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1. QA: QA

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2. Record Date 11/8/01	3. Accession Number MOL.20011114.0263
4. Author Name(s) V. PASUPATHI, F. HUA, J.SARVER, W MOHN, G GORDON	5. Author Organization BSC, MCDERMOTT TECHNOLOGY INC, FRAMATOME
6. Title/Description CREVICE CORROSION BEHAVIOR OF CANDIDATE NUCLEAR WASTE CONTAINER MATERIALS IN REPOSITORY ENVIRONMENT PAPER # 02529	
7. Document Number(s) CORRESPONDENCE NUMBER 1108010402; PAPER NUMBER 02529	8. Version Designator N/A
9. Document Type CORRESPONDENCE/REPORT	10. Medium OPTIC/PAPER
11. Access Control Code PUBLIC	
12. Traceability Designator 1108010402; 02529	
13. Comments THIS ONE OF A KIND COLOR DOCUMENT CAN BE LOCATED THROUGH THE RECORDS PROCESSING CENTER	

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MOL.20011114.0263

To:	File	**No.:**	1108010402
From:	Venkatamaran Pasupathi	**Date:**	November 8, 2001
Re:	Crevice Corrosion Behavior of Candidate Nuclear Waste Container Materials in Repository Environment	**CC:**	G. M. Gordon J. H. Lee RPC = 35

Enclosed is subject report submitted by Fred Hua, Jeff Sarver and Walter Mohn of McDermott Technology, Inc., Alliance, OH; and Gerald Gordon of Framatome ANP/BSC.

CORROSION2002

Paper No.
02529

CREVICE CORROSION BEHAVIOR OF CANDIDATE NUCLEAR WASTE CONTAINER MATERIALS IN REPOSITORY ENVIRONMENT

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ABSTRACT

Alloy 22 (UNS N06022) and Ti Grade 7 (UNS R52400) have been proposed as the corrosion resistant materials for fabricating the waste package outer barrier and the drip shield, respectively for the proposed nuclear waste repository Yucca Mountain Project. In this work, the susceptibility of welded and annealed Alloy 22 (N06022) and Ti Grade 7 (UNS R52400) to crevice corrosion was studied by the Multiple Crevice Assembly (ASTM G78) method combined with surface morphological observation after four and eight weeks of exposure to the Basic Saturated Water (BSW-12) in a temperature range from 60° to 105°C. The susceptibility of the materials to crevice corrosion was evaluated based on the appearance of crevice attack underneath the crevice formers and the weight loss data. The results showed that, after exposed to BSW-12 for four and eight weeks, no obvious crevice attack was observed on these materials. The descaled weight loss increased with the increase in temperature for all materials. The weight loss, however, is believed to be caused by general corrosion, rather than crevice corrosion. There was no significant difference between the annealed and welded materials either. On the other hand, to conclude that these materials are immune to crevice corrosion in BSW-12 will require longer term testing.

Keywords: Crevice Corrosion, General Corrosion, BSW, Alloy 22, UNS N06022, Titanium Grade 7, UNS R52400, Waste Container, Yucca Mountain Project, HLW

INTRODUCTION

The Nuclear Waste Policy Act of 1982 as amended in 1987 designated Yucca Mountain in Nevada as the proposed site to be characterized for high level nuclear waste (HLW) disposal [1]. The design concept for geological containment of HLW is a double wall canister structure with an inner structural container and an outer concentric barrier made of the corrosion resistant material.. Earlier designs used Alloy 825, later changed to Alloy 22 as the inner corrosion resistant barrier, with an outer structural barrier of "corrosion allowance" carbon steel. This concept was later modified to the current so-called "Enhanced Design Alternative" (EDA) [2]. With EDA design concept, the outer corrosion resistant barrier is made of a 20 mm thick Alloy 22 cylinder concentric with a 50 mm thick inner structural barrier cylinder fabricated from Type 316 NG stainless steel.. The weld sealed waste packages will be emplaced in the drifts (tunnels) under a self-supported 15 mm thick Ti Grade 7 mailbox shaped drip shield [3]. The minimum target lifetime for containment of HLW without failure is 10,000 years [4]. In this most current design, test results to date [2] indicate Alloy 22 will not undergo localized corrosion in the range of expected aqueous environments.

