electrolytic refining of blister copper. It is quite scarce - concentration in the Earth's crust < 0.002 ppm, about 1/50 that of its sister element, selenium. Annual world production is less than 1/2 million kg (1.1 million lbs.), more than half of which is consumed in iron and steelmaking.

## AVAILABLE FORMS

Metallic tellurium is sold as sticks, slabs, tablets and powder. Ferrotellurium, preferred for large-tonnage steelmaking, is sold in lump form: it nominally contains 45% Fe, 55% Te. Copper-tellurium is largely used in nonferrous alloys, but some iron foundry operators prefer it as well, claiming it gives better recoveries. Lump manganese telluride (70% Te, 25% Mn, 5% Fe) is also available, and may be a better addition agent when subsequent hot working problems are anticipated (see below).

Tellurium will not recycle through electric furnace or oxygen steelmaking processes, but will be retained to a considerable extent in the induction remelting of tellurium cast iron scrap.

## ADDITION PRACTICE

Stick tellurium is generally added to the pouring stream during ingot teeming, while ferrotellurium is used for ladle additions. The latter practice gives better uniformity, but recovery is generally lower than with ingot mold inoculation. However, manganese tellurium will give high recoveries even as a ladle addition. Adding tellurium through a funnel in a covered continuous caster tundish is claimed to improve both distribution and recovery. All tellurium addition agents are reasonably dense but are subject to oxidation if trapped on the surface of the bath or slag. The boiling point of tellurium is considerably below steelmaking temperatures and careless addition can result in high fuming losses unless a high-melting alloy is used.

Fumes from tellurium compounds can be noxious, and proper venting must be provided wherever additions are made. Atmospheric exposure to less than 0.01 mg/m<sup>3</sup> produces the characteristic "tellurium breath" with a strong garlic-like odor. OSHA regulations cite a time weighted average (TWA) concentration limit of 0.1 mg/m<sup>3</sup> in any 8-hour shift of a 40-hour workweek.

## ROLLING/FORGING

Low manganese, low sulfur tellurium steels are notoriously difficult to hot work and will be subject to hot cracking at temperatures below 1150 C (2100F). The presence of nickel aggravates this embrittlement, and 18/8 stainless steels, for example, may never be tellurium treated. This adverse behavior has been traced to the intergranular formation of iron and nickel tellurides when Mn/Te or S/Te ratios are low. It is claimed that the use of manganese telluride addition agents mitigates the problem but in any event, the Mn/Te ratio of the steel should be well over 20. If hot workability is questionable the steel should be soaked at 1100 C (2010 F) for prolonged periods before forging or rolling.

## HEAT TREATMENT

Tellurium has no effect on transformations in steels, nor does it adversely affect their hardenability or weldability. It has been reported that tellurium is a grain refiner in heat treated steels although there may a measurable degradation of notch impact properties.

In cast irons, tellurium is an extremely potent carbide stabilizer, to the extent that graphitization during the annealing of malleable irons is excessively retarded. For this reason, these irons are frequently inoculated with a

combination of bismuth and tellurium. The two elements act together to inhibit graphitization during solidification, but the milder effectiveness of bismuth does not inhibit breakdown of carbide during heat treatment (see Bismuth).

## **APPLICATIONS**

Tellurium is added to steel to improve machineability. It may be added alone or in combination with lead; in the latter case tellurium will be associated with the lead inclusions in the steel, enhancing their "internal lubricant" property. Tellurium has a very high surface activity, greater even than arsenic, bismuth or selenium. It is thought that this property reduces the surface energy of telluride-iron interfaces, lowering resistance to shear and promoting the generation of microcracks during cutting operations. Also, the elevated temperatures produced by high-speed machining soften the tellurides, allowing them to form a lubricating film as they smear out between tool and workpiece.

Tellurium is an optional constituent in standard free-machining grades but is routinely added to a number of proprietary steels. Because tellurium addition commands a considerable cost premium, its use must be justified on the basis of over-all product economics.

