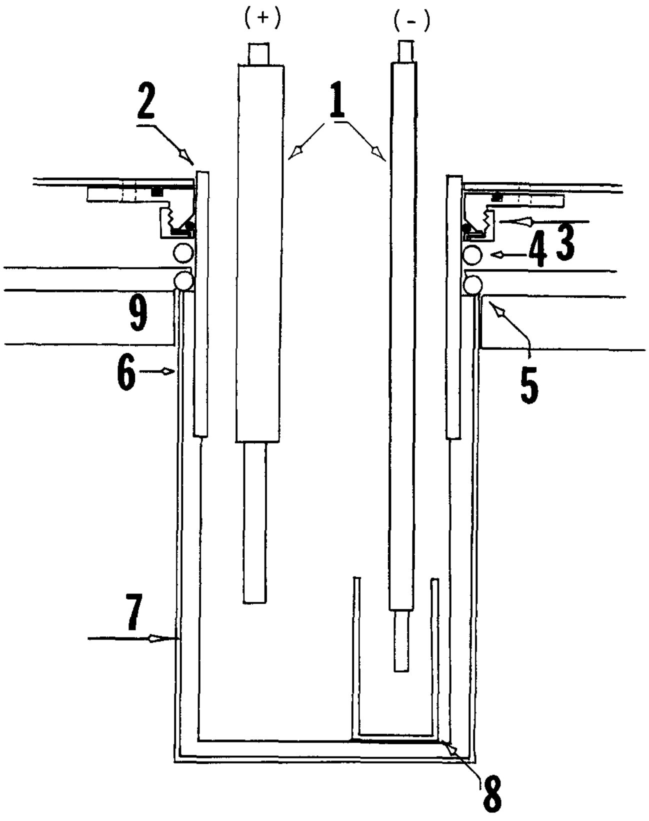

Fig. 1—Sketch of electrochemical cell: (1) alumina electrode sheaths, (2) alumina tube, (3) O-ring flange, (4) copper cooling coil, (5) HASTELLOY C-276 coil, (6) INCO 182 weld metal, (7) steel crucible, (8) alumina metal collection crucible, and (9) insulation.

This produced a material which had a water content of about 1 to 1.5 pct with negligible (0.4 pct) oxychloride formation.

Seon *et al.*[5] have shown that a cathode current density of 1.15 A/cm^2 is best. In experiments performed at Dow Chemical Company, Freeport, TX, it was found that current densities above 1.55 A/cm^2 were detrimental; neodymium was won faster than it could alloy with the cathode.

The ability of a cathode to form the eutectic with the electrodeposited neodymium is dependent on the impurity levels in the cathode, the most important impurity being carbon. Since the steel cathode will decarburize at the temperatures employed during electrowinning, it is hypothesized that formation of a neodymium carbide on the surface passivates the cathode.

Neodymium forms two carbides, NdC_2 and Nd_2C_3,[6] that appear to be stable at the temperature at which the cell is operated. Commercial steels are readily available with carbon levels as low as 0.03 pct. For an electrolytic process to be viable, the cost of the raw materials must be minimized. A steel of sufficient purity is necessary for a successful electrowinning process; as carbon levels fall, the cost of cathodes increases. Commercial AISI 1003 steel is readily available and relatively inexpensive. Metallurgical iron flake, which must be consolidated, has a cost of about \$4.4/kg, while high-purity iron cost is much higher, on the order of \$0.45/g, which would be prohibitively expensive. Transformer cores may

Table I. Carbon Level and Current Yield at 770 °C and $NdCl_3$/LiF/LiCl Bath

Cathode	Carbon Level	Current Yield
A36	0.30 pct	0
AISI 1010	0.10 pct	0
AISI 1003	0.03 pct	0
AISI 1001	0.09 pct	0
Electrolytic flake	0.0060 pct	6.9 pct
ESPI pure iron	0.0020 pct	50 to 90 pct
ESPI pure iron	0.0010 pct	50 to 90 pct

offer the required levels of carbon at a somewhat lov cost. Cathodes of differing carbon levels were tested consumable cathodes. The data are presented in Table

Consumable cathodes used in the formation neodymium-iron alloys must have carbon levels ne 0.002 pct, which are an order of magnitude lower th commercially available steels. This affects the econo ics of the route for eutectic manufacture since very l carbon steel cathodes would have been specifically m for this purpose.

