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Corrosion Resistance of Friction Surfaced AISI 304 Stainless Steel Coatings

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Corrosion resistance of friction surfaced AISI 304 coating in boiling nitric acid and chloride containing environments was found to be similar to that of its consumable rod counterpart. This was in contrast to the autogenous fusion zone of GTAW weld which showed inferior corrosion resistance with respect to the consumable rod. The superior corrosion resistance of friction surfaced coatings was attributed to the absence of δ-ferrite in it.

Keywords coatings, corrosion testing, stainless steels, surface engineering

1. Introduction

Traditionally, fusion welding based methods are used for producing corrosion resistant overlays. However, these techniques suffer from problems such as dilution with the base metal, microsegregation, cracking, porosity, entrapment of slag inclusions, etc. Friction surfacing is an upcoming solid state coating technique where melting and solidification are absent. This process has been used for obtaining various dissimilar metal coatings such as tool steel coating, stainless steel coating, Inconel coating on mild steel, and MMC coatings on titanium and aluminum (Ref 1-4). Dissimilar coatings were made possible by the generation of high contact stress and intimate contact between the coating material and substrate (Ref 5). A schematic of the friction surfacing process is shown in Fig. 1. The coating material in rod form is rotated under pressure over a substrate. Frictional heat generates a plasticized layer at the interface between the rod and the substrate. By moving the substrate across the rubbing face of the rotating consumable, a relatively thick plasticized layer is deposited.

Austenitic stainless steel weld overlays are highly resistant to general corrosion in moderately oxidizing environments in which they exhibit passivity. On some occasions, they may be exposed to mildly reducing environments such as hydrochloric acid for pickling, borderline active passive environment such as sulfuric acid and highly oxidizing conditions such as urea industry. Sulfuric acid attack of a phase or of chromium and molybdenum depleted regions next to σ-phase precipitates is commonly reported (Ref 6). Highly oxidizing environments such as those found in bleach plants could conceivably attack δ-ferrite networks and σ phase. However, this mode of attack is not often a cause of failure, probably because free-corrosion potentials are generally lower (less oxidizing) than that required to initiate attack. Preferential attack of δ-ferrite in type 316L weld metal is most often reported after prolonged HNO_3 exposure, as in nuclear-fuel reprocessing or urea production (Ref 6). In all the above cases, other than mildly oxidizing conditions, their corrosion resistance is significantly diminished. This is directly attributed to the attack on δ-ferrite in the austenitic matrix. European welding acceptance tests for urea synthesis demand absence of δ-ferrite for corrosion resistance (Ref 7). However, some amount of δ-ferrite has to be maintained in austenitic weld overlays to avoid solidification cracking (Ref 8).

The objective of this work was to evaluate the corrosion resistance of friction surfaced AISI 304 coatings and compare it with that of GTAW fusion zone. Experiments were carried out to analyse the performance of the coatings in aggressive corrosive environments and for pitting corrosion.

2. Experimental Methods

AISI 304 rods (Chemical composition (wt.%) 17.75 Cr, 7.7 Ni, 0.77 Si, 1.17 Mn, 0.08 C, and balance Fe.) of dimensions 18 mm diameter and 100 mm length were used for producing the friction surfaced coatings. The substrate used was low carbon steel AISI 1012 (chemical composition (wt.%) 0.12 C, 0.4 Mn, 0.02 P, 0.01 S) of dimensions 200 mm × 150 mm × 10 mm. A friction surfaced coating was produced on the substrate with the following parameters which were found to be optimum to produce thin and metallurgically bonded coatings: traverse speed 4.4 mm/s, axial load 10 kN, and a rotational speed 800 rpm (Ref 9). Test coupons were sliced out from the friction surfaced coating as well as GTAW autogenous fusion zone using EDM wire cut. The δ-ferrite content in test samples was measured using Fischer Feritscope (model FMP 30). Corrosion resistance was evaluated by accelerated boiling acid test and electrochemical tests. The boiling nitric acid test conducted was as per ASTM A262 practice 'C'. The test specimens were observed under scanning electron microscope (SEM) after the corrosion test. Pitting resistance was evaluated for friction surfaced coating and as-received consumable rod in