# Tungsten

Atomic number	: 74
Density, 20° C	: 19.3 g/cm <sup>3</sup>
Atomic weight	: 183.92
Melting point	: 3410° C (6170° F)
Boiling point	: 5400° C (9752° F)

## GENERAL

Tungsten is known chiefly for its strong tendency to form extremely hard and stable carbides. This property, in fact, is the basis for the most important use of tungsten in steels: as a constituent of high speed and other tool steels. About 30% of all tungsten produced is used in this fashion. Carbide cutting tools account for one-half of the total tungsten market; alloy steels, superalloys, lamp filaments and miscellaneous applications make up the remainder.

The economic history of tungsten has been one of the most erratic of all steel alloying constituents. Prices have risen and fallen abruptly in irregular cycles throughout the years. Adequate supply has been an occasional problem, despite massive government and private stockpile accumulation.

It has been estimated that China holds over 50% of world tungsten reserves, followed by Canada and the U.S. Bolivia, Peru, Thailand and Korea also have important reserves. The Chinese and, more recently, the Russians have taken over.

## AVAILABLE FORMS

Tungsten is supplied to steel mills in the form of ferrotungsten, melting base alloy, and natural or synthetic scheelite (Ca<sub>2</sub>WO<sub>4</sub>). The choice of addition agent used is determined largely on the basis of steelmaking practice (see below), although product requirements and economics also play an important role.

Standard ferrotungsten is available in four grades. High (0.60% C) and low (0.10% C) carbon varieties usually contain 75-80% W. These may be produced either in an electric furnace or by aluminothermic or silicothermic reduction. Aluminum and silicon contents will vary accordingly. Molybdenum is the remaining majority impurity; it may run from 1-3% in high carbon grades to only 0.35% in the low carbon product. A special high purity grade containing 85-90% W, 0.050% C, 0.010% P, 0.020% S, 0.10% Si, 0.20% Mo, 0.10% Al, bal. Fe is also available.

Because of its high density and somewhat sluggish solution rate, ferrotungsten is normally crushed to 1/4 in. x D. This small size permits slow, careful additions with less chance for "sinkers". The product is shipped in bags, cans or bulk containers.

Melting base is the generic name given to a 30/70 tungsten/iron alloy produced from high speed steel scrap, iron, wolframite ((Fe, Mn)WO<sub>4</sub>) and scheelite. It may contain silicon, aluminum, and other impurities depending on raw materials chosen for its production. It is supplied as piglets, lump, or broken ingots.

Scheelite, natural or synthetic, is very popular, especially in specialty steel mills equipped with an AOD. Theoretical oxide content is approximately 80%, although concentrates will typically run 77-78% WO<sub>3</sub>. Silica is the major impurity.

## ADDITION PRACTICE

Usage patterns for tungsten addition agents have closely followed those of molybdenum (see Molybdenum). That is, whereas ferroalloys were long the traditional and accepted means of adding tungsten to the electric furnace, widespread adoption of the AOD has resulted to an overwhelming shift to the use of scheelite. It should be noted that an AOD is not necessary for a producer to make use of scheelite: it may be added directly to the electric furnace in much the same way as molybdic oxide. A layer of light scrap is put down first to protect the tungstate from contact with refractories. Cans of oxide are next placed in areas somewhat away from the electrodes and covered by ferrosilicon and the balance of the charge.

Practice will, of course, vary according to the product being made, i.e., to the aim tungsten content, and to the

availability of (usually high speed or tool steel) scrap. For low-tungsten alloys, many producers find it simpler to melt down, take a preliminary analysis, and trim with ferrotungsten or melting base.

The AOD has been responsible for most of the shift to scheelite use, however. The ability to add large quantities of tungsten (theoretically up to about 18% W, but practically up to around 10%) to the AOD gives the steelmaker greater freedom in scrap selection, for one thing. Addition control can be somewhat better as well although, like molybdenum, tungsten recoveries are usually quite high (90%), no matter what the practice. Since the tungstate is easily reduced, losses will chiefly be due to mechanical causes. One of these factors derives from the extremely high density of metallic tungsten addition agents. For example, if large lumps of ferrotungsten are added to the melt as a trim addition they may sink directly to the bottom before dissolving completely. There, they may become trapped against or combined with the refractories and thus give reduced or erratic recoveries. When making such additions, therefore, best practice is to use fine (1/4 in. x D) product, adding it slowly so that it can all dissolve before tap or teeming.

