

THERMOCHEMISTRY OF JOINING

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ABSTRACT

The joining processes of soldering, brazing and fusion welding each involve a number of complex chemical interactions. Unfortunately, many researchers have felt that it is impractical to apply equilibrium thermodynamics to processes which are inhomogeneous both thermally and chemically; nonetheless, there have been a number of successful applications of thermochemistry to joining processes. For example, the reduction of surface oxides in soldering and brazing is readily explained by application of thermochemical principles. In recent times such approaches have been used to aid in development of brazing alloys for new ceramic/metal systems and in joining of metal matrix composites.

In fusion welding, thermochemical analysis has been used to aid in development of self-shielded steel welding electrodes; in prediction of fume formation during arc welding; in understanding evaporation-limited weld pool temperatures in arc, laser and electron beam processing; and in development of welding fluxes for both steel and titanium alloys. Similarly, thermochemical analysis of diatomic gas dissociation in welding arc plasmas can provide insight into the mechanisms of gas absorption during welding.

INTRODUCTION

Most joining processes have been developed empirically, which has resulted in a deficiency in our understanding of the scientific foundations of these processes [1]. Indeed, many researchers consider it impractical to apply quantitative analysis to processes which are strongly inhomogeneous both thermally and chemically. For example, in arc welding, temperature gradients can exceed 1000°C per centimeter and alloy chemistry can vary several-fold during reactions which occur in less than five seconds! Even if one is successful in developing a theoretical mechanism for a reaction, it is often difficult to test the hypothesis experimentally. Nonetheless, thermochemical analysis can be a powerful tool in determining which chemical steps control the joining process. Unfortunately, most engineers working in joining have meager education in chemistry and are unlikely to develop the quantitative chemical analyses which are necessary. Thus, thermochemical analysis of joining processes provides a fertile area for future research.

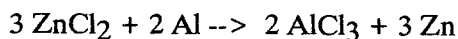
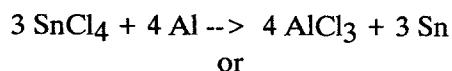
In this paper, a selection of some of the successful applications of thermochemistry to joining processes is presented. These examples show that such analysis can provide significant advances in our understanding.

Soldering and Brazing

There has been relatively little use of thermochemistry to explain soldering processes, in spite of the obvious importance of chemistry in the fluxing reactions. This is due both to the paucity of thermochemical data on the organic compounds which are used, and to decomposition of these organics during the fluxing process. Although soldering fluxes are characterized by their chemical "activity", this term is used only in a qualitative sense. The activity is often strongly time dependent and can be influenced markedly by surface contamination and moisture.

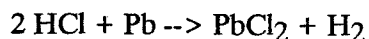
The action of the inorganic fluxes is much more amenable to quantitative thermochemical analysis. Clearly, ZnCl_2 or HCl in aqueous carrier systems can reduce copper oxides or sulfides, yet this author has not seen quantitative analyses of these processes. Most people appear satisfied to know that the flux works rather than worrying about the details.

Aluminum provides one successful application of thermochemistry to solder flux analysis. Anhydrous fluxes containing SnCl_4 or ZnCl_2 are capable of cleaning the surface of aluminum at temperatures below 400°C . Analysis shows that these chlorides are incapable of reducing aluminum oxide at these temperatures; rather, it has been shown that the tin chloride penetrates the surface scale and reacts with the aluminum metal to form aluminum chloride and metallic tin or zinc, viz.

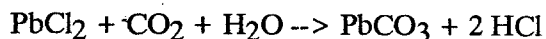


The free tin or zinc wets the aluminum and undermines the surface oxide, causing it to float away and combine with the flux [2]. If moisture is present, aluminum oxides, hydroxides or oxychlorides will form in preference to the aluminum chloride, thus reducing the activity of the flux.

Manko [3] explains the corrosion of lead-base solders in the presence of chlorides, moisture and carbon dioxide, as



followed by



It is seen that the HCl is regenerated in this process. Thus, even small amounts of chloride can create significant corrosion over a long period of time. This is why many specifications require chloride free fluxes for soldering of electrical circuits.

Metal-metal oxide equilibria in hydrogen atmospheres (see Figure 1) are useful for predicting brazing behavior in hydrogen and in

vacuum [4].

Kapoor and Eagar [5] have used thermochemical arguments to explain the greater activity of titanium as compared with zirconium in reactive solder and braze alloys for joining ceramics. For example, pure zirconium has a stronger affinity for reduction of nitride ceramics than does titanium; however, using Miedema's model for heats of mixing, they have shown that titanium possesses a greater activity as compared with an equal level of zirconium in liquid tin solders. These predictions are supported by experimental studies of wetting of ceramics by Sn-Ti and Sn-Zr alloys, as shown in Figure 2. Note that the Sn-Ti alloys are more reactive than the Sn-Zr alloys, even though pure Zr should have a greater affinity for Si_3N_4 than would pure titanium. The greater reactivity of titanium in these tin based solders can be explained by the higher activity of titanium as compared to zirconium in tin alloys.

