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Corrosion Behavior of Weldments of Ti and Ti-5Ta for Nuclear Fuel Reprocessing Plants

U. Kamachi Mudali, R.K. Dayal, and J.B. Gnanamoorthy

Corrosion studies on specimens of nuclear-grade type 304L stainless steel, titanium, Ti-5Ta, and their respective weldments were carried out in a boiling nitric acid medium, as well as in boiling nitric acid containing hexavalent chromium and divalent silver ions. The weldments were prepared using a tungsten inert gas welding process. Titanium and its weldment showed excellent corrosion resistance in both media compared to 304L stainless steel. Specimens of Ti-5Ta alloy base showed excellent corrosion resistance, whereas its weldment showed higher corrosion rates in boiling nitric acid medium. Scanning electron microscopy and x-ray diffraction analyses were carried out on the tested specimens to examine the scale morphology and the phases present on the surface.

Keywords

304L stainless steel, corrosion, nitric acid service, nuclear fuel reprocessing plant, structural materials, titanium, Ti-5Ta, weldments

1. Introduction

NITRIC ACID is used extensively in nuclear fuel reprocessing plants, fertilizers, petrochemicals, and other chemical industries for various unit operations involving a broad range of concentrations, operating temperatures, and other chemical additives. In general, AISI (American Iron and Steel Institute) type 304L austenitic stainless steel is widely used for the construction of piping, vessels, pumps, and other equipment for nitric acid service. The corrosion resistance of this alloy is attributed to the stable chromium oxide film formed on the surface during service (Ref 1).

The reprocessing of the spent fuel from a nuclear reactor employs a series of complex chemical processes in complicated equipment and systems such as (1) dissolvers, where hot or boiling nitric acid is used; (2) solvent extraction vessels for the separation of uranium, plutonium, and fission products, where nitric acid is used at ambient temperature; (3) evaporators to concentrate the products in hot nitric acid; and (4) storage tanks for holding concentrated, warm nitric acid containing radioactive wastes. The selection of materials of construction for these vessels and tanks has a direct influence on the integrity of the equipment and the primary containment of radioactivity, which indirectly affects plant availability (Ref 2-4). In general, the temperatures of the process streams used in reprocessing operations are from room temperature to boiling conditions. The concentrations range from dilute to concentrated, containing ions such as Cr^{6+}, Ag^{2+}, Ce^{4+}, $Cr_2O_7^{2-}$, and Fe^{3+}.

The use of stainless steels for construction is not favorable under these highly oxidizing conditions, because such steels may undergo intergranular corrosion even in the nonsensitized condition (Ref 5-7). Many reported cases of failures in equipment made of austenitic stainless steels during plant operation have led to shutdown of the unit (Ref 4, 7, 8). Major causes of failure include sensitization; secondary phases such as sigma, $M_{23}C_6$, TiC, NbC, and delta ferrite; inclusions along the plane parallel to the rolling direction; and segregation of impurities such as boron, sulfur, and phosphorus along the grain boundaries. Titanium, tantalum, and their respective alloys as well as cleaner low-carbon, impurity-controlled nitric acid grade (NAG) stainless steels are considered as candidate materials for applications that face severe corrosion problems (Ref 8-15).

Welding is an indispensable process for joining of components fabricated for nitric acid service. It is well known that welding introduces secondary precipitates and makes the structure more heterogeneous compared to the base metal. Austenitic stainless steels have been reported to form delta ferrite, sigma, $M_{23}C_6$, and other precipitates during welding (Ref 16, 17). Also, the multipass welding of thicker components can lead to the formation of secondary precipitates in the welded region and sensitization in the heat-affected zones, significantly affecting corrosion resistance. In order to compare the corrosion resistance of weldments of 304L stainless steel, titanium, and Ti-5Ta with that of their respective base metals, experiments were conducted in boiling nitric acid as well as in boiling nitric acid with additives such as CrO_3 and $AgNO_3$. These additives represent the hexavalent chromium and divalent silver ions present in process streams of reprocessing plants, and they significantly affect the corrosion resistance of the materials of construction. The surface morphologies of the specimens tested were examined in a scanning electron microscope (SEM), and the scales formed on the surface in boiling nitric acid medium were analyzed by x-ray diffraction (XRD). Results of the investigations are discussed in this paper.