The objectives of the current investigation were 1) to evaluate the susceptibility of Alloy 22 and Ti Grade 7 to crevice corrosion in a potential waste package/drip shield surface environment and 2) providing the material exhibited susceptibility to corrosion, to determine the critical crevice corrosion temperature. The objectives were to be achieved by studying the crevice corrosion behavior of welded and annealed Alloy 22 and welded and annealed Titanium Grade 7 in a highly concentrated site groundwater, Basic Saturated Water (BSW-12) at six selected temperatures (60°C, 70°C, 80°C, 90°C, 100°C, and 105°C). The evaluation was primarily based on weight loss and morphological observations after the test. All tests, except the SEM and EDS, were performed in compliance to the Nuclear Quality Assurance (NQA-1) procedures.

EXPERIMENTAL PROCEDURES

Materials and Test Specimens

Solution annealed and welded Alloy 22 and solution annealed and welded Ti Grade 7 were tested in this work. The welded Alloy 22 was prepared by Machine Gas Tungsten Arc Welding (Amperage: 0-170 A; Voltage: 3-6 V; Wire Feed Speed: 25-200 ipm) with filler metal ERNiCrMo-10 (0.045" in diameter) and 1" thick plates. The welded Ti Grade 7 was prepared by Machine Hot Wire Gas Tungsten Arc Welding (Amperage: 0-170 A; Voltage: 2-6 V; Wire Feed Speed: 25-200 ipm) with filler metal ERTi-7 (0.045" in diameter) and 5/8" thick plate.

The chemical compositions of the materials are shown in Table 1. Also shown in Table 1 are the major mechanical properties of the materials. The materials were machined into nominally 2×2× 0.1875 inch square coupons with a 0.385 inch center hole for mounting a crevice former. All as-received specimens were cleaned with distilled water and acetone prior to testing.

Table 1 Chemical compositions and mechanical properties of the testing materials

Ti Grade 7							
Element	C	Fe	N	H	O	Pd	Ti
Base metal	0.009	0.07	0.005	< 20 ppm	0.14	0.16	Bal.
Filler metal	0.02	0.07	0.012	0.0016	0.06	0.19	Bal.
Mechanical properties	UTS 70,500 psi		$\sigma_{0.2}$ 45,000 psi		Elongation 32.0% (1.4 inches)		

Alloy 22														
Element	C	Mn	P	S	Si	Cr	Mo	Co	Fe	V	W	Ti	Ni	Cu
Base metal	0.010	0.29	0.009	0.001	0.05	22.49	12.58	1.07	4.61	0.19	3.14	0.01	Bal.	NR
Filler metal	0.00	0.21	0.008	0.001	0.06	20.72	14.17	0.04	2.07	0.03	3.21	NR	59.24	0.04
Mechanical properties	UTS 109,000 psi					$\sigma_{0.2}$ 50,000 psi				Elongation 67.0% (2 inches)				

Equipment Setup and Testing Program

The test was performed in so-called basic saturated water-12 (BSW-12) simulating evaporatively concentrated Yucca Mountain J-13 ground water which contains ~9% dissolved chloride ion concentration and exhibits a pH of ~12. The chemical composition of the BSW-12 solution is shown in Table 2. The test temperatures were chosen at 60°, 70°, 80°, 90°, 100° and 105°C, respectively. After heating, the testing solutions were maintained at the desired temperatures (±5°C) and CO_2-free air was continuously purged through the solutions.

The Multiple crevice assembly (MCA) method, as described in ASTM G78-98, was employed to study crevice corrosion resistance of the materials. The test setup is shown in Figures 1 (a) and (b). The crevice specimen was a 2×2×0.1875 in. square coupon with a 0.385 in. center hole for mounting the crevice former. The crevice was formed between the specimen and the serrated polytetrafluoroethylene (PTFE) crevice former. Racks of prepared specimens were assembled and torqued to 20 kg-cm, and immersed in baths containing approximately 30 liters of BSW-12 solution in each bath at various temperatures. A total of 89 specimens were tested (18 welded Alloy 22, 24 annealed Alloy 22, 24 annealed Titanium Grade 7 and 23 welded Titanium Grade 7 specimens). About half of the specimens were removed from the testing baths after 4 weeks of exposure time for evaluation. These racks were rinsed in deionized water and methanol, then placed in a low-temperature drying oven prior to disassembly and specimen inspection. The rest of the specimens remained in the baths for an additional 4 weeks (for a total of 8 weeks exposure time), then removed, rinsed, dried, and disassembled for evaluation.

