Slag Metal Reactions in Binary CaF_2-Metal Oxide Welding Fluxes

Some otherwise chemically stable fluxes may decompose into suboxides in the presence of welding arcs, thereby providing higher levels of O_2 in weld metal than those oxides which do not form suboxides

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ABSTRACT. The stability of metal oxides commonly used in welding fluxes has been studied by producing binary CaF_2-metal oxide fluxes. The oxides investigated include SiO_2, MnO, MgO, Al_2O_3, Na_2O, TiO_2 K_2O and CaO. A binary SiO_2-MnO flux was also produced for purposes of comparison. The fluxes were fused, crushed, sized and used to make submerged arc welds on carbon steel plate. Supplementary argon shielding was used to prevent atmospheric contamination which might distort the effect of metal oxide decomposition. Silicon and manganese recoveries were also measured.

The results show that the stability of metal oxides during welding is not directly related to their thermodynamic stability. Some fluxes, which are otherwise very stable chemically, may decompose into suboxides in the presence of the welding arc plasma. Such oxides produce higher levels of oxygen in the weld metal than chemically stable oxides which do not form suboxides.

It is also shown that CaF_2 tends to reduce the amount of oxygen in the weld metal, but the effect is believed to be due to dilution of the metal oxide rather than to a direct chemical reaction. The effect of CaF_2 in reducing the level of weld metal oxidation is dependent upon the stability of the metal oxide which is present.

The results indicate that the stability of metal oxides during welding decreases in the following order:

1. CaO.
2. K_2O.
3. Na_2O and TiO_2.
4. Al_2O_3.
5. MgO.
6. SiO_2, MnO.

FeO was not tested as it is usually excluded from most submerged arc fluxes.

Introduction

Oxygen in steel weld metal causes a number of problems including porosity, loss of fracture toughness and reduced ductility. In order to improve the mechanical properties of the weld metal, many investigators have sought more effective means of reducing the level of oxygen contamination.

Rein has described both the oxygen and the nitrogen levels typical of the common welding processes (Ref. 1). Figure 1 is taken from his analysis. It will be noted that the greatest variations occur in the flux shielded welding processes. A general description of the reasons for impurity concentration differences, which are produced by different welding processes, has been given previously (Ref. 2).

It has been shown that the oxygen content of submerged arc weld metal decreases with both increasing flux basicity (Ref. 3) and with increasing CaF_2 content of the flux (Ref. 4). Indeed, the present (IIW) International Institute of Welding flux basicity formula includes CaF_2 as a basic constituent of the flux. The reason for this has been questioned (Ref. 5), because CaF_2 is not found to significantly alter the activity of the metal oxides contained in the flux.

Most theories of welding flux reactivity have assumed that each of the components behave in a manner similar to that found in steelmaking thermochemistry, in which the oxides with the lowest activity and the lowest free energy of formation are the least reactive. Most of these analyses consider only the direct decomposition of the metal oxides to the pure metal and oxygen. Recently, however, it has been shown that the formation of suboxides can dramatically alter our conceptions about the relative stability of metal oxides in welding fluxes (Ref. 2). In particular, SiO_2 can be shown to be more reactive than FeO if the formation of SiO is considered.

Heile and Hill have proposed silicon monoxide as one of the principle sources of fume generation in gas metal arc welding (Ref. 6). The formation of such suboxides is very likely in the high temperature plasma of the welding arc. North has suggested that CaO contributes oxygen to the weld metal (Ref. 7). His analysis assumes unit activity and his experimental data are based upon $CaCO_3$ rather than CaO; hence, the generality of his results are questionable.

The present study was undertaken to determine the relative stability of several oxides commonly used in welding fluxes. CaF_2 was added in order to reduce the melting temperature of the more refractory oxides.

