WELD-OVERLAY IRON-ALUMINIDE COATINGS FOR USE IN HIGH-TEMPERATURE OXIDIZING/SULFIDIZING ENVIRONMENTS

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Abstract

The development of iron-aluminide weld overlay coatings for high-temperature oxidation and sulfidation resistance critically depends on the determination of the aluminum concentration range for which good corrosion behavior and weldability coexist. This study demonstrated that a sound weld overlay composition with about 30 at.% Al has relatively low corrosion rates in a highly aggressive oxidizing/sulfidizing ($\text{H}_2\text{S} - \text{H}_2 - \text{H}_2\text{O} - \text{Ar}$) environment at 800°C . Its corrosion resistance was superior to alloys with compositions like that of type 310 stainless steel and FeCrAlloy. The results with this overlay composition can be explained on the basis of what is known about the effects of variations in aluminum and chromium concentrations on high-temperature oxidation/sulfidation from studies with bulk iron aluminides. While higher aluminum concentrations are even better for long-term corrosion resistance, the ability to reliably produce weld overlays of such compositions without hydrogen cracking is problematical and is the subject of continuing development.

IRON ALUMINIDES have several attractive attributes that have prompted many alloy development studies of these systems (see, for example, refs. 1 and 2). Alloys based on Fe_3Al and FeAl have been shown to have good-to-exceptional resistance to degradation in high-temperature oxidizing, oxidizing/sulfidizing, sulfidizing, and oxidizing/chlorinating gases (1,3-9). Indeed, the oxidation/sulfidation resistance of iron aluminides containing greater than about 18 - 25% Al (at.% unless noted otherwise) is maintained at temperatures that are well above those at which these alloys have adequate mechanical strength (for example, 800°C). Because of this and possible cost considerations, it is anticipated that appropriate compositions of iron aluminides may find application as coatings or claddings on more conventional higher-strength materials which are generally less corrosion-resistant at high temperatures.

In a previous paper (10), initial results from 800°C exposures of weld-overlay iron-aluminide specimens to a highly aggressive ($\text{H}_2\text{S} - \text{H}_2 - \text{H}_2\text{O} - \text{Ar}$) environment were reported. The investigation involved the characterization of the thermodynamic stability and reaction kinetics of these coatings, but did not determine their ability to physically separate the corrosive species from susceptible substrate material. Under conditions that produced coatings with ~35% Al, corrosion resistance equivalent to the best wrought iron aluminides was observed. A second set of weld deposits, with Al concentrations < 23%, showed significantly less sulfidation resistance.

A key issue in the development of appropriate weld deposit compositions is the determination of the optimal Al concentration. Based solely on oxidation/sulfidation considerations, higher Al levels are preferable (8). However, the susceptibility to hydrogen-induced (cold) cracking of the weld overlays increases with the concentration of aluminum in the deposit (11,12). This type of cracking occurs due to the combined influence of stress and available hydrogen. Stresses arise during cooling from the melt temperature after welding or from thermal cycling or impacts during service. As shown previously (5,10), lower levels of aluminum (~20 - 25% or less) don't appear to be sufficient to assure corrosion resistance of bulk aluminides or weld overlays in the mixed-gas ($\text{H}_2\text{S} - \text{H}_2 - \text{H}_2\text{O} - \text{Ar}$) environment, particularly if a significant amount of chromium is present. Therefore, it is of crucial importance to the overall iron-aluminide weld-overlay developmental effort to establish the compositional window, as schematically illustrated in Fig. 1, where high-temperature sulfidation resistance and weldability coexist. This paper addresses this issue by reporting recent oxidation/sulfidation results for an iron-aluminide weld-overlay deposit with an aluminum concentration that falls between the high (~35%) and low (11 - 23%) levels of the deposits studied previously (10). It also includes preliminary data on the cyclic oxidation behavior of type 304L stainless steel coated with this weld overlay as an initial indicator of the influence of thermally induced stresses on coating and corrosion product (scale) integrity.