Table 2 The chemical composition of the testing solution

Chemicals	Quantity
KCl	127.9 g/L
NaCl	116.2 g/L
NaF	2.9 g/L
$NaNO_3$	191.2 g/L
Na_2SO_4 (anhydrous)	20.6 g/L
1 N NaOH (1.0428 g/ml)	2 ml
CO_2 Partial Pressure	0
Nominal pH	12

The initial weight, the post-test weight without descaling and the post-test weight after descaling were obtained for each specimen to the nearest 1 milligram.

While all specimens were weighed for their post-test weights without descaling, only 63 post-test specimens were weighed for their post-test and descaled weights. The purpose of descaling is to remove corrosion products and deposits without significant removal of base metal. This allows for an accurate determination of the mass loss of the metal or alloy that occurred during exposure to the corrosive environment. The basic procedure utilized alternating exposures to acetone and inhibited hydrochloric acid. The cleaning was enhanced by the use of an ultrasonic cleaning bath, light brushing with a nylon brush, and temperature. Steps were repeated, as necessary, to effect complete removal of the scale. To ensure that the cleaning procedure did not cause the loss of the substrate metal *per sé*, several control specimens were cleaned by the same cleaning procedure. The weight loss on the control specimens was found to be negligible. The detailed cleaning procedures can be found elsewhere [5].

Post-test specimens were visually inspected and examined using stereo light microscopy up to 25X for signs of crevice attack. The surface appearance of each specimen was also documented in a digital image at a magnification of 6X. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis were performed on several post-test specimens to detect and identify chemical species present in different areas of the exposed surface.

RESULTS AND DISCUSSION

Weight Loss Analysis

Before the post-test specimens were descaled, most specimens showed slight weight gains, regardless of materials and whether the materials were annealed or welded. Both Alloy 22 and Ti Grade 7 showed a 1 ~ 3 milligram weight gain for almost all specimens except three annealed Ti Grade 7 specimens. The three annealed Ti Grade 7 specimens showed significant weight loss from 5 to 12 mg before descaling. For the rest of the specimens, no appreciable differences were observed between those that were annealed and welded and those that were exposed for 4 weeks and 8 weeks in BSW-12.

A total of 63 out of 89 post-test specimens (18 annealed Alloy 22, 12 welded Alloy 22, 17 annealed Ti Grade 7 and 16 welded Ti Grade 7) were descaled and re-weighed. 26 remaining specimens were kept undescaled for future analysis. After descaling, all specimens had positive weight loss. Figure 2 and Figure 3 show the results of the descaled weight loss of Alloy 22 and Ti Grade 7, respectively, as functions of exposure temperature. For both annealed and welded materials, the descaled weight loss of Alloy 22 and Ti Grade 7 increased slightly, but systematically, with the increase in temperature. However, no appreciable difference in weight loss was observed between the annealed and welded materials, especially for Ti Grade 7.

The effect of temperature on corrosion rate of Alloy 22 in dilute chloride solutions has been demonstrated in the work of Dunn et al [6]. The passive dissolution rate of Alloy 22 in 0.028 M chloride at 95°C was 10 times higher than that measured at 20°C. In the present work, the corrosion rate of both Alloy 22 and Ti Grade 7 increased by about threefold as temperature increased from 60°C to 105°C. Note in the work of Dunn et al [6], in solutions of 4.0 M chloride concentration, the corrosion rate of Alloy 22 increased by about threefold as temperature increased from 20°C to 95°C and the corrosion rate of Alloy 22 in 4.0 M chloride solution at 20°C is same as that in 0.028 M chloride solution at 95°C. Although the possibility that the lower corrosion rate at lower temperature is caused by the artifact of higher oxygen solubility at lower temperature cannot be ruled out, the synergetic effect of chloride concentration and temperature may also play an important role.

The average nominal surface area of the MCA used in this work is 9.65 square inch (including the areas underneath the crevice formers). The densities of Alloy 22 and Ti Grade 7 are 8.69 g/cm^3 and 4.51 g/cm^3, respectively. The corrosion rate corresponding to a 1 to 3 milligram weight loss over a 4-week period is 0.010 to 0.030 mpy (0.25 to 0.76 microns/year) for Alloy 22 and 0.020 to 0.054 mpy (0.51 to 1.4 microns/year), for Ti Grade 7, respectively. The corrosion rate of Ti Grade 7 is about twice as high as that of Alloy 22. These ranges of corrosion rate are in agreement with the available literature data mostly for relatively short-term tests including linear polarization and potentiostatic polarization tests. Table 3 compares the relevant literature data with the corrosion rates obtained in this work.