REFERENCES

1. E. Morrice and M.M. Wong: *Miner. Sci. Eng.*, 1979, vol. 11 (pp. 125-36.
2. I.S. Hirschhorn: *J. Met.*, 1968, vol. 20 (3), pp. 19-22.
3. S. Singh, A.L. Pappachan, and H.S. Gadiyar: *J. Less-Com Met.*, 1986, vol. 120, pp. 307-15.
4. L.F. Druding and J.D. Corbett: *J. Am. Chem. Soc.*, 1961, vol. pp. 2462-2567.
5. F. Seon, G. Barthole, and P. Bobrue: European Patent 0184515, Rhone-Poulenc Co., France, 1986.
6. F.H. Spedding, K. Gschneider, Jr., and A.H. Daane: *J. Am. Ch Soc.*, 1958, vol. 80, pp. 4499-4503.

Modeling of Interfacial Phenomena in Welding

T. ZACHARIA, S.A. DAVID,
J.M. VITEK, and T. DEBROY

Variable depth of penetration during the welding different heats of the same material (compositions wit the specified allowable range) is a significant probl that has received much attention over a number years.[1–7] Previous work[6–12] by the authors as well other investigators has shown that knowledge of interfacial phenomena that occur during welding is key to understanding and ultimately controlling the p etration behavior. Often, the critical variable that c trols the variation in the weld pool size and shape is

---

T. ZACHARIA, S.A. DAVID, and J.M. VITEK, are with the Ridge National Laboratory, Oak Ridge, TN 37831-6095. T. DEB is with the Department of Materials Science and Engineer Pennsylvania State University, University Park, PA 16802.

Manuscript submitted November 8, 1989.

amount of surface active elements that is present in commercially available alloys. Several mechanisms have been proposed by which the surface active elements present in the molten metal could influence the depth of penetration during welding.[1-5] Of the various models proposed, the most widely accepted explanation is credited to Heiple and Roper[2] and Heiple *et al.*[3] They showed that surface active elements can significantly influence the development of the weld bead by altering the surface tension of the molten metal, thereby altering the surface tension gradient driven flow within the weld pool.

The development of the weld pool is controlled by the convective heat transfer in the weld pool during welding. In most cases, weld pool convection is influenced, and to a large extent controlled, by the spatial variation of surface tension (surface tension gradient) on the weld pool surface. Surface tension gradients are generated on the weld pool surface because surface tension is temperature- and composition-dependent, and large temperature gradients are generated on the weld pool surface during welding. The spatial variation of surface tension causes the molten metal to be drawn along the surface from a region of lower surface tension to that of a higher surface tension, resulting in large surface flows. Experimental investigations of surface tension gradient driven flows in the weld pool are extremely difficult and limited in scope. Computational modeling is an alternative approach that can provide an insight into the weld pool fluid flow and heat transfer. A serious limitation, however, in computationally studying the interfacial phenomena is the lack of adequate surface tension data.

For pure metals and alloys, surface tension decreases with increasing temperature. However, surface active impurities present in the molten metal segregate preferentially to the weld pool surface, altering the temperature dependence of surface tension. In iron-base alloys, sulfur and oxygen are the most important surface active elements commonly found. The surface tension of these alloys is a function of the oxygen and sulfur content and may increase or decrease with temperature depending on the thermodynamics of the segregation process. Belton combined Gibbs and Langmuir adsorption isotherms to describe the effect of surface active elements on the interfacial tension of liquid metal:[13]

$$\gamma_0 - \gamma = \mathrm{R}T\Gamma_s \ln\,[1 + Ka_i] \qquad [1]$$

where γ and γ_0 are the surface tensions of the solution and the pure metal, respectively, at the temperature of interest T; R is the gas constant, Γ_s is the surface excess at saturation; K is the adsorption coefficient of the solute; and a_i is the activity of the solute. This equation has been widely used to represent the surface tension of liquid iron as a function of sulfur and oxygen content. Recently, Sahoo *et al.*[14] expressed γ_0 in Eq. [1] explicitly as a function of temperature to obtain the following relation between surface tension of solution and temperature:

$$\gamma(T) = \gamma_m - A(T - T_m) - \mathrm{R}T\Gamma_s \ln\,[1 + Ka_i] \qquad [2]$$

$$K = k_1 \exp\left(\frac{-\Delta H^\circ}{\mathrm{R}T}\right) \qquad [3]$$

where A is a constant, γ_m is the surface tension of the pure metal at the melting point T_m, k_1 is a constant which is related to the entropy of segregation, and ΔH° is the standard heat of adsorption.