2. Experimental Method

The chemical compositions of the materials used in the present work are given in Table 1. Welding of titanium and of Ti-5Ta was carried out by the tungsten inert gas (TIG) process using argon as a cover gas in a special atmosphere chamber. Details of the welding parameters are given in Table 2. Nuclear-grade type 304L stainless steel was also welded by the TIG process using 308L filler wires (see Table 2). Nitrogen gas was partly mixed with the shielding argon gas in order to reduce the consumption of argon gas as well as to eliminate the formation of the secondary delta ferrite phase (Ref 18). The presence of

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Table 1 Chemical composition of materials (wt%)

Element	304L SS	Titanium	Ti-5Ta
Iron	bal	0.041	0.028
Chromium	18.33	...	...
Nickel	10.12	...	...
Oxygen	...	0.096	0.091
Nitrogen	...	0.003	0.005
Sulfur	0.004	...	...
Phosphorus	0.030	...	...
Tantalum	...	...	5.000
Carbon	0.033	0.015	...
Manganese	1.640	...	...
Silicon	0.064	...	...
Titanium	...	bal	bal

Table 2 Welding parameters

Titanium and Ti-5Ta	
Process	TIG
Current, A (dc)	60-85
Thickness, mm	3
Filler wire, diam	2.6 mm Ti/Ti-5Ta
Argon gas flow, L/h	700-850
Speed, mm/min	100
304L stainless steel	
Process	TIG
Current, A (dc)	60-65
Voltage, V	20
Thickness, mm	6
Filler wire, diam	1.6 mm 308L SS
Interpass temperature, °C	120
Number of passes	Four
Shielding gas	Argon + nitrogen

such phases significantly affects the localized corrosion behavior of austenitic weld metals (Ref 18, 19).

Specimens measuring 50 by 15 by 1.5 mm were taken from titanium, Ti-5Ta, and type 304L stainless steel and their respective weldments; they were polished using up to 600-grade SiC paper. The specimens were degreased in acetone, dried in hot air, weighed, and then immersed in a test solution of boiling concentrated (65 mass%) nitric acid. The corrosion tests in boiling nitric acid were conducted per ASTM A 262, practice C (Ref 20). A cold finger condenser was used to reflux nitric acid vapors into the test solution during the test. The ratio of solution volume to specimen surface area was about 50 cm^3/cm^2. Each specimen was suspended in the test solution by a Teflon thread and exposed for a total period of 240 h. Necessary care was taken to avoid the formation of crevices on the specimens. To observe changes in appearance and to measure changes in weight, the specimens were removed after every 48 h, and fresh test solution was used for each period. After testing, corrosion rates were calculated in both mils per year (mpy) and millimeters per year (mm/yr).

Experiments were also conducted in a test solution containing boiling nitric acid with 300 mg/L CrO_3 and 30 mg/L $AgNO_3$. The tests were interrupted every 100 h and changes in specimen weight recorded. This was done five times, for a total test duration of 500 h. Each time, fresh test solution was used for the study. Corrosion rates were calculated for each 100 h period. After the corrosion tests, the specimens from both experiments were examined using SEM to observe the changes in surface morphology, and the specimens tested in boiling nitric acid were examined using XRD to analyze the scales formed.