Gas Welding

Use of thermochemistry to calculate adiabatic flame temperatures is neither novel nor unique to joining. Nonetheless, such calculations can provide considerable insight for selection of fuels for welding. The two most common fuels for gas welding are acetylene (C_2H_2) and methyacetylene-propadiene (C_3H_4). Estimates of the adiabatic flame temperature for these two gases are 3100°C and 2870°C respectively [6]. There is considerable debate as to which fuel is best. Using the adiabatic flame temperature and knowing that the rate of heat transfer from the flame varies roughly as the square of the flame temperature [7], one can estimate the useful heating value of these two gases on molten iron. Taking 1600°C as the temperature of the iron, the rate of heat transfer from C_2H_2 is proportional to $(3100-1600)^2$ while for C_3H_4 it is $(2870-1600)^2$. Thus the C_3H_4 produces approximately 30% less useful heat as compared with C_2H_2 . It is seen that even a 230°C increase in flame temperature can have a significant effect on the efficiency of the

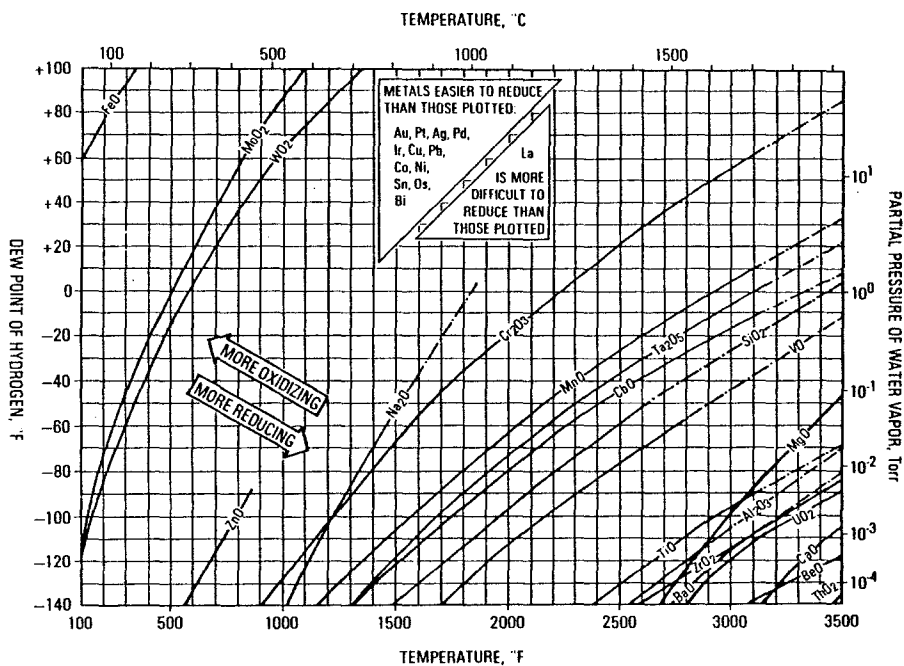


Fig. 1. Metal-metal oxide equilibria in hydrogen atmospheres. [Brazing Manual, 1976, American Welding Society, used by permission.]