The equation described above (Eq. [2]) was used to represent the surface tension of molten Type 304 stainless steel as a function of temperature and sulfur content, and the results are presented in Figure 1. The values used for the calculations are presented in Reference 11. The results indicate that in the absence of sulfur in the weld pool, the surface tension of the molten metal, as would be expected, decreases with increasing temperature. In this case, surface tension would be highest near the periphery of the weld pool, thereby drawing liquid metal from the center to the sides and resulting in a recirculating outward flow. On the other hand, when the metal contains small quantities of surface active elements, the temperature dependency of surface tension of the material is drastically altered. Surface active elements present in the molten metal segregate preferentially to the weld pool surface causing the surface tension to be lowered. As the temperature of the melt increases, these elements desorb from the melt surface causing the surface tension to increase. Consequently, under certain conditions during welding, the surface tension of the liquid metal may be higher at the center of the pool due to the higher temperature directly below the heat source, thereby drawing liquid metal from the sides to the center of the pool and resulting in an inward recirculating flow. This phenomenon has been experimentally observed[2] using Al_2O_3 particles floating on the surface of the weld pool. However, the calculated surface tension data clearly show that this phenomenon can occur only within a particular temperature regime. As the surface temperature increases beyond a particular temperature, the temperature coefficient of surface tension reverses and the surface tension tends to decrease with increasing temperature, as shown in Figure 1.

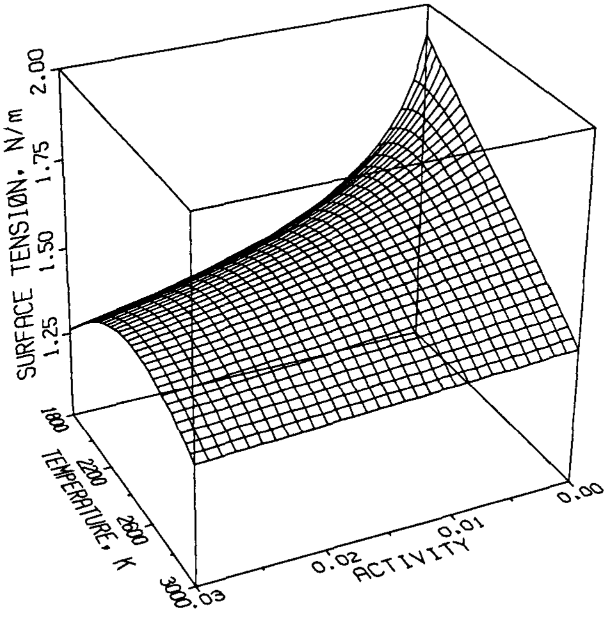

Fig. 1—Calculated surface tension as a function of temperature and sulfur content.

Previous computational studies[8,9,10] of weld pool fluid flow implicitly assumed that the surface tension of the molten metal continuously increased with increasing temperature for metals containing surface active impurities, thereby overestimating the effect of surface active impurities on the interfacial phenomena that occur. The results presented in Figure 1 indicate that surface tension gradients of opposing signs can exist on the weld pool surface depending on the weld pool surface temperatures. Therefore, the fluid flow in the weld pool is likely to be more complicated than a simple recirculation, as predicted by earlier investigations, since the peak surface tension is likely to be somewhere between the center and the periphery of the weld pool. The surface tension model described here was used to study interfacial phenomena and their effect on convective heat transfer during stationary gas tungsten-arc (GTA) and laser welding of Type 304 stainless steel.[11,12] The study showed that even when an alloy contained significant levels of sulfur, the flow field need not necessarily be a simple, recirculating, inward flow as suggested by previous investigations.[8,9,10] On the contrary, for the conditions investigated, it was shown that the weld pool fluid flow was predominantly outward, resulting in relatively shallow penetration. The higher surface temperatures and the associated melt surface tension gradient present during stationary GTA and laser beam welding resulted in an outward flow even though the molten metal contained significant levels of sulfur. The results of the study are presented in detail in References 11 and 12.