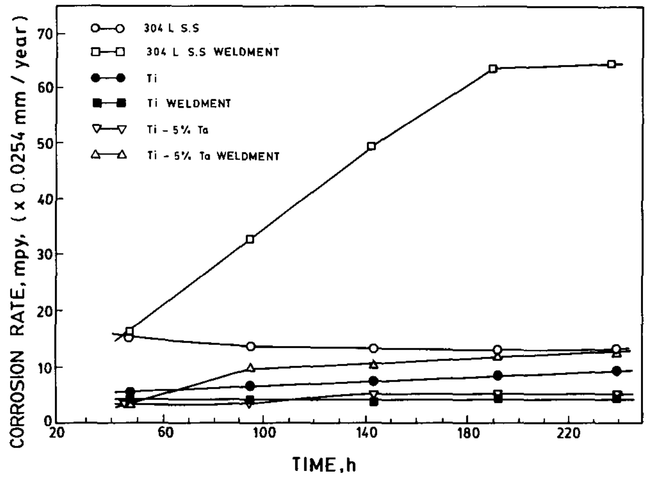

Fig. 1 Corrosion rate of materials in boiling nitric acid medium

3. Results and Discussion

3.1 *Corrosion Behavior in Boiling Nitric Acid Medium*

Figure 1 shows the corrosion rates obtained for the specimens in boiling nitric acid medium for different test durations. The corrosion rates of titanium specimens increased as the test progressed to 240 h. Since fresh test solution was used for every 48 h period, continuous dissolution of the film could take place, resulting in the increased corrosion rate values. In comparison with the base metal, the titanium weldment showed a lower corrosion rate (Fig. 1). However, the corrosion rate values of both were in the acceptable range (<20 mpy) for use of titanium in nitric acid service (Ref 14). The specimens of titanium and its weldment showed significant changes in their surface appearance as the testing progressed (Ref 15). The decrease in the corrosion rates of the titanium weldment compared to its base metal can be attributed to the change in the kinetics of the film growth due to the combination of both weld- and base-metal regions of the weldment. It was interesting to note that the weldment of titanium behaved in a similar manner as the Ti-5Ta alloy base, with identical corrosion rate values throughout the study. The heterogeneous microstructure containing base metal, heat-affected zone, and weld metal seems not to have affected corrosion behavior. The increase in the corrosion rate of the weldment of Ti-5Ta as the immersion period increased (Fig. 1) could be attributed to intermetallics as well as to the complex microstructure that is formed during welding. The addition of body-centered cubic tantalum would have influenced the formation of beta-phase secondary precipitates.

The specimens of type 304L stainless steel and its weldment showed high corrosion rate values (Fig. 1) compared to titanium and Ti-5Ta alloy and their respective weldments. Spallation of grains and visible roughening of the surface were

