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 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 phosphorus 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:

$$\Gamma_{11} = -\frac{\delta\gamma}{\partial a_2}$$

where \(\gamma \) = surface tension; \(a_2 \) = activity specie 2; \(\Gamma_{11} \) = 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 FeP would exist. These are the high temperature stable compounds of iron with sulfur and phosphorus, respectively. Kozakevitch and Urban (Ref. 13) have measured the surface tension of molten FeS at 1550°C.
(2822°F) and found it to be at a very low
350 dynes/cm ($2 \times 10^{-4}$ lb-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 tem­
perature. 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 $-1.639 \times 10^4 K$.
The heat of decomposition for the solid
$H_{D(s)}$, is related to the slope, $M(S)$ by
equation 2:

$$M(S) = -H_{D(s)}/R(2.303)$$

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 decom­
position 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:

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

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

In Table 4, the extent of decomposi­
tion of FeS, based upon the data extrap­
olated 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 vari­
ance in sulfur concentration on the pool
surface caused by temperature and
entropy considerations, a critical tem­
perature 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. Further­
more, the change in surface tension with
temperature $\frac{\Delta \sigma}{\Delta T}$ 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 pool. Thus, the
direction of flow would reverse at the
locus of the critical temperature, $T_{C}$, as
shown in Fig. 3.
The compound Fe₃P 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 Fe₃P, a compound less stable than Fe₂P, 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 Fe₂As and Fe₃As 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

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**Table 4—log K as a f(T)**

<table>
<thead>
<tr>
<th>Temperature T, °C</th>
<th>log K</th>
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<tbody>
<tr>
<td>1375</td>
<td>-4.024</td>
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<tr>
<td>1500</td>
<td>-3.4</td>
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<tr>
<td>1600</td>
<td>-2.96</td>
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<tr>
<td>1700</td>
<td>-2.57</td>
</tr>
<tr>
<td>1800</td>
<td>-2.21</td>
</tr>
</tbody>
</table>

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**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 is liquidus of the base material.**

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**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

The authors gratefully note the support of NSF contract MEA82-08950 in this study, and the many helpful discussions with Dr. P.J. Ficalora of the Center for Integrated Electronics at R.P.I.

References