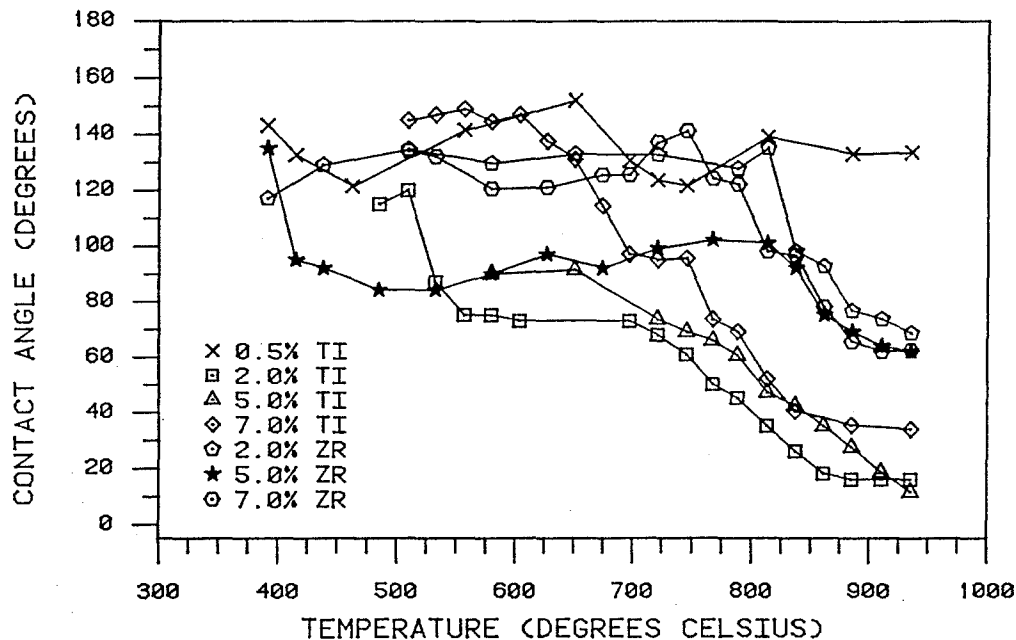


Fig. 2. Flow behavior of tin based alloys on silicon nitride. Heating rate of 5°C/minute.

flame. In practice, weldors know that one can weld more quickly with C_2H_2 than C_3H_4 , but few people realize that the improved performance is such a strong function of the adiabatic flame temperature. These calculations apply only to welding and not to oxy-fuel cutting. The two fuels perform essentially the same when used for cutting since the majority of the heat generated in the cutting process comes from oxidation of the iron, but this is a topic that will not be discussed further in this paper. The interested reader is referred to the excellent work by Wells [8].

Arc Welding

A number of successful thermochemical analyses have been applied to arc welding. Only a brief selection of these are presented below.

1. Fume Formation and Metal Evaporation

Increasing concern for environmental health has created an interest in both the rate and the composition of fumes generated during arc welding. Heile and Hill [9] have used thermochemical arguments to show that silicon in the fume is vaporized as silicon monoxide rather than metallic silicon. Indeed, the concentration of silicon in the fume increases significantly as the oxidizing potential of the shielding gas increases (see Table I).

From the oxygen concentration in Table I, it is clear that some of the fume is still in a metallic state. This is because much of the iron and manganese in the fume evaporates in an elemental form and condenses before becoming fully oxidized.

Block-Bolten and Eagar [10] have measured and calculated the ratio of iron, manganese and chromium evaporated from arc weld pools at various temperatures. Their analysis shows that the maximum temperature of a steel arc weld pool is approximately $500^{\circ}C$ less than the boiling temperature of the steel. This is due to the fact that the rate of heat loss due to evaporation at the

TABLE I. Composition of Gas Metal Arc Welding Fume on Steel at 300 amperes. (After Heile and Hill [9])

Shielding Gas	Mn, percent	Si, percent	Fe, percent	Oxygen, percent
Argon	4	1	46	49
Ar - 2% O_2	9	7	63	22
Ar - 5% O_2	6	14	47	33
Ar - 25% CO_2	8	17	52	23
CO_2	8	27	47	18

TABLE II. Estimated maximum weld pool temperatures of aluminum alloys based upon evaporative cooling. (After Gedeon [11])

Alloy	Theoretical Maximum Arc Weld Pool Temperature $^{\circ}C$	Theoretical Maximum Electron Beam Weld Pool Temperature $^{\circ}C$	Measured Electron Beam Weld Pool Temperature $^{\circ}C$
1100	1614	2091	1900 $\pm$ 100
2024	1290	1751	1700 $\pm$ 100
5083	1126	1491	1250 $\pm$ 100
6061	1358	1882	1800 $\pm$ 100
7075	909	1242	1080 $\pm$ 100

boiling temperature of the metal is many times greater than the rate of heat input to the weld. Thus, the maximum temperature of the weld pool is controlled by evaporation of metal from the pool. In the case of alloys with volatile components, the maximum temperature of the weld pool can be strongly influenced by the alloy composition. Table II shows how strong this effect is for several

aluminum alloys.

2. Gas Metal Reactions

The first arc welds, made over one hundred years ago, were performed without any gas shielding. Nitrogen in the arc was strongly absorbed by the steel weld pool, creating severe porosity in the solidified weld deposit. Major advances occurred independently in the United States and in Europe around the turn of the century. In the U.S., an enterprising weldor found that wrapping paper around the bare electrode eliminated porosity in the weld deposit. This was due to the formation of a hydrogen-carbon monoxide atmosphere as the paper burned. In Europe, another weldor found that an electrode coated with mud eliminated the porosity. This was the first flux shielded welding process.

For many years, the high levels of nitrogen or hydrogen absorbed in arc weld pools have been explained by application of Sievert's law. Such calculations required weld pool temperatures in excess of the boiling temperature of the metal in order to achieve agreement between theory and experiment. The model also predicted that the maximum gas absorption occurred in the hottest portion of the weld pool. Recently Gedeon and Eagar [12] have shown that consideration of monatomic hydrogen (or nitrogen) absorption provides more realistic weld pool temperatures. Clearly, monatomic gases are present in the arc and the presence of these highly reactive gases may dominate the gas absorption process.