Table 3 Comparison of corrosion rates of Alloy 22 and Ti Grade 7

Material	**Testing Environment**	**Corrosion Rate, mpy**	**Reference**
Alloy 22	SAW, 90°C	0.04	[7]
Alloy 22	Modified SAW, 90°C	0.013	[7]
Alloy22 welds	70,000 ppm Cl$^-$, pH 1, 105°C	0.011	[7]
Alloy 22	0.028 ~ 4.0 M NaCl, 95°C	0.021	[8]
Alloy 22	SCW, 90°C	0.09	[7]
Alloy 22	0.1 ~ 10% NaCl, 95°C	0.04	[9]
Alloy 22	ASTM G 28B, 105°C	4 ~ 5	[9]
Alloy 22	SAW, 60oC	Negligible	[10]
Alloy 22	4.0 M Cl$^-$, pH 8.0, 95°C	0.012 `0.021	[6]
Alloy 22	SAW, SCW, SDW, 60°C, 90°C	≤0.029 (6 month tests) and ≤ 0.003 (2 year tests)	[11]
Alloy 22	BSW-12, 60° ~105°C	0.010 ~ 0.030	This work
Ti Grade 7	5 M Cl$^-$ + 0.1 M HCl, 95°C	0.026	[12]
Ti Grade 16	SAW, SCW, SDW, 60°C, 90°C	≤ 0.014 (one year test)	[11]
Ti Grade 7	BSW-12, 60° ~ 105°C	0.019 ~ 0.055	This work

The exposure time in BSW-12 did not seem to significantly effect the weight loss. Figure 4 (a) compares the descaled weight loss of four materials exposed in BSW-12 at 105°C for 4 weeks and for 8 weeks. Prolonged exposure time did not cause further increase in the weight loss consistent with the corrosion rate decreasing with exposure time. A possible hypothesis to explain this phenomenon is that significant corrosion occurred during the earlier stage of exposure (e.g. the first 4 weeks) as schematically illustrated in Figure 4(b). The corrosion became insignificant at prolonged exposure. Several wastage container lifetime prediction models assume a uniform passive dissolution rate throughout the lifetime and then calculate for how long it will take to corrode the 20 mm thick container wall [6,8, 11]. If further experimental work supports the hypothesis illustrated in Figure 4(b), the real lifetime of the container is likely to be much longer than what has been predicted based on short term tests, as long as localized corrosion does not occur.

It should be pointed out that the corrosion rate obtained in this work does not reflect the crevice corrosion susceptibility of the materials as was discussed in another paper of this conference [13]. This corrosion rate is more likely the general corrosion rate of the materials.

Macroscopic Visual Examinations

Most of the post-test specimens exhibited discoloration after exposure to BSW-12 solution at various temperatures. The discoloration became more severe at higher temperatures. The post-test Alloy 22 generally exhibited faint blue color while Ti Grade 7 specimens exhibited faint blue at lower temperature but turned to faint golden at higher temperature. A characteristic "crevice pattern" matching the shape of the serrated Teflon crevice former that contacted the specimen surface was observed on annealed and welded Alloy 22 specimens at temperatures higher than about 80°C. The characteristic "crevice pattern" appeared on annealed and welded Ti Grade 7 at all temperatures and became more significant at higher temperatures. After descaling, all the "crevice patterns" on Alloy 22 specimens were completely removed. The "crevice patterns" on Ti Grade 7 specimens, however, were only partially removed by the descaling process.

Effect of Temperature

Figure 5 and Figure 6 show low magnification optical macroscopic morphologies of post-test welded and annealed Alloy 22 specimens, respectively, tested at 60° ~ 105°C for 8 weeks. While the discoloration of the whole specimen surfaces did not increase significantly, the "crevice pattern" underneath the crevice former became visible at temperatures higher than 80°C and became more obvious with increase in temperature. Figure 7 and Figure 8 show low magnification optical macroscopic morphologies of post-test welded and annealed Ti Grade 7 specimens, respectively, tested at 60° ~ 105°C for 8 weeks. In case of Ti Grade 7, the color of the specimen turned from faint blue at lower temperature to faint golden at higher temperature. The "crevice patterns" underneath the crevice formers were much clearer and more crevice-attack-like than those on Alloy 22 specimens. The "crevice patterns" on Ti Grade 7 specimens appeared at all temperatures but became more distinctive at higher temperatures.