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Fig. 1. Schematic representation of dependence of sulfidation resistance and cracking susceptibility on aluminum concentration of iron-aluminide weld overlays. White area is aluminum concentration window where excellent sulfidation resistance and good weldability coexist. Actual boundaries depend on concentrations of other elements in weld deposits (particularly, Cr) and particular processing conditions. Adapted from ref. 12.

Experimental Procedures

Weld-overlay deposits of Fe-Al alloys were produced using conventional manual gas tungsten arc techniques employing 3.2 mm-diam filler metals and argon shielding gas (11). Weld current was 80 - 120 amps DCEN at 10 - 12 volts. Travel speed was approximately 50 - 100 mm/min. A single layer of about 10 cm², and a thickness of 2 - 3 mm, was produced by overlapping stringer beads. Preheat was accomplished using an oxyacetylene torch with the interpass temperature maintained at a minimum of 350°C. Immediately after the welding process, the specimens were postweld heat treated at 750 - 800°C for 1 - 2 h followed by air cooling.

Rectangular pieces, approximately 18 x 12 mm, were cut from a weld overlay on type 304L stainless steel that was produced using filler metal H4 (Table I). A significant fraction of the deposits exhibited cracking following welding (11,12). However, the coupons used in the present corrosion experiments were taken from a sound weld overlay. For the sulfidation experiment, a specimen was prepared by grinding away the substrate material so that only weld metal (approximately 1 - 2 mm thick) remained. (The same procedure was used in the previous similar study - see ref. 10.) Oxidation/sulfidation behavior was then characterized by use of a microbalance to continuously measure specimen weight during exposure at 800°C to a flowing (~2 cm³/s) mixed gas consisting of 5.4% H₂S - 79.4% H₂ - 1.6% H₂O - 13.6% Ar (by volume). The oxygen partial pressure, as determined by a solid-state oxygen cell, was 10⁻²² atm, and the sulfur pressure was calculated to be 10⁻⁶ atm. The mixed gas represents an extremely aggressive environment and can be considered representative of a coal gasification application in which the temperature is high, the gas composition is very sulfidizing, and the oxygen partial pressure is sufficiently low to preclude formation of many surface oxides (but not alumina on Fe₃Al - see refs. 4 and 5). This type of experiment has been used to characterize the sulfidation resistance of many iron aluminides and several other alloys (5-8,13). More details regarding this type of experiment can be found in ref. 13. Specimens for

cyclic oxidation were cut from the weld pad, but, in this case, part of the type 304L stainless steel substrate (about 1 mm) was left attached to the deposits. These coupons were then exposed in individual pre-annealed alumina crucibles to static air at 1000°C for either 12 2-h or 2 24-h exposure periods. At the end of each period, the crucibles were taken from the furnace hot zone into the ambient atmosphere over a period of about 2 min. Both the weight of the specimen and that of any spalled scale (as collected in the crucible holding the coupon) were measured after every thermal cycle.

Table I. Nominal Composition (at.%) and Cracking Resistance of Developmental Iron Aluminide Filler Metals

Wire	Al	Cr	Other	Weld Deposit
O1-1	47	-	Ti, Zr, B	Cracks
O1-2	47	6	Ti, Zr, B	Cracks
O1-3	47	-	C, Mo, Zr, B	Cracks
O2-1	47	4	Nb, Ti, C, Mo, Zr, B	Cracks
O2-2	41	4	Nb, Ti, C, Mo, Zr, B	Cracks
O2-3	34	4	Nb, Ti, C, Mo, Zr, B	No Cracks
H1	47	4	Nb, Ti, C, Mo, Zr, B	No Cracks
H3-1	47	6	Nb, Ti, C, Mo, Zr, B	No Cracks
H3-2	47	-	Mo, Zr, B	No Cracks
H4	41	6	C, Mo, Zr, B	No Cracks

^a Determined by spark source mass spectrometry. Balance is Fe.