The absorption of monatomic hydrogen is exothermic, hence the solubility decreases with increasing temperature. The absorption of diatomic hydrogen is endothermic, hence, its solubility increases with increasing temperature. The combination of absorption of both monatomic and diatomic gases results in a weak dependence of gas absorption versus temperature as the two species tend to compensate for one another as the temperature is changed. (Note that at the lower temperatures when absorption of monatomic

hydrogen is high, the fraction of monatomic hydrogen in the welding plasma is reduced.) Gedeon's estimates of solubility considering both forms of hydrogen at a constant concentration of 0.01 atm is shown in Figure 3. The calculated spatial distribution of absorption due to monatomic and diatomic species in the arc is shown in Figure 4. It is seen that most of the hydrogen is absorbed in the cooler regions of the weld pool. Previous hypotheses which were not based upon thermochemical analysis suggested that the gas is absorbed in the hottest portions of the weld pool. Thus, the thermochemical analysis has provided not only a more realistic estimate of weld pool temperature, but has shown a completely new trend of absorption versus temperature.

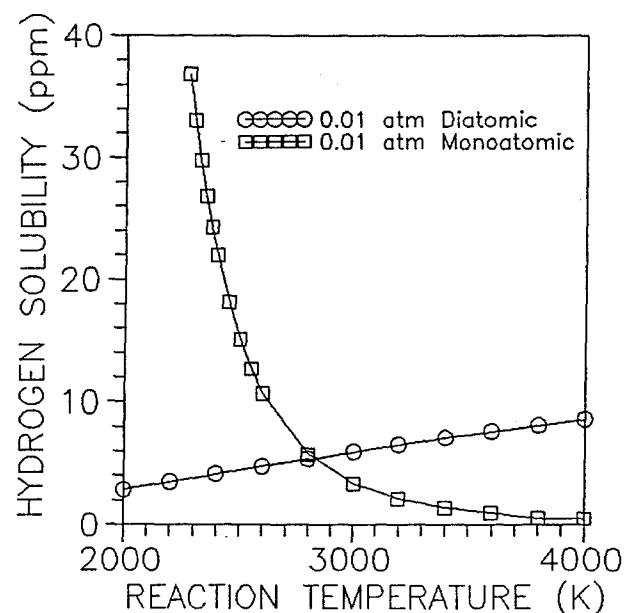


Fig. 3. Total solubility of hydrogen in a steel weld pool assuming that both diatomic and monatomic forms of hydrogen are present in the atmosphere. (After Gedeon [11])

Approximately twenty-five years ago, the welding industry developed self-shielded electrodes which do not require a shielding gas. These electrodes contain a powder core of aluminum and titanium which combine with the nitrogen in the weld pool to prevent evolution of nitrogen gas during solidification. Kaplan and Hill [13] have provided a thermochemical analysis of

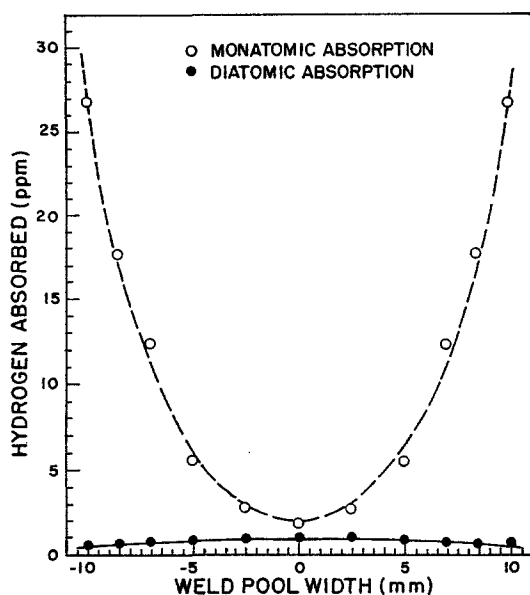


Fig. 4. Estimated spatial distribution of hydrogen absorption in an arc weld pool considering both diatomic and monatomic hydrogen species. Note that this was calculated based on measurements of the temperature gradient across the weld pool surface. (After Gedeon [11])