Effect of Exposure Time

Figure 9 compares the morphologies of welded (a) and annealed (b) Alloy 22 specimens after 4 weeks and 8 weeks of exposure at 105°C. Figure 10 compares morphologies of annealed Ti Grade 7 specimens after 4 weeks and 8 weeks of exposure at (a) 105°C and (b) 60°C. Figure 11 compares the morphologies of welded Ti Grade 7 specimens after 4 weeks and 8 weeks of exposure at (a) 105°C and (b) 60°C. In all these cases, both annealed and welded Alloy 22 and Ti Grade 7 showed no significant dependence of exposure time in terms of the degree of discoloration and the "crevice pattern" underneath the crevice former. This is in agreement with the similarity in weight losses after 4 weeks and 8 weeks exposure (Figure 4(a)).

Effect of Welds

For both Alloy 22 and Ti Grade 7, no obvious difference between the annealed materials and the welded materials was observed.

In fact, some welded specimens were not composed of whole welds but only a portion of the specimen was weld metal. Figure 12 (a) shows an example of the location of the welds in one of the post-test welded specimens. The disposition of the welded metal was not intentionally arranged. On the other hand, the disposition of the welds provided an additional way to evaluate the difference in corrosion behavior between base metal and welded metal. Figure 12 (b) to (e) show the macroscopic morphologies of some selected post-test welded Alloy 22 and Ti Grade 7 specimens with the assumed locations of the welds. All specimens chosen for Figure 12 have been tested at 105°C for 8 weeks. From Figure 12, no noticeable difference in morphology across the welds/base metal boundaries can be observed.

Microscopic Optical Observations

Selected post-test specimens were examined under the optical microscope for signs of crevice attack. Figure 13 shows the optical micrographs of annealed Ti Grade 7 after exposure for 8 weeks at (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, (e) 100°C, (f) 105°C and (g) after exposure for 4 weeks at 105°C. Figure 14 shows the micrographs of welded Ti Grade 7 after exposure for 8 weeks at (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, (e) 100°C, and (f) 105°C (200×). As temperature increased, the original surface characteristics (e.g. the 600 grit polishing scratches) remained for both annealed and welded specimens in both creviced and uncreviced areas. In both creviced and uncreviced areas, some pit-like defects were observed. The defects were found not to be pitting-related but were the inclusions or the processing defects of the materials since they were present in all the untested specimens (not shown).

Figure 15 shows the optical micrographs of (a) annealed Alloy 22 after 4 weeks exposure at 60°C, (b) annealed Alloy 22 after 8 weeks exposure at 105°C and (c) untested annealed Alloy 22. Figure 16 shows the optical micrographs of (a) welded Alloy 22 after 4 weeks exposure at 60°C, (b) welded Alloy 22 after 8 weeks exposure at 105°C and (c) untested welded Alloy 22. For both annealed and welded Alloy 22, exposure to BSW-12 solutions at temperatures from 60°C to 105°C for 4 and 8 weeks did not change the overall appearance of the specimen surface morphology. Again, the pit-like defects on the post-test specimens are the results of materials processing, rather than corrosion testing, as can be verified by the similarity in surface morphologies of the tested and untested Alloy 22 specimens (Figure 15 (c) and Figure 16 (c)).

SEM and EDS Analysis

Figure 17 shows the representative SEM images of welded Alloy 22 after 4 weeks exposure in BSW-12 environment at 105°C and the semi-quantitative chemical compositions at the areas of interest. Although the macroscopic appearance of the creviced areas had a clear "crevice pattern", the microscopic views revealed similar surface morphologies and chemical composition at the creviced and uncreviced areas. In both areas, no signs of localized attack were observed. No obvious EDS signals from species possibly contained in corrosion product were detected either. At location 1 of the specimen (Figure 17), the abnormal EDS spectra containing all kinds of species are presumably either from an inclusion in Alloy 22, which contained a large amount of titanium carbides, or from the deposits from the BSW-12 solution in which the Ti Grade 7 specimens were also tested at same time.

Figure 18 shows the SEM and EDS analysis of the welded Ti Grade 7 specimens tested in BSW-12 solution at 105°C for 8 weeks. Figure 19 shows the SEM and EDS analysis of the annealed Ti Grade 7 specimen tested in BSW-12 solution at 105°C for 4 weeks. In either case, the microscopic surface morphologies of the creviced and uncreviced areas were similar. The EDS analysis showed that no obvious chemical species possibly contained in corrosion product was detected. The imperfect area at location 1 of Figure 19 is not caused by corrosion but inherited from the testing material, as can be concluded by comparing the microstructures of the tested and untested Ti Grade 7.