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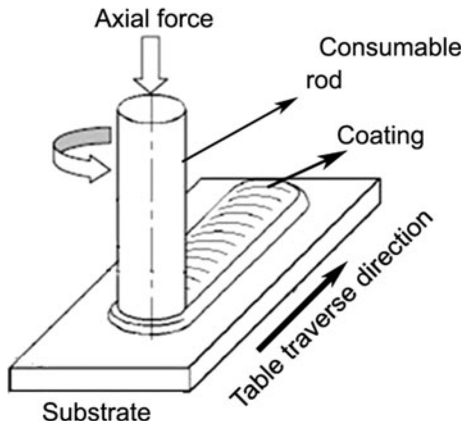

Fig. 1 Schematic of friction surfacing process

1 M H_2SO_4 + 0.1 M NaCl solution by electrochemical anodic polarization method.

3. Results and Discussion

Microstructural characterization of AISI 304 wrought material, AISI 304 friction surfaced coating and GTAW melted AISI 304 are shown in Fig. 2(a)-(c). AISI 304 wrought material showed equiaxed grains with occasional twinning (Fig. 2a). Friction surfaced coating showed a microstructure free of δ-ferrite (Fig. 2b). In contrast, the GTAW melted AISI 304 stainless steel microstructure showed δ-ferrite network in austenite matrix (Fig. 2c).

The Fischer Ferritscope measurements on the fusion zone of autogenously GTAW welded AISI 304 showed 6% δ-ferrite. It is interesting to note that the friction surfaced coating showed zero ferrite content despite the fact that the chemical compositions of the two samples is same. Autogenously GTAW welded AISI 304 showed a mixed austenite-ferrite microstructure after cooling to room temperature which is attributed to the fast cooling typical of arc welding processes. This is explained with the help of a pseudo-binary phase diagram of Fe-Cr-Ni (Fig. 3) (Ref 10). When the temperature of the liquid at dotted line is decreased it will pass through three-phase eutectic triangle $L + \gamma + \delta$ before it enters into two-phase region consisting of $\gamma + \delta$. The transformation of δ to γ will be complete with the decrease in temperature only if the cooling is very slow. As the cooling is relatively fast in welding operations, some amount of δ-ferrite will be retained in the weld metal.

The maximum temperature attained in the friction surfaced AISI 304 coating was found to be ~1350 °C (Ref 11). As can be seen from Fig. 3, in this temperature regime, the coating will enter in to the duplex structure zone $\gamma + \delta$. (It should be mentioned that the as-received rod was 100% γ due to its prior solution treatment condition.) Though, the coating entered in to duplex phase region, no δ-ferrite was observed. This could be attributed to the short dwell time in this temperature region. If the coating had been exposed to those temperatures for relatively long time, δ-ferrite could have formed. Different amounts of δ-ferrite were obtained in wrought austenitic stainless steel sheets when exposed to temperatures above 1200-1350 °C for 1 h (Ref 12). In the present case, the friction