At the same time, previous experimental observations[2–8] of weld pool fluid flow during GTA welding have conclusively shown that surface active elements in the weld pool can result in an inward flow producing increased depth of penetration. However, these results were obtained for linear (moving) GTA welding. It was speculated that the lower power density and associated lower surface temperatures that occur during moving arc welds may have caused a positive surface tension gradient to exist on the weld pool surface, resulting in the observed inward flow during welding.[11,12] In order to confirm this premise, the fluid flow and heat transfer that occur during moving arc welds were computationally modeled for the two heats of 304 SS containing 90 and 240 ppm sulfur that were examined earlier.[11,12]

The flow field and the temperature fields during linear GTA welding were calculated in a two-dimensional plane along the welding direction for the heats containing 90 and 240 ppm sulfur. The welding parameters used were a welding current of 150 A, an arc voltage of 14 V, and a welding speed of 2.5 mm/s. The detailed information on the computational scheme and the thermophysical properties are given in Reference 11. The calculations of minor element effects on weld pool fluid flow and heat transfer were based on the initial sulfur content in the base metal and assumed no significant loss of sulfur due to vaporization. The sulfur loss in the fusion zone of GTA weld deposits of the two heats of 304 SS was evaluated in order to verify this assumption. The results confirmed there was no significant loss of sulfur during welding.

The calculated flow field and temperature field for the heat containing 90 ppm are presented in Figure 2.

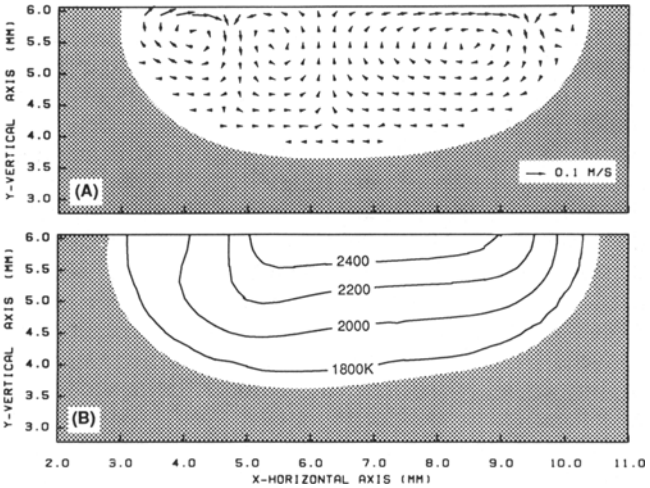

Fig. 2—Calculated heat flow and fluid flow during linear GTA we ing of Type 304 SS containing 90 ppm sulfur: (a) flow field (b) temperature field.

Figure 2(a) shows a complex flow field in the weld po with an inward flow at the leading and trailing edges the weld pool and an outward flow near the center belo the welding arc. It must be noted that for the heat co taining 90 ppm sulfur, surface tension increases with i creasing temperature until 2200 K and subsequent decreases with further increase in temperature. Ther fore, at the trailing edge of the weld pool where the te perature of the weld pool is below 2200 K, a positi $d\gamma/dT$ prevails on the weld pool surface and, con quently, the flow field is radially inward. Also, at t leading edge of the weld pool, there is a narrow regi where the surface temperature is below 2200 K ar consequently, a small inward loop which appears to ha a minimal effect on the overall flow and temperature fie exists at the leading edge. In the middle of the weld po the temperature is marginally above 2200 K and t negative $d\gamma/dT$ causes a radially outward flow. T calculated flow field is not a simple recirculating flo as one would have expected based on previous studi The maximum calculated velocities are of the order 0.1 m/s. The calculated velocities agree qualitatively w previous theoretical investigations. Figure 2(b) shows significant influence of fluid flow on the temperatu distribution in the weld pool. The inward flow at t trailing edge of the weld pool results in an increased de of penetration at the trailing edge of the pool.