The escape-depth of SEM and EDS is normally much larger than the thickness of the oxide film formed on nickel alloys and Ti Grade 7. In order to confirm that the metal underneath the crevice formers were not attacked by localized corrosion, SEM was further performed on the descaled specimens. Descaling the post-test specimens completely removed discoloration and the "crevice pattern" on all Alloy 22 specimens. Some faint blue or faint golden color remained on Ti Grade 7 specimens after the descaling. The "crevice pattern" on Ti Grade 7 specimens was not completely removed either. Figure 20 shows the optical and SEM post-descaling morphologies of an annealed Ti Grade 7 specimen tested in 105°C BSW-12 for 8 weeks. showing the remaining "crevice pattern" and similarity in surface morphologies in the creviced and uncreviced areas

Alloy 22 as a potential candidate nuclear waste container material has received extensive studies for its stress corrosion cracking, passive dissolution and localized corrosion [1, 6, 11], galvanic corrosion [14, 15], and microbial corrosion [11, 16,18]. The excellent corrosion resistance of Alloy 22 cannot be attributed to chromium content alone. Alloy 625 contains similar Cr as Alloy 22 (about 21wt%). However, Alloy 625 is much less corrosion resistant than Alloy 22 [19]. It is the higher Mo content and addition of W that significantly improves the corrosion resistance of Alloy 22 [20, 21]. In present work, no attempts were made to monitor the changes of Mo and W contents in passive films formed under different temperature for different exposure time. From the present results, crevice corrosion was not initiated within the 8 weeks testing time and 60° ~ 105°C temperature range of the present work. However, the general corrosion rate of Alloy 22 was found to increase with the increase in temperature. Moreover, the characteristic "crevice patterns" formed underneath the crevice formers at the temperatures higher than about 80°C. It is worthwhile to further study the corresponding evolution in oxide film composition and thickness in term of temperature and exposure time.

Ti Grade 7 is considered as the candidate material for the drip shield to divert the incoming water from the container [22]. Ti and Ti alloys owe their excellent corrosion resistance to the spontaneous formation of a protective passive film (TiO_2). Ti alloys, however, suffer from significant corrosion in highly reducing acidic environments. The underground and rock pore-water ~~water~~ chemistry in Yucca Mountain region is near-neutral to slightly basic and oxidizing. Therefore, the main potential but unexpected failure mechanisms under the anticipated repository conditions are hydrogen embrittlement, which could result from galvanic coupling to ferrous components or through development of localized corrosion in which a reducing acidic environment can develop. Pd-bearing Ti Grade 7 is a α titanium that has similar mechanical properties to commercial purity (CP) Ti but exhibits considerably superior corrosion resistance than CP Ti. The localized corrosion and general corrosion [11,12, 23], stress corrosion cracking [24, 25], and microbial corrosion [26] of Titanium Grade 7 have been extensively studied.

Ti Grade 7 [27] and Pd bearing Ti alloys [28] are generally found to be immune to crevice corrosion in oxidizing Cl^- environment. Brossia and Cragnolino compared the localized corrosion and uniform corrosion behavior of Ti Grade 2 (UNS R50400) and Pd-containing Ti Grade 7 (UNS R52400) in chloride containing environments and found that Ti Grade 7 was immune to crevice corrosion under conditions where Ti Grade 2 was susceptible to crevice corrosion [12]. It was found that the Pd improved the localized corrosion resistance of Ti but had little effect on the passive dissolution rate nor did it mitigate the deleterious effects of fluorides. The authors explained the effect of Pd on Ti based on the effect of Pd on hydrogen evolution reaction (HER). It has been reported that the surface Pd concentration was progressively increased during corrosion of Ti and increased with increasing exposure time as well [29, 30]. According to Brossia and Cragnolino, the accumulation of Pd in Ti oxide film could be due to rapid active dissolution of titanium, which leads to the subsequent decrease in uniform corrosion rate [12]. While the decrease in general corrosion rate was observed, no accumulation of Pd in oxide film on Ti Grade 7 was found in this work. In the present work, although after 4 to 8 weeks exposure to BSW-12 solution at elevated temperature led to the significant discoloration and obvious "crevice patterns" on Ti Grade 7 specimens, no obvious crevice corrosion attack was observed, even under SEM and EDS. However, the discoloration of the specimens and progressively increased "crevice patterns" at higher temperature and more prolonged exposure time were observed. The "crevice patterns" could not be completely removed even after descaling. This suggested that crevice corrosion might be initiated at still longer exposure time. However, no evidence of crevice corrosion was observed in much longer term exposure tests at Lawrence Livermore National Laboratory (LLNL) that included 60° and 90°C exposures on analogous but lower Pd level Ti Grade 16 creviced specimens in a range of relevant environments (SAW,SCW and SDW) [11] and on Ti Grade 7 creviced double-U-bend specimens exposed in 105°C BSW for 18 months [31]. Longer-term testing of Ti Grade 7 now planned will provide additional insight into the potential of this material to undergo crevice corrosion after still longer exposure in BSW-12 environment at elevated temperature.