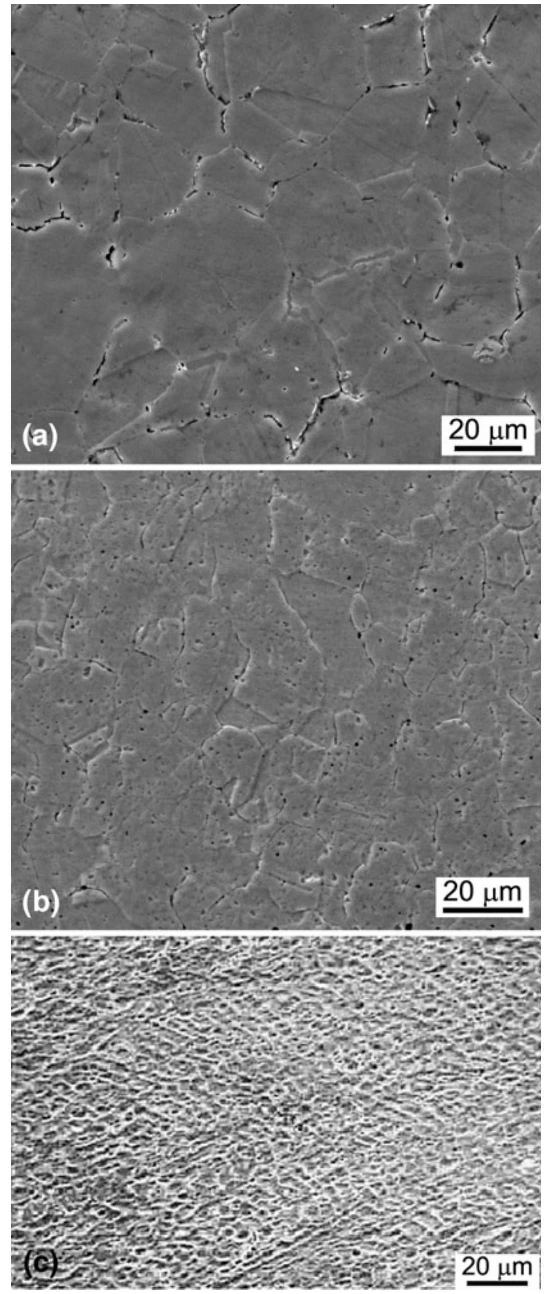

Fig. 2 SEM-SE image: (a) as-received AISI 304, (b) friction surfaced AISI 304 coating, (c) autogenous GTAW melted AISI 304

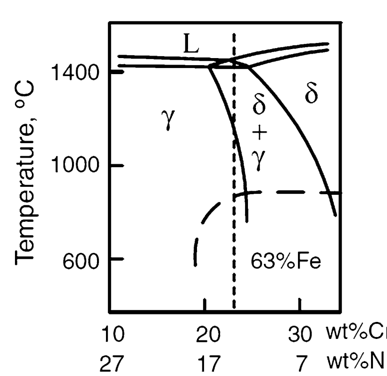

Fig. 3 Fe-Cr-Ni pseudo-binary phase diagram at 63% Fe (Ref 10)

surfaced coating cooled down to room temperature rapidly as the rod was moving further to make a continuous coating.

Therefore, single-phase austenitic consumable rods can be coated by friction surfacing to obtain a single-phase austenitic coating. Further, absence of δ-ferrite implies the absence of subsequent metallurgical transformations which are often disadvantageous from the point of view of mechanical properties. The δ-ferrite transforms into brittle intermetallic phases, such as σ and χ, at temperatures ranging from 500 to 850 °C for σ and 650 to 950 °C for χ (Ref 13). Continuous intergranular networks of a phase reduce the toughness, ductility, and corrosion resistance of austenitic stainless steels (Ref 14).

An important and significant advantage of friction surfaced AISI 304 coating over steel substrate is the absence of dilution with the base metal. Figure 4 shows the SEM-EDS line scan across the interface between coating and substrate. It was observed that there is no mixing of base metal with the coating. It means that one can get coating conforming to AISI 304 composition with a consumable rod of same composition. This is not possible by fusion welding processes. In order to compare the chemical composition of coating obtained by fusion welding, AISI 304 was deposited on steel substrate using GTAW welding process. It was found that the resultant coating contained chromium below 12% (Table 1). Further, the fusion welding based coatings showed martensitic microstructure (Fig. 5) which will impair the bend ductility requirement of coatings. In order to realize 18% Cr containing coating on steel substrate by fusion welding process, one should start with a highly alloyed consumable rod such as AISI 309 (containing about 25% Cr) (Ref 15). AISI 309 is costlier than AISI 304 in view of its higher alloying contents. The study showed that AISI 304 austenitic consumable rod can be coated by friction surfacing to obtain a AISI 304 austenitic coating.