The calculated flow field and temperature field for t heat containing 240 ppm sulfur are presented in Figure Figure 3(a) shows a radially inward flow in the weld po as suggested by previous experimental investigations. T higher sulfur content causes the surface tension to crease with temperature until 2450 K (Figure 1). Sir most of the weld pool surface is below 2450 K, t positive $d\gamma/dT$ over much of the weld pool surface p vails, producing an inward recirculating flow. The ma mum calculated velocities are once again of the order 0.1 m/s. Figure 3(b) shows the calculated temperatu distribution in the weld pool. The inward flow transpo hot liquid metal from directly below the arc to the b tom of the weld pool, causing an increased weld pe tration directly below the arc.

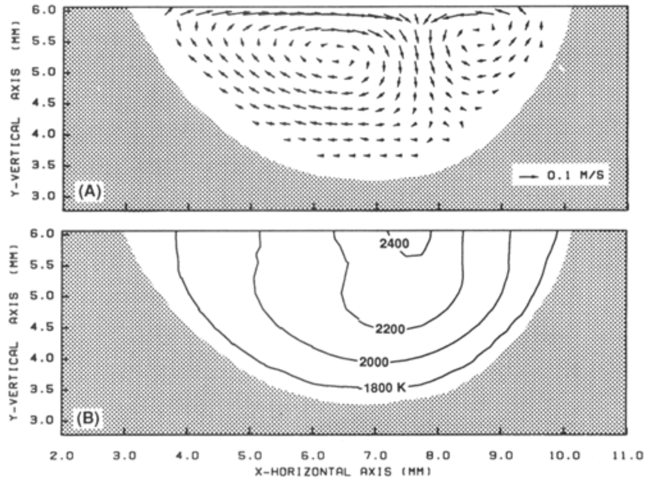

Fig. 3 — Calculated heat flow and fluid flow during linear GTA welding of Type 304 SS containing 240 ppm sulfur: (*a*) flow field and (*b*) temperature field.

The results presented here clearly show the significant influence of interfacial phenomena on the development of the weld pool. The results confirmed the modifying effect of surface active elements on the weld pool fluid flow and heat transfer. It has also been demonstrated that the effect of surface active elements on interfacial phenomena is a strong function of surface temperature and, hence, the welding parameters.

The authors would like to thank E.P. George and N.A. Morgan for reviewing the manuscript. The research was sponsored by the Division of Materials Sciences, United States Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. W.F. Savage, W.F. Nippes, and G.M. Goodwin: *Weld. J.*, 1977, vol. 56 (4), pp. 126s-132s.
2. C.R. Heiple and J.R. Roper: *Weld. J.*, 1982, vol. 61 (4), pp. 97s-102s.
3. C.R. Heiple, J.R. Roper, R.T. Stagner, and J.J. Alden: *Weld. J.*, 1983, vol. 62 (3), pp. 72s-77s.
4. G.W. Oyler, R.A. Matuszek, and C.R. Carr: *Weld. J.*, 1967, vol. 46 (12), pp. 1006-11.
5. S.S. Glickstein and W. Yeniscavich: *Weld. Res. Counc. Bull.*, May 1977, no. 226.
6. C.R. Heiple and J.R. Roper: *Weld. J.*, 1981, vol. 60 (8), pp. 143s-145s.
7. C.R. Heiple and P. Burgardt: *Weld. J.*, 1985, vol. 64 (6), pp. 159s-162s.
8. R.E. Sundell, S.M. Correa, L.P. Harris, H.D. Solomon, L.A. Wojcik, W.F. Savage, D.W. Walsh, and G.-D. Lo: GE Report No. 86SRD013, General Electric Company, Corporate Research and Development, Schenectady, NY, 1986.
9. S. Kou and D.K. Sun: *Metall. Trans. A*, 1985, vol. 16A, pp. 203-13.
10. T. Zacharia, A.H. Eraslan, and D.K. Aidun: *Weld. J.*, 1988, vol. 67 (1), pp. 18s-27s.
11. T. Zacharia, S.A. David, J.M. Vitek, and T. DebRoy: *Weld. J.*, 1989, vol. 68 (12), pp. 499s-509s.
12. T. Zacharia, S.A. David, J.M. Vitek, and T. DebRoy: *Weld. J.*, 1989, vol. 68 (12), pp. 510s-519s.
13. G.R. Belton: *Metall. Trans.*, 1972, vol. 3, pp. 1465-69.
14. P. Sahoo, T. DebRoy, and M.J. McNallan: *Metall. Trans. B*, 1988, vol. 19B, pp. 483-91.