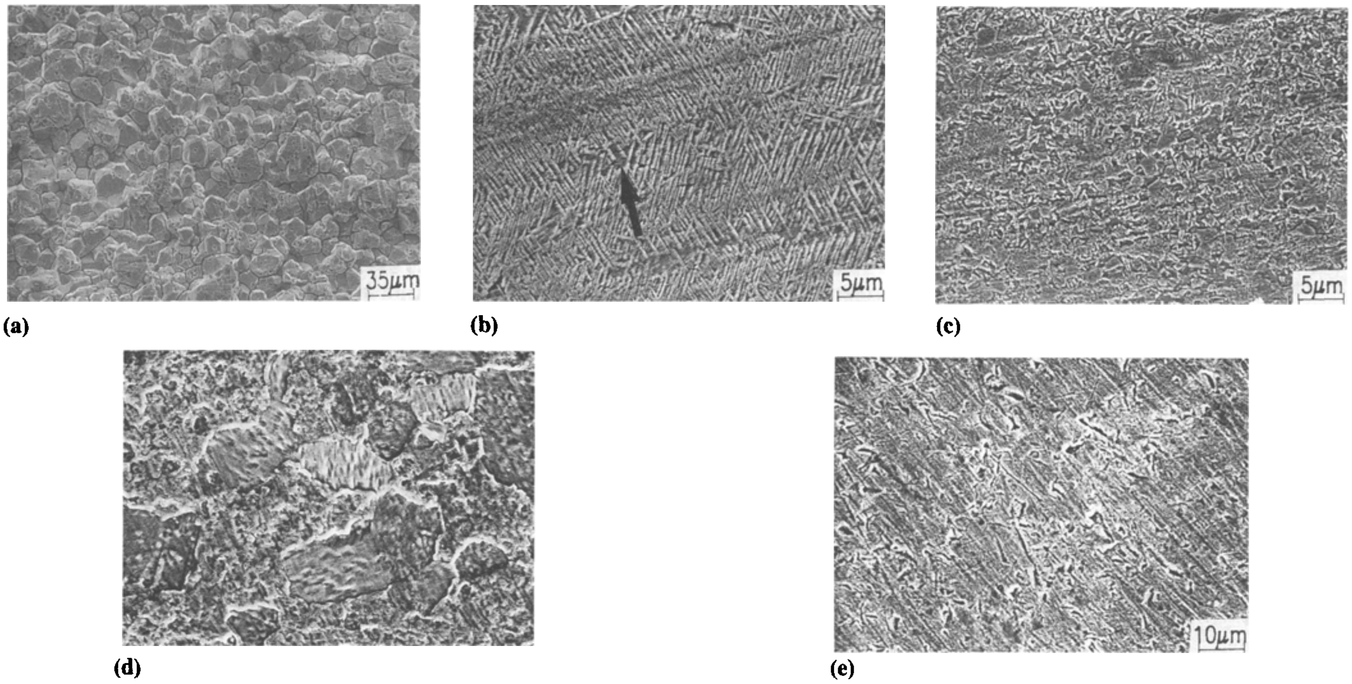

Fig. 2 SEM micrographs of specimens tested in boiling nitric acid medium for 240 h. (a) 304L stainless steel with spalling of grains and grain-boundary grooving. (b) Ti-5Ta weld with dissolution around needle-shaped secondary precipitates. (c) Ti-5Ta weld with uniform dissolution. (d) Titanium with uniform dissolution. (e) Titanium weld with a uniform oxide coating

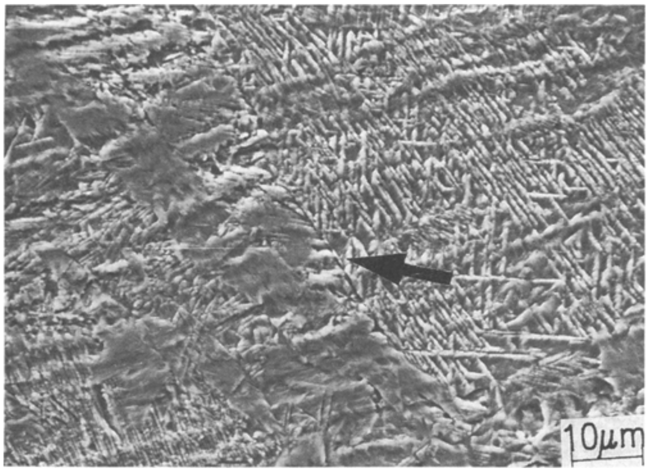

Fig. 3 SEM micrograph of Ti-5Ta weld after testing in boiling nitric acid for 240 h