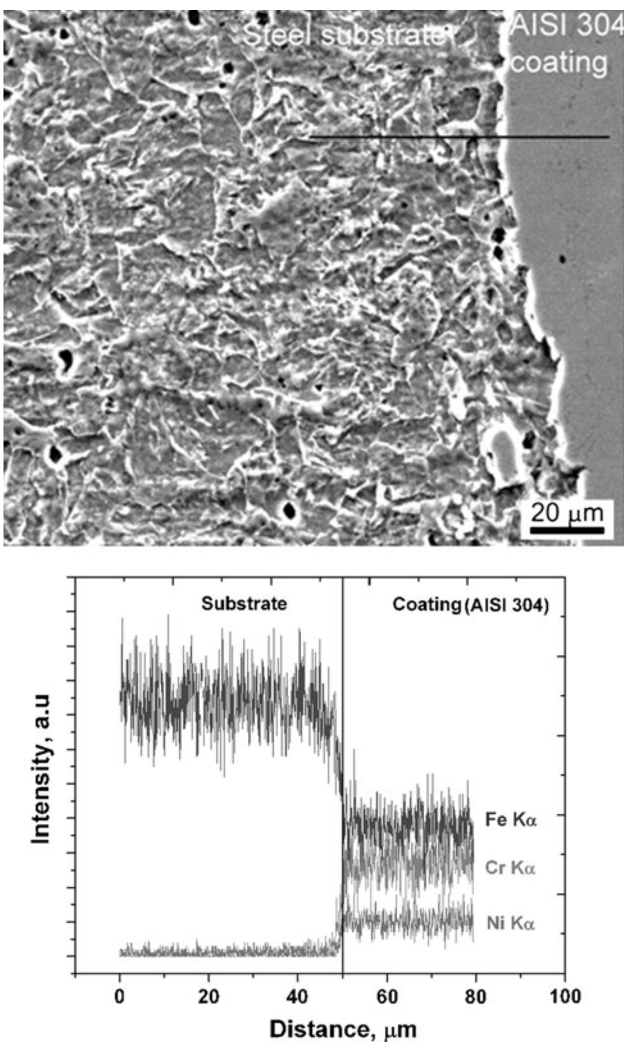

Fig. 4 SEM-EDS line scan across the substrate/coating interface

To compare the difference in corrosion resistance, as-received AISI 304 rod, friction surfaced AISI 304 coating and autogenously made GTAW fusion zone of AISI 304 were subjected to 65% boiling nitric acid test. SEM images of the tested samples after boiling nitric acid test are shown in Fig. 6(a)-(c). The as-received material and friction surfaced coatings did not exhibit any selective corrosion attack and were free from intergranular corrosion (Fig. 6a, b). In contrast, the fusion zone of AISI 304 GTAW sample exhibited selective attack on δ-ferrite (Fig. 6c).

Preferential attack associated with δ-ferrite and σ can be a problem in an austenitic stainless steel weldment when it is used close to the limit of corrosion resistance in environments represented by three types of acidic media:

- Mildly reducing (e.g., hydrochloric acid, HCl)
- Borderline active-passive (e.g., sulfuric acid, H_2SO_4)
- Highly oxidizing (e.g., nitric acid, HNO_3)

Acid cleaning of type 304 and 316 stainless steel evaporators in the pulp and paper industry with poorly inhibited HCl can lead

Table 1 Chemical composition from AISI 304 friction surfaced coating and AISI 304 coating by GTAW welding over low carbon steel substrate

	Cr, wt.%	Ni, wt.%	Fe, wt.%
Friction surfaced coating	17.78	8.63	73.59
Coating by GTAW welding	7.52	3.43	89