Results and Discussion

Development of Aspiration-Cast Filler Metal.

Examination of eleven compositional variants of wire, produced by aspiration casting at Oak Ridge National Laboratory or by a commercial supplier (Haynes International, Kokomo, IN) has helped define compositions which provide crack-free deposits on type 304L stainless steel and two Fe-Cr-Mo (2.25 and 9 Cr, 1 Mo, wt%) substrates. (See refs. 11 and 12 also.) These developmental compositions and the general cracking tendencies of weld deposits produced with the respective filler metals are shown in Table I. Although crack-free deposits can be produced with several of these filler metal compositions, preheat and immediate PWT must still be employed (typically at 350 and 750°C, respectively) to avoid cracking. Filler metals for alternate welding processes such as mechanized gas-tungsten arc and shielded-metal arc are being developed so as to achieve broader application of these alloys as weld-deposited coatings (12). For example, the availability of powder-cored filler wire in coil form for use in these processes would permit much better control of final deposit composition (see below) and decrease the cost of producing the overlays.

Dilution Effects. Due to the nature of the weld-overlay process, there is a loss of alloying elements during welding from vaporization and significant mixing of the filler metal and substrate materials during deposition. The final concentrations of the various elements in the weld deposit will therefore be between those associated with the respective filler metals and substrates. In the present study, because there is

no aluminum in the substrate, this element is diluted with respect to the filler material. As shown in Table II, which contains an analysis of a weld specimen taken from the same plate as used to make the respective coupons for the corrosion exposures, the aluminum concentration of the C4 overlay (30%) was significantly less than that of the filler metal used to make it (H4, Table I). The extent of this reduction in aluminum depends on losses during welding and the total amount of substrate material melted and thus depends on parameters such as current, voltage, travel speed, etc.

Similar dilution/enrichment considerations apply to the other elements. For example, Table II shows that the chromium and nickel concentrations of the deposit are greater than those of the weld rod due to pickup of these elements from the stainless steel substrate. The composition of the weld overlay is qualitatively consistent with the simple rules of mixing and with the general dilution/enrichment factors found previously (10).

Table II. Composition of Weld Deposit On Type 304L Stainless Steel (C4) Using Filler Metal H4

	at. % ^a
Al	30.4
Cr	9.0
Ni	2.5
Mn	0.5
Si	0.3
Mo	0.1
Ni	0.1

^a Determined by spark source mass spectrometry. Balance is Fe.

High-Temperature Sulfidation and Oxidation.

The gravimetric results for a corrosion specimen with the composition shown in Table II (C4) are shown in Fig. 2 for exposure to the H₂S - H₂ - H₂O environment. This figure also includes previous data (10) on compositions C1 - C3 (35 - 37% Al) and O1 - O3 (11 - 23% Al). (The complete compositions of these specimens are listed in Table III.) The measured weight gains of C4 are intermediate between these groupings of high- and low-aluminum alloys. Based on work with bulk iron aluminides (5), the aluminum concentration of C4 would be sufficient to yield the lower corrosion rates shown by the C1 - C3 specimens if its chromium concentration were limited to about 2%. - see Fig. 3. However, there is a substantial amount of chromium in this deposit (Table II) due to the mixing of the filler metal and substrate during welding (see above) and, as shown in Fig. 3 for bulk iron-aluminum alloys, such levels significantly increase the sulfidation rate (8). The increased weight gain with chromium concentration is probably due to this element disrupting the initial formation of a protective alumina scale that would otherwise grow on the alloy during exposure to the mixed gas (7). Based on what is known for bulk iron aluminides, the chromium level of the C4 deposit is certainly sufficient to increase the corrosion rate relative to the C1 - C3 specimens. Figure 3 also shows that the sulfidation of C4 is not as severe as a 27% Al alloy with 10% Cr. Based on simple rules of mixing, the use of the same filler metal to make overlays on Fe - 2.25% Cr - 1% Mo and - 9% Cr - 1%

Mo (wt%) steel substrates should result in coatings that have lower sulfidation rates than those shown by C4 because of the significantly lower chromium levels that would be incorporated into the deposit.