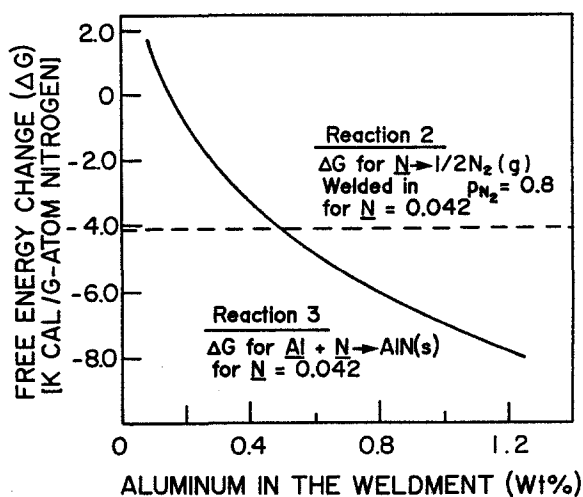


Fig. 5. Estimated free energy changes for reactions between aluminum and nitrogen in steel weld pools during solidification. (After Kaplan and Hill [13], reprinted with permission of the American Welding Society)

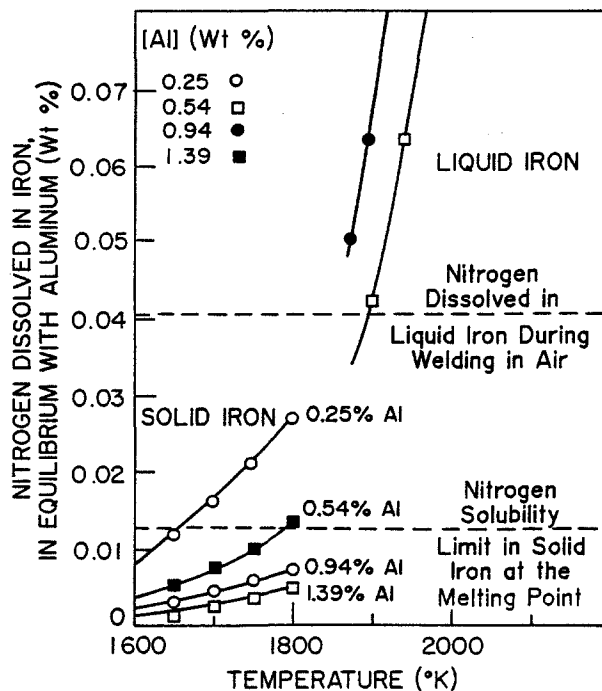


Fig. 6. Graphical solution of the aluminum-nitrogen equilibrium in iron. (After Kaplan and Hill [13], reprinted with permission of the American Welding Society)

this process. They note that the solubility of nitrogen in liquid steel at the melting point in air is 0.042 wt%. On solidification, the solubility drops to 0.012 wt% and the excess nitrogen creates porosity in the weld. By addition of more than 0.5 wt% aluminum, the pool is killed due to formation of AlN. Figure 5 shows Kaplan's theoretical analysis, while Figure 6 gives a graphical solution based upon the actual aluminum content of several tests welds. The welds made with 0.94 and 1.39% Al were porosity free, while welds with lower Al contents contained porosity. It is clear that the thermochemical analysis provides an accurate explanation of elimination of porosity in air-operated flux cored electrodes, in spite of uncertainties concerning the reaction temperature of the weld pool.

Another potential source of porosity in steel welds is carbon monoxide. The more oxidizing shielding gases such as carbon dioxide for gas metal arc welding can remove as much as 0.5% Si and Mn from the pool. If the Si level falls below approximately 0.1 wt%, carbon monoxide will form. Eagar [14], following work by Wright and Elliott [15], provided an estimate of the silicon content required to prevent CO porosity as shown in Figure 7. In practice, welding electrodes used with argon rich shielding gases typically contain a minimum of 0.5% Si and a similar level of Mn. Electrodes used with carbon dioxide shielding may contain both Si and Mn in excess of 1% since much of the silicon and manganese are oxidized by the carbon dioxide during welding. High initial Si and Mn are used such that the final weld deposit contains in excess of 0.25% Si and 0.5% Mn. Such silicon-killing prevents the formation of carbon monoxide porosities in the weld bead.

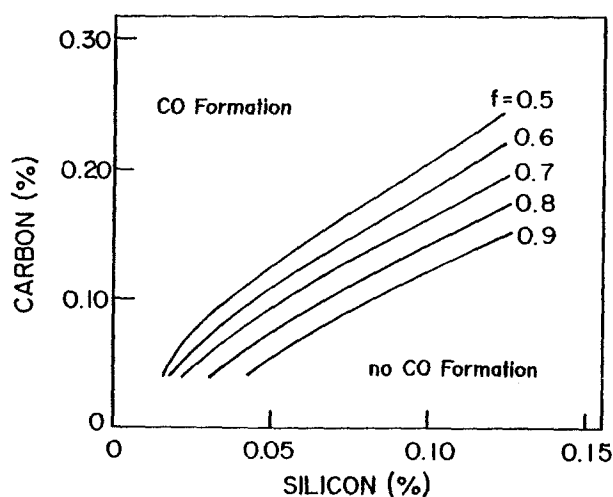


Fig. 7. The weld metal silicon content required to suppress CO gas formation (one atmosphere) as a function of weld metal carbon content for various fractions solid. (After Wright and Elliott [15])