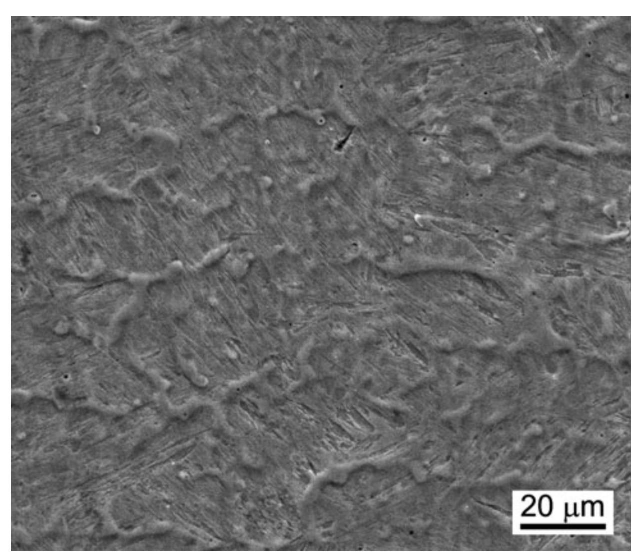

Fig. 5 SEM-SE image of AISI 304 deposited on steel substrate using GTAW welding process

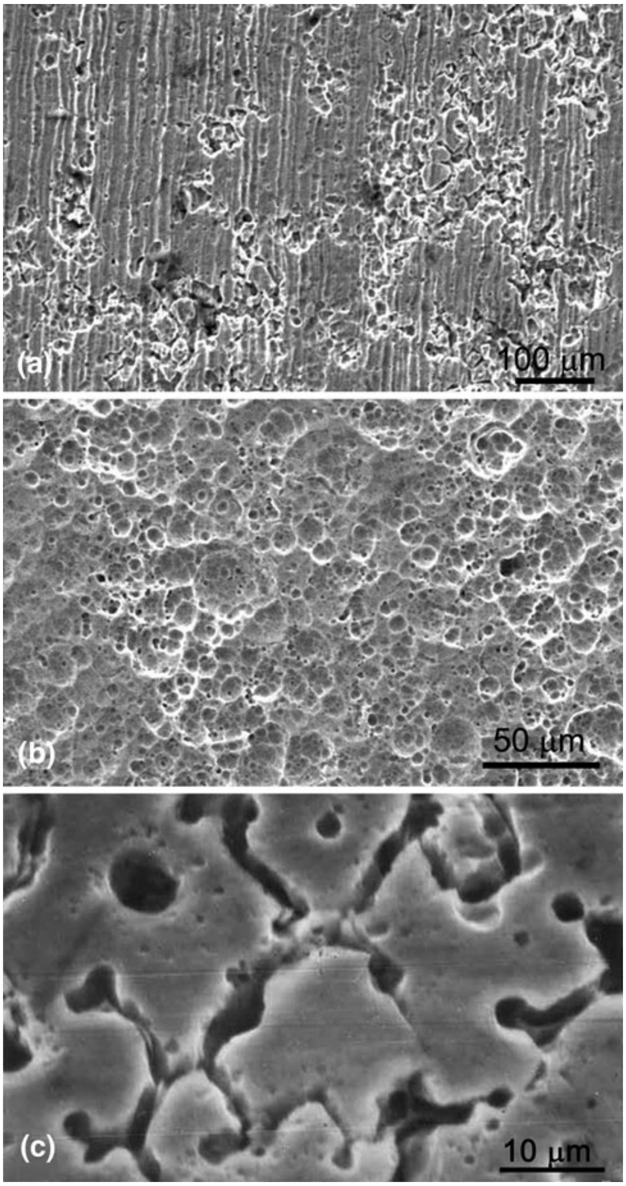

Fig. 6 SEM-SE image of samples after boiling nitric acid test: (a) as-received AISI 304, (b) friction surfaced AISI 304 coating, (c) autogenous GTAW melted AISI 304

to weld metal δ-ferrite attack (Ref 16). Under moderately oxidizing conditions, such as a pulp and paper bleach plant, weld metal austenite may suffer preferential pitting in alloy-depleted regions. This attack is independent of any weld metal precipitation and is a consequence of microsegregation or coring in weld metal dendrites (Ref 16).