Fig. 2. Weight change versus time for iron-aluminide weld overlays exposed to 5.4% H₂S - 79.4% H₂ - 1.6% H₂O - 13.6% Ar at 800°C. See Tables II and III for the compositions of the various specimens.

Table III. Deposit Compositions Of Other Weld Overlays Referenced In Paper

	Concentration (at.%) ^a		
	Al	Cr	Other
C1	35.4	2.5	0.2 Nb, 0.4 Ti, 0.6 Mo, 0.2 Zr, 1.0 C
C2	36.7	4.7	0.2 Nb, 0.4 Ti, 0.6 Mo, 0.2 Zr, 1.0 C
C3	35.5	0.7	0.7 Mo, 0.1 Zr, 1.0 C
O1	11.1	6.7	6.6 Ni, 0.2 Mo, 0.03 Zr, 0.5 C
O2	23.1	6.3	6.3 Ni, 0.1 Nb, 0.1 Ti, 0.2 Mo, 0.1 Zr, 0.5 C
O3	21.7	2.1	0.1 Nb, 0.7 Mo, 0.1 Zr

^aDetermined by spark source mass spectrometry. Balance is Fe.

While the mass gain of C4 under exposure to the H₂S - H₂ - H₂O gas is significantly higher than that of the higher-Al C1, C2, and C3 compositions (Fig. 2), its corrosion resistance in this type of environment is still relatively good, not only when compared with the O weld-overlay specimens, but also with respect to austenitic stainless steels and FeCr alloys. This is illustrated in Fig. 4, which compares the

Fig. 3. Weight change versus time for weld overlay C4 and various bulk iron aluminides exposed to 5.4% H_2S - 79.4% H_2 - 1.6% H_2O - 13.6% Ar at $800^\circ C$. See Table II for the composition of C4.

Fig. 4. Weight change versus time for weld overlay C4 and other alloys exposed to 5.4% H_2S - 79.4% H_2 - 1.6% H_2O - 13.6% Ar at $800^\circ C$. See Table II for the composition of C4.

data for C4 with prior results (5,8) for Fe-27% Cr-18%Ni (similar Cr and Ni concentrations to that of type 310 stainless steel) and Fe-18% Cr - 12% Al (Fecralloy) exposed under similar conditions.

The gravimetric results for the cyclic oxidation of the two type 304L stainless steel specimens coated on one side with the C4 overlay are shown in Fig. 5. Each data point represents one thermal cycle (weight after cooling to room temperature from $1000^\circ C$). Filled symbols are used to denote

the specimen weights; the corresponding open ones are the weights of the spalled material. Evaluation of the effects of thermal cycling on the physical integrity of the deposit and on cracking and spallation of the protective alumina that forms is a key part of the development of these weld overlays as corrosion-resistant coatings for high-temperature oxidizing and sulfidizing environments. Because only one of the two major faces of the respective stainless steel coupons was coated, the gravimetric data shown in Fig. 5 are not a true indicator of the protectiveness of the coating. However, as an initial assessment of the influence of (albeit relatively mild) thermal cycles on deposit integrity, these results do not reflect any damage to the coatings. This conclusion is based not only on the lack of visible observations of cracking, but also by the absence of any rapid increase in weight after the first thermal cycle. Comparison of the 24-h data for the two coated coupons shows higher specimen weight gains for the coupon with 12 thermal cycles (versus one). This indicates some damage to the chromia and/or alumina scales due to thermal cycling, but the effect is not large - indeed, the total weight changes are fairly low and are comparable to what is measured for bulk iron aluminides exposed under similar conditions (14).