It is advisable, especially if large amounts of tungsten scrap or melting base or ferrotungsten are added with the original scrap charge, to rabble the bath before taking a test or perhaps stir it up by a short argon blow. This reduces the gravity segregation (stratification) of tungsten towards the furnace bottom and gives a more representative or at least more reliable sample.

Since tungsten may be partially oxidized under steelmaking conditions, slag rabbling should be employed after adding the mentioned fine sized ferrotungsten to the slag, especially if this is done close to tap.

Tungsten has a tendency to stick to furnace bottom refractories or be partially absorbed by them. For this reason a "tungsten reversion" can occur when making a non-tungsten bearing heat after a series of heats with tungsten additions to the furnace. Occasionally, the reversion may be high enough to make a low tungsten grade without any use of strong reducing agents; if no tungsten is permitted in the heat, a "wash heat" may have to be made first. Thus careful scheduling of furnaces according to the tungsten content made may result in significant economies.

The above mentioned problems associated with tungsten-bearing steels have recently been practically eliminated in modern melt shops equipped with an AOD, and at least two melting furnaces to feed it. Careful operation of the AOD will allow alternate sequencing of high nickel and high tungsten heats to the vessel with no carryover of nickel to tungsten heats or tungsten in nickel heats.

Scheelite can be used directly in the AOD bath as a source of oxygen as well as tungsten units with special precautions to avoid boil-over.

## **ROLLING/FORGING**

High-tungsten products such as the T-series high speed steels and their molybdenum counterparts are extremely susceptible to ingot segregation. Massive amounts of hot work (90% is the figure normally given) are required to break up this segregation and provide for a uniform structure in the final product (see Molybdenum).

One practice that has become increasingly popular is to avoid the ingot stage completely by means of powder metallurgy. That is, instead of being poured into ingot molds, the molten steel is atomized by teeming into a blast of high-pressure inert gas, usually argon. The rapidly solidified spherical particles formed in this way are inherently low in segregation. After cooling, they are screened, canned, cold compacted by isostatic pressure, reheated, hot isostatically pressed (HIP process) and rolled or forged to final billet shape. The result is a product with much better microstructural uniformity, improved cutting performance, greater dimensional stability during heat treatment, higher mechanical properties and simplified grindability. The process is applicable to all high-alloyed tool steel compositions.

## **HEAT TREATMENT**

Tungsten's behavior during heat treatment follows the same pattern as other strong carbide forming elements. It stabilizes ferrite, being stronger than chromium in this respect. It has an inherently high hardenability factor, but the net effect of large tungsten additions may be to decrease hardenability due to the removal of carbon from solution by the formation of stable tungsten carbides and the subsequent grain refining action these carbides provide.

Tungsten raises both the eutectoid temperature and the A3. Thus, tungsten steels will require higher austenitizing

temperatures (see below). Tungsten decreases the eutectoid carbon content: a minimum of about 0.2% C occurs at a tungsten content of 5%. There is a slight increase in eutectoid carbon content as tungsten content is raised above this level.

Tungsten decreases the MS temperature but, again, the situation is complicated by the presence of stable carbides. When dissolution of these carbides is incomplete, as with too low austenitizing temperatures, the MS temperature may actually appear to be raised by tungsten additions.

Tungsten steels will show a definite secondary hardening peak upon tempering. This phenomenon is an important contribution to the high hot hardness for which high speed steels are known.

The heat treatment of tungsten-type (T-series) high speed steels is essentially similar to that for the molybdenum grades discussed elsewhere (see Molybdenum). The same precautions regarding slow heating, dwell periods at specified temperatures and the avoidance of incipient melting should be observed. Tungsten grades are less susceptible to decarburization than moly high speed steels, but heat treatment temperatures are somewhat higher and chances of "burning" the steel by overheating are increased accordingly. Tungsten steels should be preheated at 815-870 C (1500-1600 F) and austenitized in the range 1260-1300 C (2300-2375 F). Refrigeration and double tempering are recommended to transform residual austenite.

## APPLICATIONS

As the above discussions imply, the overwhelming domestic use of tungsten as a constituent of steels is in applications requiring the wear resistance and hot hardness imparted by tungsten carbides. This encompasses most, though not all, of the standard tool and die steels as well as the tungsten- and tungsten-molybdenum high speed steels.