Short-Term Testing versus Long-Term Prediction

It is clear that during the maximum testing time of the present work, no crevice corrosion occurred on either Alloy 22 and Ti Grade 7. Combined with the weight loss data and surface morphological observations on creviced and uncreviced areas, it can be concluded that the weight losses after descaling were the consequence of general corrosion (passive dissolution), rather than localized corrosion (crevice corrosion). It has been argued that the localized corrosion susceptibility studies conducted by simply immersing a specimen in a test environment for a specific period without measuring the corrosion potential during the test are not useful for predicting the long-term performance of the material [6]. It is possible that the corrosion potential could become more positive with time and eventually exceed the critical potential for passive film breakdown and lead to localized corrosion. The corrosion potentials in the BSW environment has been monitored for both Alloy 22 and Ti Grade 7 as a function of time at 110°C in other tests [25] and was found to be stable over the several thousand hour test period with values well below the critical potentials for localized corrosion.

For predictions over times as long as 10,000 years, any short-term laboratory study can only provide, and should focus on the *changes* in passive films in and outside of the localized areas. Many studies have focused on the formation and compositional changes of the passive films formed on Fe-Cr [32] and Fe-Cr-Ni-Mo [33, 34]. The composition of the oxide film has been related to the passive dissolution rate [35]. The passive film on Ni-Cr or Ni-Cr-Mo alloys is composed of mainly an inner layer of Cr_2O_3 and an outer layer of nickel oxide [36]. Significant enrichment of Cr in the oxide film has been observed and the enrichment of Cr increased with the increase in temperature [37], possibly due to the faster dissolution rate of Ni and Mo at elevated temperature. On the other hand, Dunn et al studied the long-term dissolution behavior of Alloy 22 under various chloride concentrations and temperatures [8]. The preferential dissolution of alloying elements such as Fe, Ni or Mo was not observed. The evolution of the oxide film composition and layered structure with temperature and exposure time has not yet been well characterized for Alloy 22 although testing is underway for both Alloy 22 and Ti Grade 7 and initial results are reported[38]. The present test lasting for 8 weeks may not be long enough to reveal the changes in oxide film composition and thickness.

In case of Ti Grade 7, the different discoloration of the oxide films formed under various temperatures for various exposure time suggested the changes in the oxide chemical composition and possibly the structure. The SEM and EDS used in this work are not sensitive enough for elemental analysis.

In order to predict the long term behavior of the materials by conducting short-term laboratory immersion tests, further analysis of the oxide composition (*e.g.* Cr/Ni ratio in case of Alloy 22 and oxide structure in case of Ti Grade 7) and its change with temperature and exposure time is critically important. The extrapolation of long-term behavior from the short-term test results based on *changes* could be more reliable than assuming a never-changing passive dissolution rate over 10,000 years. Studies in this connection are under way along with the development of a passive film kinetic model based on the Point Defect Model.

CONCLUSIONS

Annealed and welded Alloy 22 and Ti Grade 7 have been tested in BSW-12 environments from 60° to 105°C for their susceptibilities to crevice corrosion. Based on the weight loss analysis and surface morphological examinations, none of these materials suffered from crevice corrosion under the present test conditions. No significant difference in both the general corrosion rate and crevice corrosion susceptibility between the annealed and welded materials was observed either. The critical crevice corrosion temperature was, therefore, not obtained. However, the general corrosion rates as reflected by the weight loss data increased with the increase in temperature for all materials tested. An approach for long-term prediction based on short-term laboratory testing has been proposed in light of that the changes in the composition and thickness of the oxide films as obtained in short-term testing may lead to a better understanding of the long-term behavior of the materials.

