Technical Note: Autogenous GTA Weldments—Bead Geometry Variations Due to Minor Elements

The nature of surface regions in a weld pool
are critical to the determination of weld bead shape

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Background

Investigations into the causes of variable weld depth-to-width ratios in materials of nominally the same composition have indicated that surface active elements and the Marangoni effect (Refs. 1, 8) play major roles. Simply stated, the Marangoni effect is nothing more than surface tension driven convection. All pure metals and many alloys exhibit a negative surface tension coefficient wherein the surface tension of a liquid decreases as the temperature is increased.

Since the temperature of a weld pool decreases from the center of the arc plasma column radially to the solid-liquid interface, a radial surface tension gradient exists on the weld pool surface. In the absence of surface active elements, the surface tension gradient leads to a radially outward flow from the weld pool center. If surface active elements are present, a positive surface tension gradient can be produced over a particular surface region in the weld pool. In this case, the surface tension driven flow leads to a radially inward flow and lower surface tension fluid. The fluid of lowest surface tension is located in the outer regions of the weld pool and flow is inward to displace high surface tension fluid closest to the weld pool center.

The investigations have centered on the Group VI (O, S, Se, Te) elements in the periodic table. These elements have low surface tensions and are surface active in iron-based alloys. Several investigations have considered the surface activity of selected Group V elements (N, P, As, Sb) and found that those studied

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are not surface-active in iron, despite having low surface tensions as elemental species. During welding, however, there is an interaction between the surface tension effects of Group V and Group VI elements when present in combination. The purpose of this paper is to propose an explanation for this behavior, and to present circumstantial physical confirmation of the surface tension mechanisms postulated.

Theory

Surface tension is a measure of the interatomic or intermolecular strengths (*i.e.*, interatomic spacing) in a material. Therefore, just as authors have correlated cohesive energies (Refs. 2, 3), diffusion coefficients (Ref. 4) and other properties with electronic configuration, so too can surface tension be correlated. With reference to Fig. 1, note that the surface tension of both Group V and Group VI elements — most notably phosphorous and sulfur — are markedly less than that of iron.

Based on the low value of surface tension and the existence of a miscibility gap in all binary alloys of iron with Group V and Group VI elements (Ref. 5), surface activity would be predicted along with precipitous declines in surface tension of the alloy system when compared to pure iron. This decline has been noted by direct experimentation for several Group VI elements (Refs. 6, 7), and inferred by indirect results in others (Refs. 8, 9). Investigations of the Group V elements have not shown analogous results, either by direct (Ref. 6) or indirect measurement (Refs. 10, 11).

The Gibbs isotherm equation mathematically describes a basic concept, whereby elements which decrease the surface tension of a liquid will segregate to the surface at the expense of the

entropy of mixing; the equation is:

$$\Gamma_{2,1} = - \frac{\partial \gamma}{\partial \ell n a_2} \tag{1}$$

where γ = surface tension; a_2 = activity specie 2; $\Gamma_{2,1}$ = surface adsorption 2.

The extent of segregation is fixed by kinetics and the minimization of system free energy. The interplay between the thermal gradient on the surface and the effective adsorption leads to Marangoni flow as a result of the radial surface tension gradients.

Experimental

A series of welds were made on alloy CN7M material with compositions shown in Table 1. Note the similarity in composition other than sulfur and phosphorus contents. The weld pools were decanted by an impulse decanting technique developed by Zanner and Savage (Ref. 12). Silicone rubber casts of the resulting cavities were made and the dimensional variables were measured. All welds were made with the conditions shown in Table 2, and the resulting depth-to-width ratios are summarized in Table 3.

Results and Discussion

Given the similarities discussed, a question arises: Why do sulfur and phosphorus cause such different behavior in the weld pool? An answer comes from an examination of the compounds that form in the surface regions of these alloys.

In a sulfur-rich surface region the compound FeS would exist (Ref. 6), and in a phosphorus-rich region Fe_2P would exist. These are the high temperature stable compounds of iron with sulfur and phosphorus, respectively. Kozakevitch and Urbain (Ref. 13) have measured the surface tension of molten FeS at 1550°C

Fig. 1—Elemental surface tension at the melting point as a function of the atomic number (Ref. 16). Atomic numbers for phosphorus and sulfur are 15 and 16, respectively

Table 2—Weld Variables Used For Decant Testing

Current, A	250
Voltage, V	12.6 Volts
Travel speed, ipm	3
Shielding gas	Argon
Shielding gas flow rate, cfh	35
Electrode diameter, in.	⅛ EWTH-2
Tip-to-work distance, in.	⅛

Table 3—CN7M Depth-to-Width Ratios

	Treatment				
Heat	C	Si	S	P	D/W
1	low	low	high	high	0.35
2	low	low	low	high	0.30
3	low	low	high	low	0.42

And: $M_{(L)} = 1.4471 \times 10^4$ K

Extrapolation from the data for the solid state yields a decomposition temperature for FeS (lnk = 0) of 2425°C (4397°F); imposing the correction for the heat of fusion gives a decomposition temperature of 2765°C (5009°F). However, it is not necessary for the FeS to be fully decomposed for sulfur to become surface active.