Test Procedure

Reagent grade powders were dry mixed in a V-blender at 0.5 Hz for one-half hour. This mixture was then melted in an induction furnace using a graphite crucible. After solidification, the surface of the flux was scarfed by grinding to

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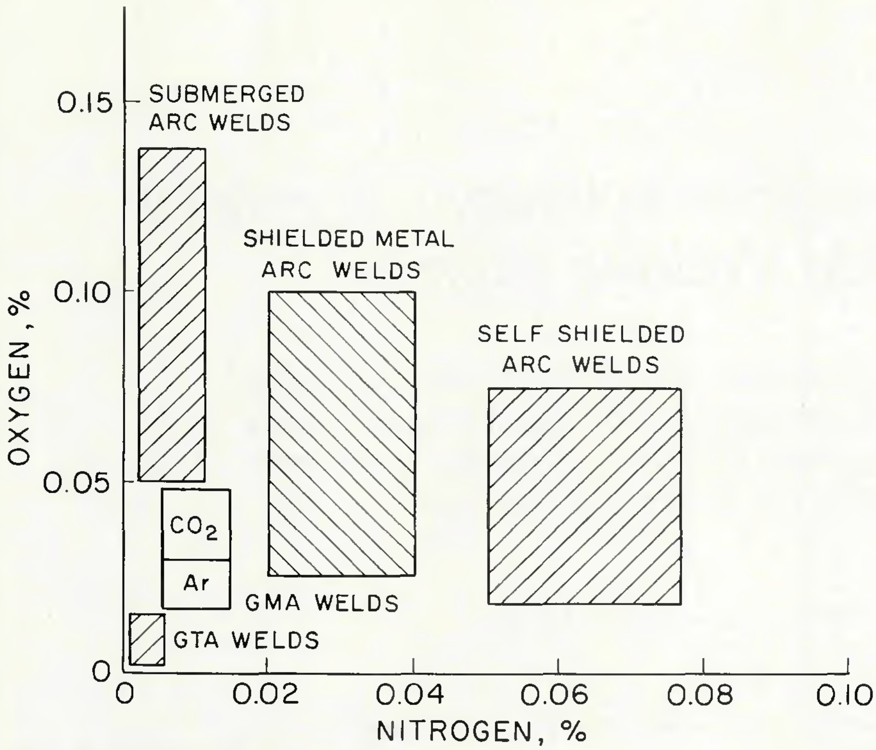

Fig. 1—Expected ranges of oxygen and nitrogen contamination of steel weld metal. After Rein (Ref. 1)

remove carbon contamination; this was followed by crushing and screening to minus 30 mesh.

Eight different metal oxides were investigated. These included CaO, MnO, MgO, SiO_2, TiO_2, Al_2O_3, Na_2O and K_2O, which are common to most welding fluxes. FeO was omitted from the study because it is generally a tramp compound in SAW fluxes and because the oxidizing potential of fluxes with more than 10% FeO is already well established (Ref. 8,9).

Due to the hygroscopic nature of CaO, and the room temperature instability of Na_2O and K_2O, fluxes containing these components were prepared from the metal carbonates. Completion of carbonate decomposition during melting was indicated by the absence of a blue flame at the top of the graphite crucible. The fluxes were maintained at 1400°C (2552°F) for 30 minutes (min) to ensure complete removal of the carbonate.

Small amounts of metal oxide, particularly MnO, were reduced by the graphite crucible during melting. Allowance for this was taken by carefully weighing all components before and after melting. In cases where metal oxide reduction was indicated, a chemical analysis was performed on the fused slag, and the adjusted composition was used in analysis of the data.

The welding conditions and metal compositions listed in Table 1 were used throughout this program in order to avoid variations due to operating parameters (Ref. 10). In order to exclude contamination from the atmosphere as a source of oxygen, external argon shielding was used.

Most of the fluxes consisted of 70 mole-% CaF_2 and 30% metal oxide, since this composition produces a flux melting temperature which is lower than the melting temperature of the base plate. A more extensive series of CaF_2-SiO_2 and CaF_2-MnO fluxes was tested, because these compositions produced the greatest level of oxygen contamination. In addition, a fluoride-free flux was included for comparison.