3. Slag-Metal Reactions

a. Flux Shielded Welding of Steel

Analysis of reactions occurring during flux shielded welding of steel requires an accurate estimate of the weld pool temperature. One of the earliest, and leading studies was performed by Christensen and Chipman [16]. Their work clearly showed that the controlling reactions occurred in the weld pool rather than in the melting droplets and that the effective reaction temperature of the weld pool is on the order of 2000°C. Unfortunately, the value of this study was lost for the next twenty-five years. Soviet researchers performed extensive studies of slag-metal reactions in welding, but their analysis was hampered by the incorrect assumption of an effective pool temperature just above the melting point of iron. Such a conclusion can easily be disproved by heat transfer analysis, but this was not done and these researchers attempted to explain the chemistry based upon incorrect process physics for over a quarter of a century. The situation was not any better in the West. Researchers ignored to work of Christensen and Chipman and attempted to prove that droplet reactions controlled the metal chemistry for many years. In addition, most researchers assumed that the oxides were present in the slag at unit activity, thus producing a number of incorrect conclusions which still persist.

One important paper during this period was a paper by Belton, Moore and Tankins [17] which showed the importance of silicon reactions on deposit chemistry. They also found an effective pool reaction temperature of 2000°C, in agreement with Christensen and Chipman. In addition, they were the first to show the deposit oxygen chemistry was controlled by the activity of silica in the slag.

Eagar [14, 18] showed that the oxygen content of weld pools made with acidic fluxes was controlled by the silicon reactions, whereas iron oxide controlled the oxygen potential of more basic

slags. He also showed that silicon monoxide was the probable specie which controlled the silicon-oxygen equilibrium.

Although Christensen [16] showed that the concept of a working temperature had physical significance in welding, the question of whether the slag and the metal attained an effective equilibrium remained actively debated. Part of the problem was selection of an appropriate temperature at which to perform the calculations. Both Christensen [16] and Belton [17] showed that 2000°C appeared to work well; but other attempts to use this "effective equilibrium" or "neutral point" temperature failed to provide consistent results. A more significant problem was the assumption that the chemistry of the weld pool was controlled at 2000°C by the same mechanisms which control the chemistry of a steelmaking bath at 1600°C. Eagar's study [14] of the silica equilibria in acidic fluxes began to break down this assumption.

Chai and Eagar [19] presented a new theory based upon four assumptions, viz.

1. The effective temperature of chemical reactions in the weld pool is 2000°C,
2. An empirical relationship exists between the basicity of the welding flux and the weld metal oxygen content,
3. The activity data of steelmaking slag may be extrapolated from 1600°C to 2000°C assuming regular solution behavior, and
4. The primary reactions of interest involve silicon, manganese and oxygen.

Although somewhat simplistic, these assumptions provide a guide for prediction of weld deposit chemistry. The 2000°C assumption was based upon the prior work of Christensen [16] and Belton [17]. The acceptance of an empirical oxygen content was key in providing a successful approach to the problem. Much prior work attempted to predict the deposit oxygen content based upon Si and Mn levels. By reversing the dependent and independent variables, a successful new theory was

developed. The final two assumptions were merely for convenience in limiting the extent of the study.

The theory did not claim to predict the final deposit composition; rather it provided a "neutral point" or effective equilibrium composition toward which the system was progressing. It was shown that true equilibrium was not always attained between the slag and the weld metal, but that the direction of the chemical change could be predicted with accuracy for a wide range of fluxes and weld metals. Table III shows that for most fluxes, the difference between the theory and the experimentally determined value was small, often being less than the uncertainty in the chemical analysis.

TABLE III. Comparison of slag-metal neutral point calculated from thermochemical data and experimentally determined values. (After Chai and Eagar [19]) ΔMn and ΔSi represent the deviation between the theoretical prediction and the experimental observation.

Flux Basicity	Mn (theory), pct.	ΔMn	Si (theory), pct.	ΔSi
0.45	0	-0.10	---	---
0.46	1.10	-0.17	0.8	-0.15
0.50	0.40	-0.04	0.25	-0.04
0.52	0.20	0.05	0.15	-0.10
0.52	0	<-0.32	1.30	<0.12
0.53	0	-0.20	---	---
0.63	1.75	0.20	---	---
0.81	0	-0.10	---	---
0.85	1.25	0.00	0.50	-0.20
1.02	0.38	-0.18	---	---
1.17	1.83	-0.02	0.33	0.05
1.45	0	<-0.50	0.32	0.07

The next major advance in understanding the deposit chemistry of flux shielded steel welds came in 1985 when Lau, Weatherly and McLean [20], showed that the oxygen content of the droplet on the end of the electrode was on the order of 1000 to 3000 ppm, whereas the deposit oxygen in the solidified weld bead, was on the order of 200 to 800 ppm. This work clearly showed a decoupling between the oxygen reaction in the droplet and the Si and Mn reactions in the weld pool. The oxygen enters the droplet from the plasma, attaining very high concentrations, while the Si and Mn are deoxidizers in the weld pool. Mitra [21] extended this work to show that the final oxygen content of the weld deposit is controlled by the solidification time of the weld pool. Smaller weld pools, which solidify more quickly, trap more oxide inclusions, resulting in a higher oxygen content of the pool.