In Table 4, the extent of decomposition of FeS, based upon the data extrapolated into the liquid state, is shown as a function of temperature. Assuming that the temperatures on the weld pool range from a peak near 2100°C (3812°F) to a low of the liquidus temperature of the alloy welded (approximately 1390°C or 2534°F for Fe), a concentration gradient will be set up on the pool surface. Thus, although flow is governed by the variance in sulfur concentration on the pool surface caused by temperature and entropy considerations, a critical temperature will have to be reached before the concentration of sulfur is great enough to effect any change. Note that this aids in the explanation of more complex flows in weld pools.

In the cooler regions of the pool, sulfur will be bound as FeS, and the surface tension in this region will be high. Furthermore, the change in surface tension with temperature $\frac{\partial \gamma}{\partial T}$ will be negative, and radically outward flows will be generated in a ring bounded by the isotherm for a critical FeS decomposition level and the liquidus of the weld pool. Thus, the direction of flow would reverse at the locus of the critical temperature, T_C, as shown in Fig. 3.

(2822°F) and found it to be at a very low 350 dynes/cm (2 × 10⁻⁴lb-force/in.). This value of surface tension is not in accordance with the compound's melting point of 1190°C (2174°F). However, it is possible that the low surface tension is caused by the decomposition of iron sulphide at elevated temperatures similar to those found in weld pools.

An extrapolation of published data on the decomposition of FeS (Ref. 14), shown in Fig. 2, can be used to define a lower limit for the decomposition temperature. Also, the slope of the line in Fig. 2 can be used to calculate the heat of decomposition of FeS. In the solid region, the slope of the line is −1.639 × 10⁴K. The heat of decomposition for the solid $H_{D(S)}$, is related to the slope, $M_{(S)}$ by equation 2:

$$M_{(S)} = -H_{D(S)}/R(2.303) \qquad (2)$$

Thus: $H_{D(S)} = (1.639 \times 10^4$ K) (2.303) 1.987 cal/M K

Therefore, $H_{D(S)} = 75$ kcal/mole

When the material transforms to the liquid state, the slope of the line will change. This slope can be approximated by subtracting the heat of fusion (i.e., 7 kcal/mole) from the heat of solid decomposition to get the heat of decomposition in the liquid state, $H_{D(L)}$ as follows:

$$H_{D(L)} = H_{D(S)} - H_f = 68 \text{ kcal/mole}$$

Then by using the relation between the slope and the heat of decomposition, one can obtain an estimate of the slope for the decomposition when in the liquid region:

$$M_{(L)} = \frac{68 \text{ kcal/mole}}{(2.303) \ 1.987 \text{ cal/M K}}$$

Table 1—Compositions of CN7M Heats Used in Decant Test, %

Heat	Cr	Ni	Mo	Ma	Cn	C	Si	S	P
1	20.01	28.36	2.76	0.54	3.58	0.008	0.020	0.020	0.019
2	20.05	28.34	2.77	0.54	3.58	0.013	0.017	0.003	0.019
3	19.85	28.82	2.78	0.43	3.39	0.015	0.015	0.022	0.007

Fig. 2 — Negative of the logarithm of the reaction constant for the decomposition of the compound FeS as a function of the inverse of the absolute temperature (Ref. 13)

Table 4—log K as a f(T)

Temperature T, °C	log K
1375	−4.024
1500	−3.4
1600	−2.96
1700	−2.57
1800	−2.21

Fig. 3 — Complex flow pattern engendered by the locus of the critical decomposition isotherm. Critical temperature is T_c where pool surface tension is a maximum; T_l is liquidus of the base material

The compound Fe_2P melts at 1365°C (2489°F), almost 200°C (360°F) above the melting point of FeS. This difference in melting temperature is indicative of a greater stability, and probably a much higher decomposition temperature. Indeed, the free energy of formation for FeS is −17.5 kcal/mole at 1200°C (2192°F), while for Fe_3P, a compound less stable than Fe_2P, it is −34.4 kcal/mole at 1200°C (2192°F) (Ref. 15).