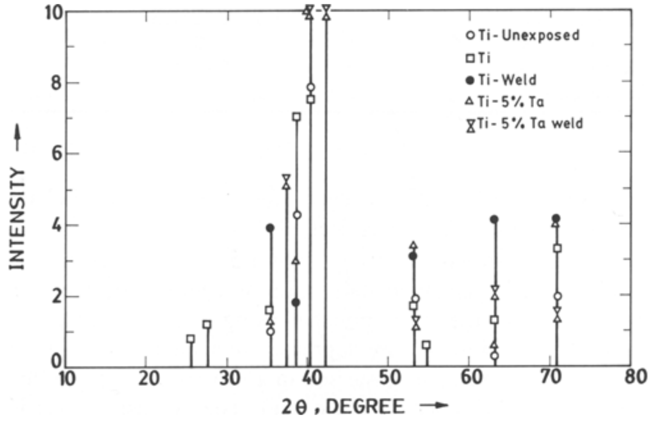

Fig. 4 XRD pattern of specimens tested in boiling nitric acid for 240 h

noticed close to the weld-metal portion in the heat-affected zone. Figure 2 shows the surface morphology of all the tested specimens examined using SEM. Type 304L stainless steel specimens underwent grain-boundary grooving and spalling of grains. Dissolution around needle-shaped secondary phase precipitates was seen in the case of the Ti-5Ta weld region, whereas uniform dissolution of the surface was observed for the Ti-5Ta base metal. Figure 3 shows the interface of the weld/base-metal region of a Ti-5Ta specimen, which exhibits severe attack at the welded region due to the heterogeneous microstructure developed during welding. The formation of the needle-shaped second-phase precipitates has been reported (Ref 14) to provide beta/alpha-phase interfaces where dissolution can initiate and propagate due to galvanic corrosion. X-ray diffraction analyses of the scales (Fig. 4) formed on titanium and Ti-5Ta as well as their respective weldments in the weld-metal regions showed the presence of TiO_2 oxide phases present on their surfaces compared to an untested specimen. The weld metal of Ti-5Ta additionally showed two peaks, indicating the presence of second-phase precipitates formed during welding.

3.2 *Corrosion Behavior in Boiling Nitric Acid Containing Chromium and Silver Ions*

Table 3 gives the corrosion rate values obtained at various intervals for the specimens tested in the present experiment.