In a series of papers recently submitted, Mitra and Eagar [22-24] show that a simple kinetic model can be applied to Chai's neutral point analysis, to provide an accurate prediction of both the extent of the slag-metal reactions and the approach to the neutral point composition. Thus, this new model provides the answer to the long sought goal of a priori prediction of weld deposit composition in flux shielded welding based upon the starting compositions of the flux, the electrode and the base plate. Specifically, they show that the droplet theory, which states that the deposit composition is controlled by reactions in the droplet rather than in the weld pool, is incorrect. The decoupling of oxygen transfer from the silicon and manganese transfer is confirmed experimentally, as is the effect of solidification time and deposit geometry on resulting weld deposit composition. The theory is shown to apply to both single pass and multiple pass weld deposits, and can be applied to reactions involving Mn, Si, Cr, P, S, Ni, Cu and Mo. Examples of the results of this work are shown in Figures 8(a), (b) and (c) for Mn, Si and Cr, respectively. In general, the prediction of weld deposit alloy content compares with the measured composition with a correlation coefficient of 0.8 or better. Most of the results are within the experimental error of the chemical analysis.

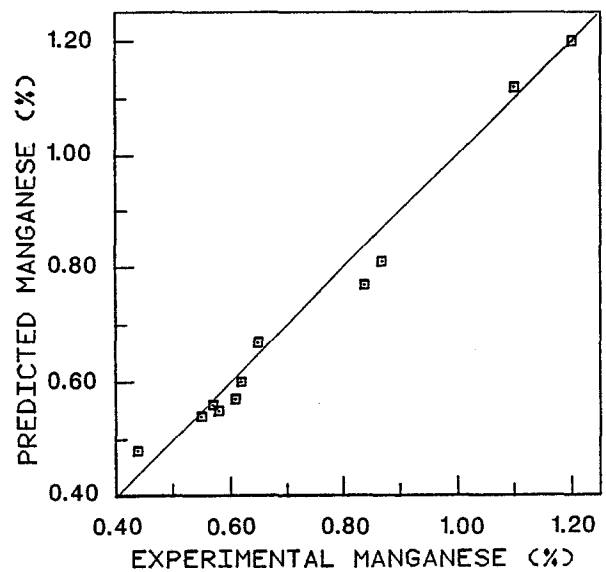


Fig. 8(a). Comparison of manganese content in single pass weld metal predicted by the kinetic model of Mitra and Eagar, to that obtained experimentally.

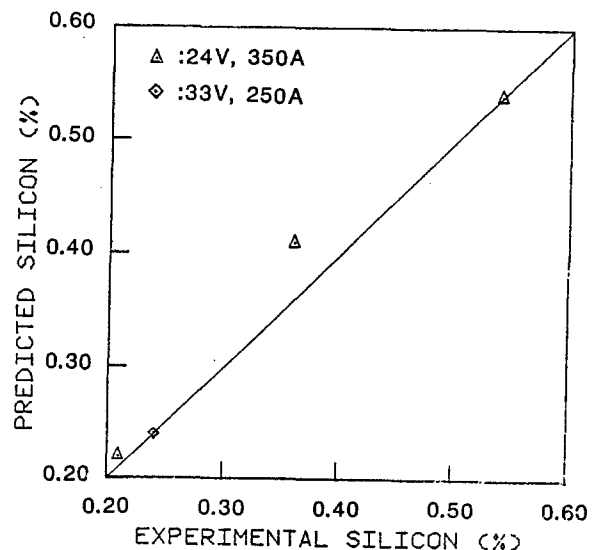


Fig. 8(b). Comparison of silicon content predicted by the kinetic model of Mitra and Eagar to that obtained experimentally. All welds made with identical flux and electrode, but performed in a water cooled copper mold in order to control the bead size and cooling rate independent of the arc voltage and current.