Pitting resistance was evaluated for friction surfaced coating and as-received consumable rod in 1 M H_2SO_4 + 0.1 M NaCl solution by electrochemical anodic polarization method. The polarization results obtained are shown in Fig. 7 and Table 2 indicating E_{pit} values. It was found that there is no significant change in the pitting potentials of the friction surfaced coating and as-received rod material. This result shows that the severe plastic deformation occurring at elevated temperatures with higher strain rates in friction surfacing process did not lead to any reduction in the corrosion resistance of AISI 304 stainless steel coating. In contrast, the autogenous welded GTAW sample

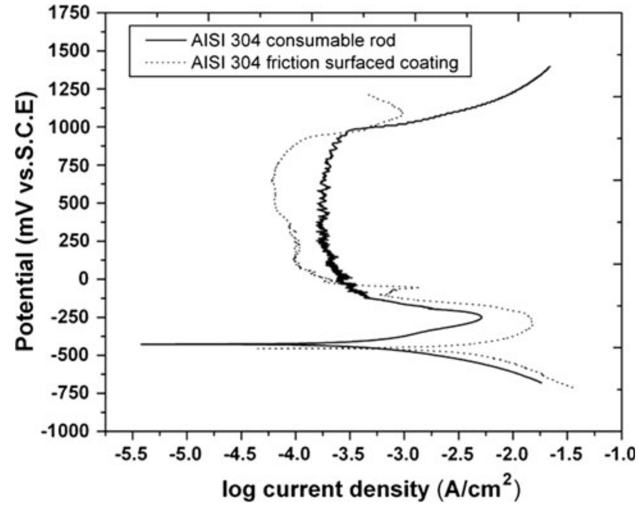

Fig. 7 Anodic polarization curve for AISI 304 as-received consumable rod and coating

Table 2 E_{pit} **for as-received AISI 304 consumable rod and AISI 304 friction surfaced coating**

	E_{pit}, mV SCE
AISI 304 As-received material	980
AISI 304 friction surfaced coating	994

showed decreased pitting potentials compared to their wrought counterparts (Ref 17). Pits develop more readily in metallurgically heterogeneous materials.

Austenitic stainless steel weld metal solidification is associated with alloy-depleted zones, alloy segregated interfaces, austenite/δ-ferrite interfaces leading to inferior corrosion resistance. δ-Ferrite in austenitic weld metals was found to be responsible for selective corrosion attack in certain environments (Ref 18). The presence of δ-ferrite also enhances the hydrogen embrittlement in austenitic weld metals by acting as hydrogen traps at ferrite-austenite interfaces (Ref 19).

The published data clearly shows that absence of δ-ferrite in stainless steel overlay coatings is very advantageous to avoid selective corrosion problems. Further, the problems associated with phase transformations and subsequent corrosion problems could also be avoided if δ-ferrite is absent in the coatings.

4. Conclusions

This study proves that AISI 304 stainless steel coatings made by friction surfacing can exhibit better corrosion resistance in various environments due to the absence of δ-ferrite. The results of the study can be summarized as follows:

1. Single-phase austenitic consumable rods can be coated by friction surfacing to obtain single-phase austenitic coatings.
2. Despite excursion to high temperatures (1350 °C), no δ-ferrite was observed in the friction surfaced coating. This could be attributed to the short dwell time in this

temperature region. In contrast, the GTAW melted AISI 304 stainless steel microstructure showed δ-ferrite (6%) network in austenite matrix despite the fact that the chemical compositions of the two samples is same.

3. Zero percent dilution was found in the friction surfaced AISI 304 coating over steel substrate. In the case of coating deposited by GTAW process, resultant coating contained chromium below 12%.
4. The consumable rod and friction surfaced coatings did not exhibit any significant selective corrosion attack and were free from intergranular corrosion. In contrast, the fusion zone of AISI 304 GTAW sample exhibited selective attack on δ-ferrite.
5. It was found that there is no significant change in the pitting potential of the friction surfaced coating when compared to consumable rod material.
6. AISI 304 stainless steel coatings made by friction surfacing exhibit better corrosion resistance than their fusion coated counterparts in various environments due to the absence of δ-ferrite.

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