Fig. 5. Weight change versus time for two specimens consisting of weld overlay C4 on one side of type 304L stainless steel exposed to air at $1000^\circ C$. Each data point represents one thermal cycle to room temperature. The filled symbols are the specimen weights and the corresponding open ones are the weights of spalled material. See Table II for the composition of C4.

General Discussion. Iron-aluminide weld overlays can provide effective corrosion resistance in high-temperature oxidizing/sulfidizing environments provided the appropriate combinations of filler metal, process parameters, and substrate are used to produce adequate aluminum concentrations and minimal chromium contents. The present data for a weld overlay with 30% Al better define the necessary clad composition to achieve low sulfidation rates relative to

previous knowledge of this system based on data for groups of weld overlays with rather large differences in aluminum concentrations (10). An aluminum concentration of 30% should provide adequate corrosion resistance in oxidizing/sulfidizing environments. Corrosion performance could be further improved if less chromium were incorporated into the weld overlay either by process modification or by the use of substrates with lower chromium concentrations (such as Cr-Mo steels). Higher aluminum concentrations in the weld deposits would delay any onset of accelerated reaction caused by aluminum depletion that occurs after extended exposure times or repeated thermal cycles and associated scale spallation (15,16) and better offset the deleterious effect of chromium on sulfidation resistance (8). However, as discussed above, weld deposits containing high aluminum concentrations are more sensitive to hydrogen-induced cracking when exposed to moist air, even after stress relief. Therefore, pending further filler alloy development, it appears the aluminum level of the C4 weld overlay is close to the maximum concentration that provides adequate corrosion resistance without a risk of hydrogen-cracking (Fig. 1). As the sulfidation resistance is quite sensitive to both aluminum and chromium concentrations, it would be of value to develop and employ mechanized welding procedures to help assure that the targeted weld deposit composition could be produced in a reproducible manner.

As in the previous study (10), only the coatings themselves were tested in the sulfidizing environment. Therefore, oxidation/sulfidation results to date only reflect the thermodynamic stability and reaction kinetics of the weld deposits and do not address the effects of extended defects. The actual protectiveness of particular layers will also depend on the ability of these layers to provide a physical barrier that doesn't delaminate or allow corrosion of the substrate by ingress of reactive species via cracks or other defects. While the preliminary thermal cycling results reported here are encouraging in this regard, these aspects will have to be much more thoroughly investigated through exposure of clad substrates to particular corrosive environments under various thermal cycling conditions.

Summary and Conclusions

Because iron aluminides containing greater than about 18 - 25% Al have oxidation/sulfidation resistance at temperatures that are well above those at which these alloys have adequate mechanical strength, these alloys may find application as coatings or claddings on more conventional higher-strength materials which are generally less corrosion-resistant at high temperatures. For satisfactory application, it is necessary to define an aluminum composition range for which good corrosion behavior and weldability coexist. This study demonstrated that weld overlay compositions with about 30% Al can meet both criteria. Careful control of filler metal compositions and process parameters is necessary to assure crack-free weld overlays. Process control (with respect to dilution) and the choice of substrate can be used to minimize the chromium concentration of the deposit, which is indirectly proportional to the sulfidation rates of iron aluminides in both bulk and coating forms. In this regard, the corrosion behavior

of the coatings can be explained on the basis of what was known from previous oxidation/sulfidation studies with bulk iron aluminides. Even with a relatively high chromium concentration from deposition on type 304L stainless steel, the weld overlay with 30% Al showed substantially better oxidation/sulfidation resistance at 800°C than Fecralloy and austenitic stainless steel.

Sulfidation characterization focused only on the weld metal. As such, the corrosion characterization principally involved an assessment of the thermodynamic stability and reaction kinetics of the coatings. Preliminary cyclic oxidation results showed no drastic damage to the coatings on thermal cycling from 1000°C. However, the ability of such weld deposits to continue to physically separate the corrosive species from the susceptible substrate by remaining adherent and free of extended cracking under imposed in-service and thermal stresses remains to be evaluated in detail.

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