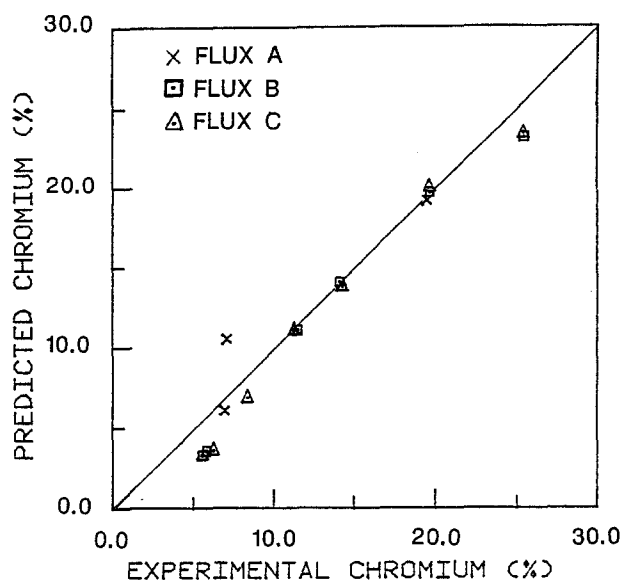


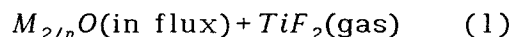
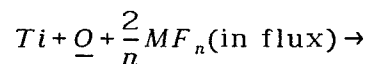
Fig. 8(c). Comparison of chromium content in single pass weld metal with the prediction of the kinetic model of Chai and Eagar. These welds were made using a number of different electrode compositions.

As noted at the beginning of this section, there are many other papers written on the subject of slag-metal equilibrium during flux shielded welding. Most of the early papers were empirical in nature. Two more recent papers which attempt a more theoretical analysis have been presented by Christensen and Grong [25] and Indacochea et al. [26]. These models are generally of more limited scope than Mitra's model, but are noted here for the benefit of the interested reader.

b. Flux Shielded Welding of Titanium

Although not generally used commercially, flux shielded welding of titanium has been studied extensively, especially in the Soviet Union [27]. The fluxes consist of pure halides, mostly based upon CaF_2 or SrF_2 . An interesting result shows that very pure halides can remove oxygen from the titanium [28]. In some cases weld metal of 2000 ppm oxygen initially was reduced to 700 ppm after melting under a CaF_2 - LaF_3 based flux.

In order to analyze which halide additions have the greatest effect on reducing the oxygen content of the weld deposit, Block-Bolten and Eagar [29] considered the metathetical reaction,



It is assumed that the metal fluorides and metal oxides in the flux are present at similar activity for equal concentration. Although very simplistic, this assumption is certainly more reasonable for these ionic halide melts than it would be for the polymeric oxide slags used with steels.

Table IV: Estimated Ability of Various Cations to Remove Oxygen from Titanium Melts in Contact with a Fluoride Flux. (After Block-Bolten and Eagar [29]) The most postent deoxidizer in titanium fluxes is judged to be tantalum pentafluoride, as it has the lowest value of ΔG based on equation 2.

Cation	Valence	ΔG (kcal/mole) [Eq. 2]	ΔG_f° (oxide) (kcal/mole)
Ta	V	63	-267
Sc	III	77	-316
Nb	V	71	-239
Ce	IV	69	-151
Y	III	93	-314
Hf	IV	79	-170
Zr	IV	96	-159
Al	III	91	-227
Cr	III	78	-137
La	III	103	-279

By comparing the estimated free energy difference between the formation of the metal oxide and the metal fluoride, i.e.

$$\Delta G = \Delta G_f^{\circ}(M_{2/n}O) - \frac{2}{n} \Delta G_f^{\circ}(MF_n) \quad (2)$$

one can predict the relative deoxidizing power of different cations in the flux. Table IV gives the expected refining power based upon this analysis. Generally, the results are consistent with the experimental results presented by Gurevich [27].

CONCLUSION

From the review presented above, it is seen that thermochemical analysis can be used successfully to define the permissible reactions occurring during a wide variety of joining processes. Generally, it is difficult to perform a complete analysis because the joining processes are inhomogeneous spatially, temporally and thermally. Nonetheless, the fact that thermochemistry can predict correct trends in the presence of such non-uniformities shows the power of the methodology. There remain a number of fruitful areas where thermochemical analysis can be employed. The oxidation of alloying elements from steel or nickel alloys in gas shielded arcs containing Ar-O₂ or Ar-CO₂ mixtures is one example. The reactive wetting of braze alloys on ceramics or metal matrix composites is yet another area capable of improved understanding through thermochemical analysis. Of course much work remains to be done in extending the work which has already been done.

One lesson to be learned from previous attempts is that the physics of the process must be understood in order to analyze the chemistry, and the chemistry must be analyzed using as complete a formalism as is available. This lesson has been taught to me powerfully by John Elliott whom we honor at this symposium. It was his approach which inspired me to apply thermochemical analysis to welding processes. For this inspiration and for his friendship, I am indeed grateful.

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