Approximately 2.0-2.75% W is present in S1 tungsten chisel steels, while up to 4% may be contained in F2 and F3 tungsten finishing steels. F1 high carbon, low alloy tool steels may contain up to 1-1/2% W, as does A10, a graphitic grade. Oil hardening cold work die steels may contain as little as 0.5% (01) or as much as 1.80% (07) tungsten. In general, the more severe the service conditions, the higher the tungsten (or molybdenum) content. Hot work die steels, for example, use tungsten or molybdenum, or both, with tungsten contents running as high as 18% (H26).

The high speed steels, and their high performance variants, virtually all contain some tungsten. Even though these alloys are classified as tungsten, molybdenum, or tungsten-molybdenum types, in point of fact most grades will contain some of both elements. An exception is the original (developed around the turn of the century) 18% W-4% Cr-1% V (T1) steel and others like it. A variety of grades take advantage of the fact that about 1.6-2.0% Mo is metallurgically equivalent to 1% W.

Beyond the tool and die steels, tungsten is an important constituent of abrasion-resistant nonferrous alloys such as the stellites, which may contain from 6 to 18% of the element. It is also used in superalloys and other heat-resisting materials. A Mo-30% W alloy resists attack by molten zinc.

# Zirconium

Atomic number	: 40
Density, 20° C	: 6.4 g/cm <sup>3</sup>
Atomic weight	: 91.22
Melting point	: 1860° C (3380° F)
Boiling point	: 4377° C (7911° F)

## GENERAL

Zirconium is highly reactive, and forms stable compounds with oxygen, sulfur, nitrogen and carbon. Its affinity for the first three of these elements accounts for its principal uses in steelmaking: the control of nonmetallic (sulfide and oxysulfide) inclusions and the fixation of nitrogen, primarily in boron steels. Zirconium will also inhibit grain growth and prevent strain aging, although its use for either of these functions is quite limited.

Although zirconium is reasonably plentiful, elaborate extractive metallurgical processes make the pure metal very expensive. Fortunately, these operations are not required for the zirconium addition agents used in steelmaking. Nonetheless, its relatively high price and the availability of cheaper replacements has restricted its general acceptance as an alloying agent in steels.

## AVAILABLE FORMS

Among the more common zirconium addition agents are iron-silicon-zirconium (35-40% Zr, 46-52% Si), nickel-zirconium (67-74% Zr, 24-30% Ni), ferrozirconium (75% min. Zr), zirconium alloy scrap and pure zirconium sponge. Tin levels are typically 1.5% max. High purity ferrozirconium grades (0.30% max. tin) are produced from zirconium sponge. Complex proprietary alloys, sometimes, but not always used as carriers for boron, may also contain manganese, aluminum, silicon and titanium. These will usually contain well less than 10% Zr. Ferrozirconium, produced by the remelting of zirconium (zircalloy) and steel scrap may contain between 40 and 90% Zr, depending on grade. Nickel zirconium (30 or 70% Zr) is used as an addition agent in superalloys.

Choice of the addition agent used depends mainly on the intended application. Equally important is the level of silicon allowed in the steel composition. This in turn is related to the product properties (e.g., weldability of plates for line pipe), steelmaking method, deoxidation and desulfurization practices and special treatment, such as vacuum degassing, if any.

## ADDITION PRACTICE

Zirconium is almost always added in the ladle, occasionally in the ingot mold. Furnace additions are not possible since high oxygen levels, in addition to the ever-present potential for reoxidation before solidification, will invariably lead to vanishingly small zirconium recoveries.

Because zirconium is so easily oxidized, it should only be added to fully (aluminum) killed steels. Thermodynamic data show that ZrO<sub>2</sub> is more stable at steelmaking temperatures, 1600 C (2912 F), than SiO<sub>2</sub> or even Al<sub>2</sub>O<sub>3</sub>. However, its stability relative to that of alumina reverses at lower temperatures.