Flux compositions were determined with an electron microprobe. Mn and Si concentrations in the weld metal were analyzed by atomic absorption spectroscopy, while oxygen content was determined by vacuum fusion.

Results and Discussion

The weld metal analyses for oxygen, silicon and manganese are presented in Figs. 2 through 4, respectively. It is seen from Fig. 2 that the oxygen content of the pure CaF_2 weld does not differ from the average base metal/electrode oxygen content. The addition of all oxides except CaO causes an increase in the oxygen content of the weld. As expected, SiO_2 and MnO are the least stable, but surprisingly, MgO and Al_2O_3, which are considered very stable (nonreactive) in steelmaking thermochemistry, are significant contributors of oxygen. The increase in oxygen is directly proportional to the concentration of MnO and SiO_2; this suggests that CaF_2 does not interact chemically to reduce the oxygen content of the weld, but reduces the oxygen level by diluting the oxygen active species.

The high reactivity of MgO is most likely due to the high vapor pressure of Mg as suggested by North et al. (Ref. 7). In the high temperature environment near the welding plasma, all oxides are susceptible to decomposition. If the metal vapor escapes rather than recombines with the oxygen, the weld will become contaminated. North's explanation, however, does not appear to apply to CaO, perhaps due to its higher stability and lower metal vapor pressure.

The reactivity of the Al_2O_3 can be explained in terms of suboxide formation as suggested previously (Ref. 2). In any case, it is clear from Fig. 2 that the presence of the welding plasma significantly alters the predictions of oxide stability based solely on free energies of formation. Traditional slag-metal thermochemistry is inadequate to describe either the equilibrium or the kinetics of these reactions during welding. However, this is not to say that thermochemical data are not useful in studying welding fluxes; rather, the traditional concepts of stability and reactivity need to be modified to accommodate some of the differences noted.

Figure 3 further illustrates that CaF_2 does not alter the activity of SiO_2 in these fluxes. It will be noted that the pure CaF_2 flux did not alter the silicon content of the weld metal, confirming that the argon shielding was sufficient to eliminate atmospheric contamination. Nonetheless, the addition of as little as 10% SiO_2 to the

Table 1—Welding Conditions and Metal Compositions Used in This Study

Welding conditions:				
Voltage, volts (V)	30			
Current, amperes (A)	400			
Travel speed, mm/s (ipm)	6.55 (15.5)			
Electrode extension, mm (in.)	20 (0.79)			
Electrode diameter, mm (in.)	2.3 (0.09)			
Polarity	DCEP			
Electrode tilt angle, deg	O			
Supplementary shielding	Argon			
Metal composition, %				
	C	*Mn*	*Si*	*O*
Electrode	0.15	1.11	0.11	0.019
Base metal	0.13	1.37	0.37	0.0025

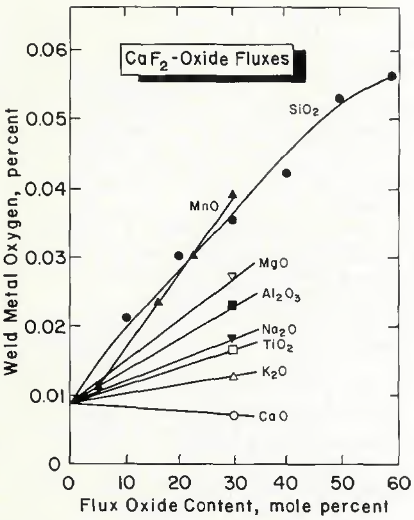

Fig. 2 — Weld metal oxygen analysis as a function of the percent metal oxide contained in the flux

CaF_2 causes a significant increase in the weld metal silicon content. If the activity of SiO_2 is altered markedly by CaF_2, it is unlikely that this small amount of SiO_2 in the flux would transfer to the weld metal. On the other hand, silicon transfer could be a two step process involving decomposition of the slag by the plasma and reaction of suboxides and oxygen in the plasma with the weld metal (Ref. 2); in this event, small amounts of unstable components in the flux will appear to react with the weld metal. This is confirmed by the strong SiO_2 reaction as shown in Fig. 3.