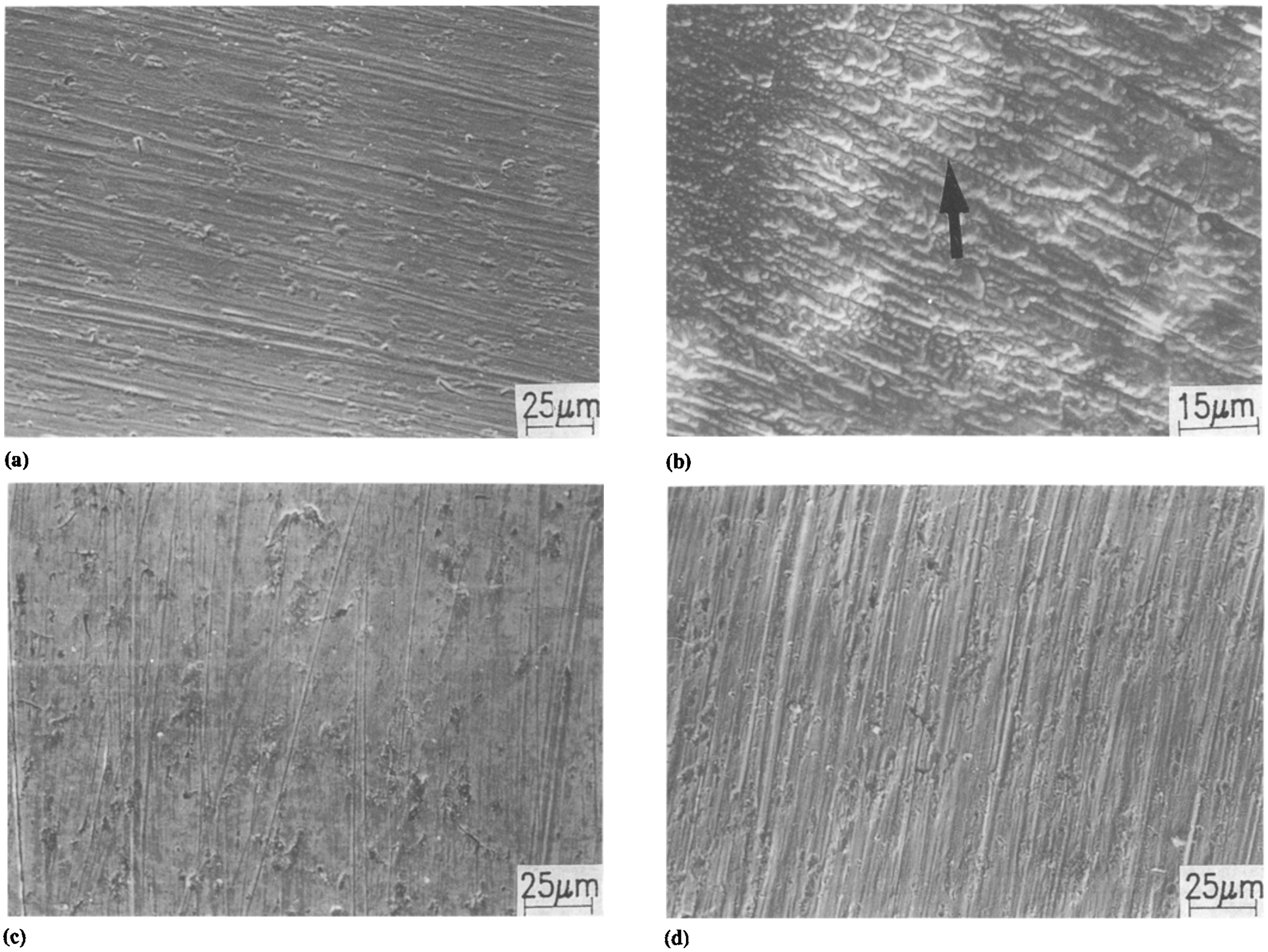

Fig. 5 SEM micrographs of specimens tested in boiling nitric acid containing CrO_3 and $AgNO_3$ for 500 h. (a) Ti-5Ta base metal. (b) Titanium base metal with thick oxide layer containing pores and microcracks. (c) Titanium weld region. (d) Ti-5Ta weld region

The base metal of 304L stainless steel completely dissolved in the test solution after four periods of 100 h, whereas its weldment completely dissolved after two 100 h periods. Both the base metals and weldments of titanium and Ti-5Ta showed nearly identical corrosion rates (Table 3). These results indicate that type 304L stainless steel may not be suitable for the conditions that arise during the dissolution of nuclear fuel.

Scanning electron microscope study of the tested specimens (Fig. 5) revealed that titanium weld metal and Ti-5Ta base and weld metals showed the presence of a uniformly developed surface coating, whereas titanium showed a dense, thick coating with pores and cracks. Thus, for applications involving nitric acid in severe corrosive conditions as used in the present tests, titanium, Ti-5Ta, and their respective weldments are not likely to pose any serious corrosion problems and are recommended for such applications.

4. Conclusions

- Titanium, Ti-5Ta alloy, and their respective weldments showed excellent corrosion resistance in boiling nitric acid medium.
- Analyses using SEM of the scales formed on the specimens revealed (1) severe corrosion attack in 304L stainless steel, (2) dissolution around secondary-phase precipitates in Ti-5Ta weld, and (3) uniform dissolution of titanium.
- Analyses using XRD of titanium, Ti-5Ta, and their weldments showed the presence of oxide phases on the surface. Also, the presence of secondary-phase precipitates formed during welding was confirmed for Ti-5Ta weld metal.
- In boiling nitric acid medium containing chromic acid and silver nitrate, 304L stainless steel showed very high corrosion rates in both the unwelded and welded conditions. Titanium, Ti-5Ta, and their respective weldments showed excellent corrosion resistance with very low corrosion rates.
- Scanning electron microscopy indicated the presence of protective coatings on the surfaces of titanium weld metal and on Ti-5Ta and its weld metal in the medium containing boiling nitric acid with chromic acid and silver nitrate.

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Table 3 Corrosion rate of materials in nitric acid with CrO_3 and $AgNO_3$

	Time,	Corrosion rate	
Specimen	h	mpy	mm/year
304L SS	100	323	8.2
	200	269	6.8
	300	243	6.2
	400	467	11.9
	500	(a)	(a)
304L SS weldment	100	386	9.8
	200	423	10.7
	300	(a)	(a)
	400		
	500		
Titanium	100	0.81	0.020
	200	0.81	0.020
	300	0.79	0.020
	400	0.76	0.019
	500	0.65	0.017
Titanium weldment	100	0.61	0.015
	200	0.72	0.018
	300	0.69	0.017
	400	0.70	0.017
	500	0.64	0.016
Ti-5Ta	100	0.007	0.0002
	200	0.1	0.002
	300	0.24	0.006
	400	0.25	0.006
	500	0.23	0.006
Ti-5Ta weldment	100	0.008	0.0002
	200	0.13	0.003
	300	0.27	0.006
	400	0.36	0.009
	500	0.31	0.007

(a) Indicates complete dissolution of the specimens

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