Precautions should be taken against reoxidation of the heat after zirconium addition. The use of shrouded nozzles, multiport nozzles, non-turbulent teeming streams and synthetic slags have all proved helpful in improving recoveries. Stable, basic ladle linings (such as magnesia) should be used since zirconium can reduce the SiO<sub>2</sub> or aluminosilicates found in acid refractories. Ladle spraying with magnesia or burned-dolomite base mix can also help. Further, the use of steel ladle desulfurization may be partially negated if acid ladle linings are used. The basic slags resulting from desulfurization can react with acid refractories to produce a sulfur-rich ladle glaze. This glaze can actually pump sulfur (and oxygen) back into the steel if powerful desulfurizers/deoxidizers such as zirconium are subsequently added.

When used as a microalloying agent, zirconium recoveries will invariably be quite low. One must bear in mind, however, that the function of zirconium in this respect is not to remain in solution in steel but to scavenge impurities (oxygen, sulfur, nitrogen) or modify inclusions through the formation of complex sulfides and oxysulfides. The efficacy of zirconium additions will therefore be measured not by the amount of residual "acid soluble" metal which remains, but by the extent to which inclusions are beneficially modified or, when so used, by the potency of desired boron additions.

## ROLLING/FORGING

With its strong ability to fix sulfur, zirconium can be used as a partial replacement for manganese to prevent hot shortness. It has alternatively been proposed that the amount of sulfur fixed is equal to  $(\%Zr-0.15)/10$  and that sulfur will be entirely combined when the (unoxidized or otherwise combined) zirconium/sulfur ratio exceeds 1.41, the stoichiometric value for  $ZrS_2$ . Further, it has been observed that whereas a Mn/S ratio of 7.5 must ordinarily be maintained to eliminate hot shortness, the addition of zirconium reduces the limiting value of  $(Mn + Zr)/S$  to about 5.0.

Of course, the fixation of sulfur has a beneficial effect on transverse ductility and impact properties as well. Levels of zirconium between 0.03 and 0.30% are known to prevent the formation of detrimental Type II grain boundary film sulfides.

## HEAT TREATMENT

The hardenability factor for zirconium probably lies between those for vanadium and titanium: moreover, unlike the case with these strong carbon scavengers, there is no drop-off in hardenability factor as zirconium levels are raised. Nonetheless, for practical and economic reasons, zirconium is not used for the sake of promoting deep hardening.

The presence of zirconium compounds does, however, reduce grain coarsening, permitting the use of higher hardening or carburizing temperatures. Zirconium produces only slight changes in the mechanical properties of quenched and tempered steels, though these changes are generally beneficial. It produces a more uniform distortion during heat treatment than, for example, vanadium. Possibly because of its modification of nonmetallic inclusions, zirconium improves ductility and impact strength with most significant changes occurring in the transverse direction. It also raises the yield/tensile ratio and improves weldability through the reduction of underbead cracking and the elimination of porosity. In high alloy steels, zirconium increases hardness but decreases ductility. In stainless steels, zirconium retards the formation of sigma phase.

## APPLICATIONS

Several quenched and tempered HSLA steels, produced domestically and in Europe, contain 0.10-0.15% Zr, mainly for sulfide shape control. These steels will have yield strengths of 550 or 690 MPa (80 or 100 ksi) depending on grade and have general structural applications. Among alloy and HSLA steels listed under ASTM/ASME specifications, grades A514 (YS = 620 MPa, 90 ksi) and A588-D (YS = 290 MPa, 42 ksi) will contain 0.05-0.15% Zr.

Zirconium is also a constituent of several nonferrous alloys, the most notable being the zircaloy series, one grade of which is used extensively as a fuel cladding material in light-water nuclear reactors.