Others (Ref. 3, 4) have suggested that CaF_2 reduces the oxidizing potential of SiO_2 by the reaction:

$$2CaF_2 + SiO_2 \rightarrow 2CaO + SiF_4 \uparrow$$

Indeed, both the smell and the taste of SiF_4 gas is present when using highly basic fluxes containing small amounts of SiO_2. The law of mass action requires that at least some SiF_4 is formed during welding; however, the quantity may be small. The human nose can detect some odors in quantities as small as 10^{-16} grams; hence, the mere presence of the SiF_4 smell does not imply that it is a significant factor in mass transport between the slag and the weld metal. If it were, one might expect a loss of silicon from the weld metal by evaporation of SiF_4 when using $CaF_2 - SiO_2$ or pure CaF_2 fluxes. As shown in Fig. 3, this is not the case. Although SiF_4 undoubtedly forms in the flux shielded welding arc, it is questionable whether its formation contributes very much to the overall mass balance of either silicon or oxygen.

The strong decrease in Si in the weld metal with MnO additions to the flux is a result of oxidation of the weld metal by the MnO while the Si in the metal acts as a deoxidizer. From Fig. 4 it will be noted that a MnO free flux containing SiO_2 will result in SiO_2 as the oxidizing species and Mn as the deoxidizer. It is clear from Figs. 2 through 4 that, in either case, the oxidizing reaction is more rapid than the deoxidizing reaction as the total oxygen content increases in all cases. This was confirmed by the results of a 35% SiO_2 — 65% MnO binary flux in which the oxygen level was 0.064%. Mn increased to 1.78% while Si decreased to 0.18%.

It will be noted that this weld had a higher oxygen content than any of the fluoride-oxide fluxes. This may be due in part to the absence of CaF_2, which as stated above, dilutes the reactive oxide components. It is also due to the rapid oxidation of the weld metal by MnO (and perhaps SiO_2). The elevated oxygen level indicates that the Si deoxidation reaction cannot keep up with the MnO oxidation reaction. This is consistent with the view that the oxidation reactions are in fact plasma-metal rather than slag-metal reactions. These plasma-metal reactions are expected to be more rapid than the liquid-liquid deoxidation reactions.

Again, it will be noted from Fig. 3 that some of the more stable oxides such as K_2O and Na_2O do decompose in the plasma, producing oxygen in the weld metal; this reduces the silicon content by the deoxidation reactions.

Although more complicated than the previous two figures, Fig. 4 provides still further evidence of processes occurring during flux shielded welding. The 25% reduction in Mn content under the pure CaF_2 flux is notable. Considering that the oxygen and silicon concentrations in this weld did not change from their initial values, the conclusion is that the Mn is lost by evaporation. It is well known that Mn vapor dominates the welding arc and that large amounts may be lost over a period of time (Ref. 11), but the loss of 25% of the total during the brief period of