Thus, unlike sulfur, phosphorus would not be present in elemental form at the surface; therefore, it is not as effective in lowering the surface tension of the weld pool. Note that, as shown in Fig. 3, the decomposition isotherm for FeS could also explain the more complex circulations observed in the weld pool by Heiple. The interaction between sulfur and phosphorus can be explained based on the effect phosphorus has on the activity of sulfur — that is, phosphorus decreases the sulfur activity by forming iron-phosphorus-sulfur and phosphorus-sulfur compounds (Ref. 17).

Similar arguments indicate that other Group V elements — most notably arsenic (As) which forms the compounds Fe_2As and FeAs with melting points of 919 and 1030°C (1682 and 1886°F), respectively — would behave as depth-to-width

enhancers. Thus, As would behave in a manner similar to sulfur, a Group VI element, and quite differently from phosphorus, which is also a Group V element.

Examples of Surface Tension Effects in Weldments

Figure 4 shows cross sections of GTAW welds made on several heats of CN7M stainless steel. Note that the weld

bead surface is consistent with the Marangoni flow mechanism postulated by Heiple and Roper et al. (Refs. 8, 9). The beads with high depth-to-width ratios, as measured by impulse decanting, show a crowning as a result of the flow of material from the sides to the weld bead center. On the other hand, those with low depth-to-width ratios show a depression caused by flow from the center to the sides.

Conclusions

1. The nature of the surface regions in a weld pool are critical to the determination of weld bead shape. The concentrations of alloy components at the surface are quite different from those in bulk. Surface active species may be present as high temperature stable compounds with iron or other surface active materials, and will be dissociated to an extent determined by the heat of decomposition of

Fig. 4 — Welds exhibiting a low depth-to-width ratio (A) and a high depth-to-width ratio (B). Weld (A) exhibits a depression not only along the length of the bead but also in its terminal crater. Weld (B) exhibits a crowning in these regions. Note the epitaxy evidenced by the maintenance of orientation from the grains bordering the fusion line to the structures in the weld beads. Divisions at base of photographs are 1/32 in. increments

the particular compound. The degree of dissociation is strongly dependent on temperature. Thus, to cause flow reversal in the pool, a critical temperature corresponding to a critical free sulfur level would exist. This mechanism aids in the description of more complex weld pool flows and in the differentiation of the effects of Group V and Group VI elements.

2. The flow pattern on a weld bead surface determines the relief of that surface with respect to the surface of the plate welded.

3. Some Group V elements, arsenic for example, may affect the weld pool flow in a manner similar to sulfur (Group VI) but unlike phosphorus, even though it too is a Group V element.

Acknowledgments

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This bulletin contains three reports of work conducted under the guidance of the Subcommittee on Failure Modes in Pressure Vessel Materials of the Pressure Vessel Research Committee of the Welding Research Council. Funding for this three year project was supplied by the American Iron and Steel Institute and the Welding Research Council.

1. "Engineering Aspects of CTOD Fracture Toughness Testing," by G. W. Wellman and S. T. Rolfe. This report presents a study of the crack-tip opening displacement (CTOD) test method as a means of evaluating elastic-plastic fracture. Correlations with Charpy V-Notch, CTOD, J-integral, and stress intensity (K) notch-toughness parameters were investigated.

2. "Three-Dimensional Elastic Plastic Finite-Element Analysis of Three-Point Bend Specimens," by G. W. Wellman, S. T. Rolfe and R. H. Dodds.
   This report summarizes the verification of analytical procedures for use in flawed structures. As a first step toward analyzing the more complex structures of a pressure vessel, the three-point bend specimen was analyzed using both 2-D and 3-D elastic-plastic finite-element analysis methods. CTOD and J values determined from these analyses were compared to the experimental results of the five steels investigated in the first paper.

3. "Failure Prediction of Notched Pressure Vessels Using the CTOD Approach," by G. W. Wellman, S. T. Rolfe and R. H. Dodds.
   This report analyzes the behavior of five notched pressure vessels tested at temperatures such that the failure mode varied from fully ductile to brittle behavior. Both 2-D and 3-D finite-element analyses were used to analytically develop curves of pressure versus opening of the flaw in the vessel. The internal pressures corresponding to the minimum CTOD values obtained from the vessel steels were within 7% of the actual burst pressures.

The results of these works contribute significantly to the understanding and predicting of the different failure modes that can occur in pressure-vessel steels.

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