# Conversions

## S.I. - METRIC CONVERSION FACTORS

To Convert from	To	Multiply by
atmosphere (760 mm Hg)	pascal (Pa)	$1.013\ 25 \times 10^5$
Btu (International Table)	joule (J)	$1.055\ 056 \times 10^3$
Btu (International Table)	watt (W)	$2.930\ 711 \times 10^{-1}$
Btu (International Table) in./s <sup>2</sup> ·ft <sup>2</sup> ·°F (k, thermal conductivity)	watt per metre kelvin (W/m·K)	$5.192\ 204 \times 10^2$
calorie (International Table)	joule (J)	4.186 800
centipoise	pascal second (Pa·s)	$1.000\ 000 \times 10^{-3}$
centistokes	centistokes metre <sup>2</sup> per second (m <sup>2</sup> /s)	$1.000\ 000 \times 10^{-6}$
circular mil	metre <sup>2</sup> (m <sup>2</sup> )	$5.067\ 075 \times 10^{10}$
degree Fahrenheit	degree Celsius	t°C=(t°F - 32)/1.8
foot	metre (m)	$3.048\ 000 \times 10^{-1}$
ft <sup>2</sup>	metre <sup>2</sup> (m <sup>2</sup> )	$9.290\ 304 \times 10^{-2}$
ft <sup>3</sup>	metre <sup>3</sup> (m <sup>3</sup> )	$2.831\ 685 \times 10^{-2}$
ft·lbf	joule (J)	1.355 818
ft·lbf/min	watt (W)	$2.259\ 697 \times 10^{-2}$
ft/s <sup>2</sup>	metre per second <sup>2</sup> (m/s <sup>2</sup> )	$3.048\ 000 \times 10^{-1}$
gallon (U.S.liquid)	metre <sup>3</sup> (m <sup>3</sup> )	$3.785\ 412 \times 10^{-3}$
horsepower (electric)	watt (W)	$7.460\ 000 \times 10^{-2}$
inch	metre (m)	$2.540\ 000 \times 10^{-2}$
in. <sup>2</sup>	metre <sup>2</sup> (m <sup>2</sup> )	$6.451\ 600 \times 10^{-4}$
in. <sup>3</sup>	metre <sup>3</sup> (m <sup>3</sup> )	$1.638\ 706 \times 10^{-5}$
inch of mercury (60F)	pascal (Pa)	$3.376\ 85 \times 10^3$
inch of water (60F)	pascal (Pa)	$2.488\ 4 \times 10^2$
kgf/cm <sup>2</sup>	pascal (Pa)	$9.806\ 650 \times 10^4$
kip (1000 lbf)	newton (N)	$4.448\ 222 \times 10^3$
kip/in. <sup>2</sup> (ksi)	pascal (Pa)	$6.894\ 757 \times 10^6$
ounce (U.S. fluid)	metre <sup>3</sup> (m <sup>3</sup> )	$2.957\ 353 \times 10^{-5}$
ounce-force	newton (N)	$2.780\ 139 \times 10^{-1}$
ounce (avoirdupois)	kilogram (kg)	$2.834\ 952 \times 10^{-2}$
ounce (avoirdupois)/ft <sup>2</sup>	kilogram per metre <sup>2</sup> (kg/m <sup>2</sup> )	$3.051\ 517 \times 10^{-1}$
ounce (avoirdupois)/yd <sup>2</sup>	kilogram per metre <sup>2</sup> (kg/m <sup>2</sup> )	$3.390\ 575 \times 10^{-2}$
Oz (avoirdupois)/gal (U.S. liquid)	kilogram per metre <sup>3</sup> (kg/m <sup>3</sup> )	7.489 152
pint (U.S.liquid)	metre <sup>3</sup> (m <sup>3</sup> )	$4.731\ 765 \times 10^{-4}$
pound-force (lbf)	newton (N)	4.448 222
pound (lb avoirdupois)	kilogram (kg)	$4.535\ 924 \times 10^{-1}$
lbf/in. <sup>2</sup> (psi)	pascal (Pa)	$6.894\ 757 \times 10^3$
lb/in. <sup>3</sup>	kilogram per metre <sup>3</sup> (kg/m <sup>3</sup> )	$2.767\ 990 \times 10^4$
lb/ft <sup>3</sup>	kilogram per metre <sup>3</sup> (kg/m <sup>3</sup> )	1.601 846 x 10
quart (U.S. liquid)	metre <sup>3</sup> (m <sup>3</sup> )	$9.463\ 529 \times 10^{-4}$
ton (short, 2000 lb)	kilogram (kg)	$9.071\ 847 \times 10^2$
torr (mm Hg, 0 C)	pascal (Pa)	$1.333\ 22 \times 10^2$
W-h	joule (J)	$3.600\ 000 \times 10^3$
yard	metre (m)	$9.144\ 000 \times 10^{-1}$
yd <sup>2</sup>	metre <sup>2</sup> (m <sup>2</sup> )	$8.361\ 274 \times 10^{-1}$
yd <sup>3</sup>	Metre <sup>3</sup> (m <sup>3</sup> )	$7.645\ 549 \times 10^{-1}$