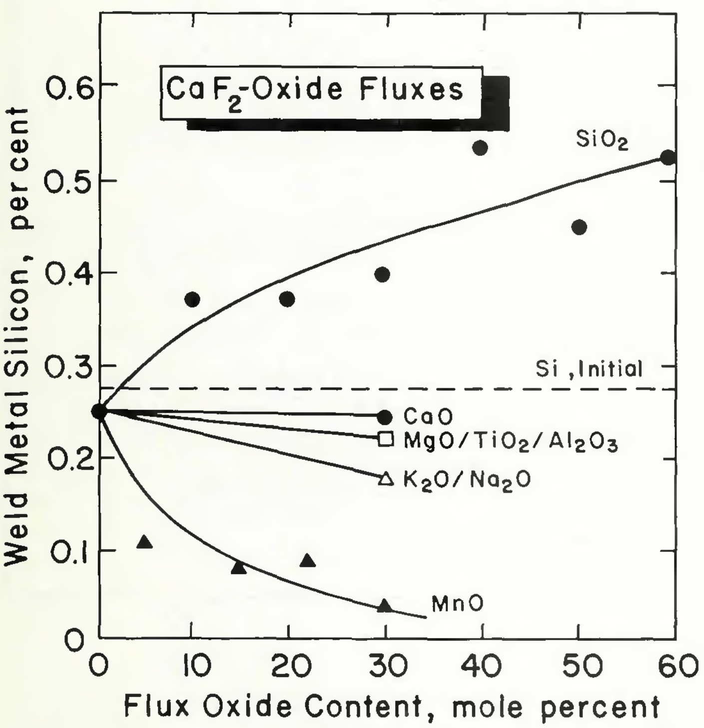

Fig. 3 — Weld metal silicon analysis as a function of the percent metal oxide contained in the flux

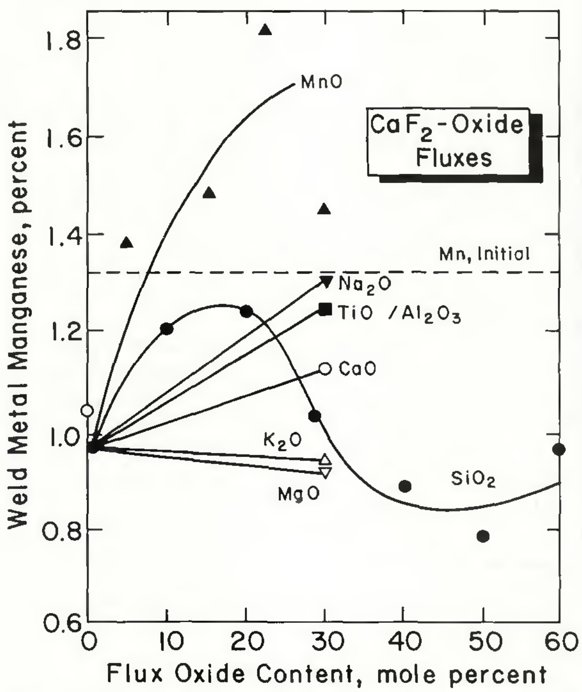

Fig. 4 — Weld metal manganese analysis as a function of the percent metal oxide contained in the flux

a single weld is most remarkable.

Both the rate and the extent of this metal transfer mechanism must be considered if one is to achieve an understanding of the kinetics of welding reactions. Unfortunately, the loss of only 13% of the Mn with the $CaF_2 - CaO$ flux and the general scatter of the data in Fig. 4 suggest that the evaporation rate is not very uniform. Figure 4 shows that as little as 5% MnO in CaF_2 causes an increase in Mn in the weld metal. This again confirms that CaF_2 is not significantly lowering the activity of the metal oxides in the flux.

The variation of Mn recovery with increasing SiO_2 in the slag is not fully understood. It may be that the oxidation of the weld surface by lower concentrations of SiO_2 tends to reduce the rate of Mn evaporation, while the oxygen contamination in higher SiO_2 fluxes decreases the weld metal manganese through a deoxidation reaction. In any case, the Mn reaction is much more complex than either the Si or the oxygen reactions if only due to the evaporation mechanism.

Conclusions

A study of oxygen, silicon and manganese recovery in binary CaF_2-metal oxides fluxes has shown the following:

1. CaF_2 reduces the oxidizing potential of welding fluxes, although the reason for the reduction is probably due to dilution of the reactive oxides by the CaF_2 rather than to reactivity of the CaF_2 itself.

2. Addition of CaF_2 will reduce the oxidizing potential of the most reactive fluxes by a significant amount, while CaF_2 has little effect on the more stable oxide components. This again suggests that CaF_2 acts as a dilutant rather than an active species.

3. In fluxes of low FeO content (less than 10%), SiO_2 and MnO are the primary sources of oxygen contamination.

4. The trend of oxide stability in welding cannot be deduced solely from steelmaking thermochemistry. The formation of suboxides and metal vapor in the plasma play important roles in establishing the reactivity of the flux.

5. Significant losses of Mn may occur by evaporation from the metal pool.

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