**Table 2 - Melting Ranges and Thermal Effects of Alloy Addition Agents**

ALLOY	Melting Range				Thermal Effect <sup>2</sup>	
	F°		C°		1 lb/ton or 1/2 kg/ton added to Steel	
	Liquidus	Solidus	Liquidus	Solidus	2902 F	1600 C
Aluminum (95 Al)	1183	1053	657	567	+0.2	+0.1
Ferroaluminum	2318	2246	1270	1230	-1.4	-0.8
Ferroboron (17 B)	2777	2687	1525	1475	-3.7	-2.1
Nickel Boron (15 B) <sup>1</sup>	2370	1620	1250	1020		
Bats 50 <sup>1</sup>	2420	1990	1440	1340	-1.3	-0.7
Grainal 79®	2950	2700	1621	1482	-1.3	-0.7
Bats TT <sup>1</sup>	2700	2335	1275	1085	-0.9	-0.5
Carbotam <sup>1</sup>	2646	2120	1400	1340	-1.7	-0.9
Calcium Aluminate Slag	2600		1425			
Calcium Carbide (72-85 CaC <sub>2</sub> )	3272-3452		1800-1900			
Calcium Silicon (30 Ca)	2192	1796	1200	980	+0.4	+0.2
Calcium Silicon Barium	1922	1778	1050	970	-0.8	-0.4
Calcium Manganese Silicon	2012	1787	1100	975	-1.5	-0.9
Hypercal	1634	1526	890	830		
Calcium Silicon Aluminum (20-25 Ca)	1751	1634	955	890	-1.8	-0.1
Calcium Silicon Aluminum	1616	1526	880	830		
Copper (99 Cu)	1981		1083		-1.8	-1.0
Ferrocolumbium Standard Grade (65 Cb)	2876	2552	1580	1400	-1.2	-0.7
ALLOY	Melting Range				Thermal Effect <sup>2</sup>	
	F°		C°		1 lb/ton or 1/2 kg/ton added to Steel	
	Liquidus	Solidus	Liquidus	Solidus	2902 F	1600 C
Nickel Columbium (65 Cb) High Purity Grade	2445	2390	1380	1280		
Cobalt (100 Co)	2723		1495		-1.5	-0.8
Manganese (99 Mn)	2300		1260		-1.8	-1.0
High Density Manganese Reg (96 Mn)	2237	2147	1225	1175	-1.8	-1.0
Massive Manganese (92-94 Mn)	2230	2135	1220	1168		
Mn N (95 Mn, 4 N)	2372	2318	1300	1270	-2.2	-1.2
Ferromanganese Nitrided (75 Mn, 4 N)					-2.4	-1.3
Ferromanganese Low Carbon Grade (88 Mn, 0.1 C)	2200	2190	1205	1200	-1.8	-1.0
Ferromanganese Standard (78 Mn, 7 C)	2310	2100	1265	1149	-2.1	-1.2
Calcium Silicon Zirconium	1832	1637	1000	925		
Carbon (Graphite)					-5.4	-3
Chromium Metal (Electrolytic)	3452		1900		-1.7	-0.9

Chromium Metal (Aluminothermic)	3362		1850		-1.7	-0.9
Low Carbon Ferrochrome (72 Cr, 0.01 C)	3074	3020	1690	1660	-1.7	-0.9
Low Carbon Ferrochrome (72 Cr, 0.05 C)	3308	2966	1670	1639	-1.7	-0.9
Low Carbon Ferrochrome (69 Cr, 0.1 C)	2920	2450	1604	1343	-1.7	-0.9
High Carbon Ferrochrome (69 Cr, 4-6 C, 1 Si)	2732	2462	1500	1350	-2.1	-1.2
High Carbon Ferrochrome (64 Cr, 5 C, 1 Si)	2660	2444	1450	1340	-2.2	-1.2
Ferrochrome, Charge Grade (63 Cr, 5.5 C, 7 Si)	2732	2552	1500	1400	-2.2	-1.2
Ferrochrome, Charge Grade (56 Cr, 6 C, 5 Si)	2720	2660	1660	1460	-2.2	-1.2
	Melting Range				Thermal Effect <sup>2</sup>	
	F°		C°		1 lb/ton or 1/2 kg/ton added to Steel	
ALLOY	Liquidus	Solidus	Liquidus	Solidus	2902 F	1600 C
Ferrochrome Silicon (36 Cr, 40 Si)	2530	2480	1388	1360	-0.8	-0.4
Ferrosilicon (75 Si)	2430	2310	1332	1266	+0.4	+0.2
Ferrosilicon (65 Si)	2320	2200	1270	1205	-0.1	-0.1
Ferrosilicon (49 Si)	2240	2210	1227	1210	-0.8	-0.4
Ferrosilicon (15 Si)	2280	2240	1249	1227	-1.6	-0.9
Titanium Scrap (90 Ti, 6 V, 4 Al)	3100		1704		-0.1	-0.1
Ferrotitanium (15 Ti)'	2740	2435	1504	1335		
Ferrotitanium (70 Ti)'	2550	2485	1135	1070	-0.5	-0.3
Ferrotitanium (40 Ti)'	2615	2465	1480	1335	-1.0	-0.6
Ferrotitanium (30 Ti)	2732	2400	1500	1315	-1.1	-0.6
Ferovan ® (43 V, 6 Si)	2675	2650	1427		-0.6	-0.3
Ferovanadium (80 V)	3218	3074	1770	1690	-1.0	-0.6
Vanadium Carbide (84 V, 13 C)	4400	3930	2430	2165	-2.8	-1.6
Vanadium Aluminum (50 V)	3038	2642	1670	1450		
Ferromanganese Silicon (67 Mn, 30 Si)	2272		1244		-1.2	-0.7
Silicomanganese (67 Mn, 17 Si)	2360	2125	1293	1162	-1.4	-0.8
Ferromolybdenum (60 Mo)	3452	3272	1900	1800	-1.2	-0.7
Nickel (99 Ni)	2650		1455		-1.2	-0.7
Ferronickel (52 Ni)	2390		1310			
Nickel Oxide Sinter (75 Ni)	3632	3452	2000	1900	-2.9	-1.6
Ferrophosphorous	2450	2305	1343	1262	-3.1	-1.7
	Melting Range				Thermal Effect <sup>2</sup>	
	F°		C°		1 lb/ton or 1/2 kg/ton added to Steel	
ALLOY	Liquidus	Solidus	Liquidus	Solidus	2902 F	1600 C
Rare Earth (Mischmetal-48 Ce)	2462		1450		-0.5	-0.3
Rare Earth Silicide (29-35 Re)	2600		1427		-0.1	-0.1
Silicon Carbide (90 min. SiC)	Sublimes at 2500 C				+0.4	+0.2

Steel Scrap	2793		1534		-1.5	-0.8
Sulfur (99 S)	240		115		+1.4	+0.8
Manganese Sulfide	2894	2822	1590	1550	+0.4	+0.2
Silicon Metal (98.4 Min Si)	2534		1440	1410	+1.4	+0.8
Ferrozirconium (85 Zr)	1832	1715	1000	935	-0.4	-0.2
Nickel Zirconium (70 Zr)	2315	2250	1600	1530		
Nickel Zirconium (36 Zr, 40 Si)	2770	2230	1130	985		
Ferrosilicon Zirconium (36 Zr, 40 Si)	2444	2282	1340	1250	-0.1	-0.1
Ferrotungsten (75-85 W)	3812	3002	2100	1650	-0.8	-0.4
Ferrotungsten (90 W)	4532	3002	2500	1650		
<b>MISCELLANEOUS</b>						
Ferroselenium (53-57 Se)	1742	887	950	475		
Manganese Sulfide (57 Mn, 35 S)	2894	2822	1590	1550	+0.4	+0.2
Manganese Tellurium (68-70 Te, 23-25 Mn)	1742		950			

1. Melting range data supplied by Prof. J. Keverian, Drexel University

2. Thermal Effects data supplied by R. J. King and W. R. Chilcott, Research Laboratory, U.S. Steel Corp., Monroeville, PA. For explanation of method, see: King, R.J. and Chilcott, W.R., "Chilling Effects of Ferroalloy Additions to Liquid Steel," Physical Chemistry of Production of Use of Alloy Additives, AIME, New York, 1974.