ACKNOWLEDGEMENT

This paper was prepared to document work performed by McDermott Technology, Inc. (MTI) for the DOE Yucca Mountain Project M&O under Contract No. DE-AC08-01RW12101. The authors wish to thank R. Pelger and B. Conrad for the MCA tests, J. Jevec for chemical cleaning work and S. Boyce for SEM/EDS analysis.

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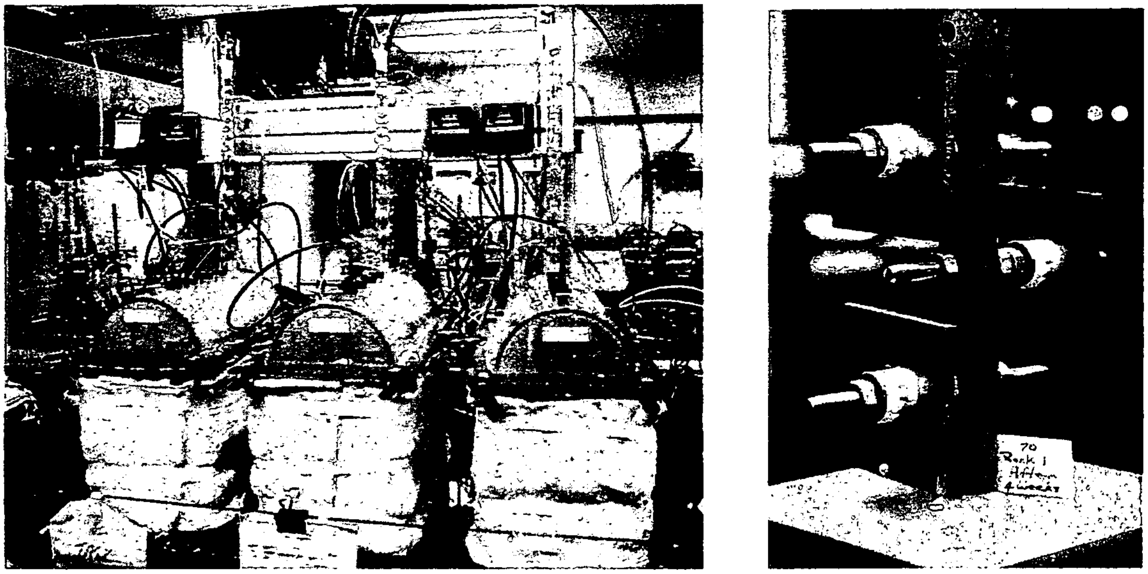


(a) (b)

Figure 1 MTI testing facility for MCA crevice corrosion test: (a) heating baths containing BSW and (b) supporting rack with MCAs

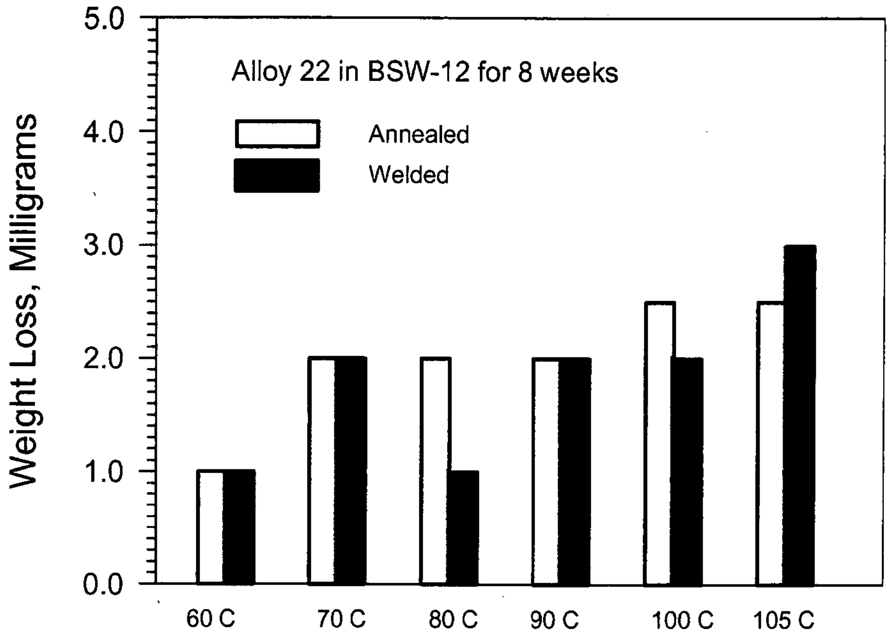


Figure 2 Descaled weight loss of annealed and welded Alloy 22 as a function of the exposure temperature

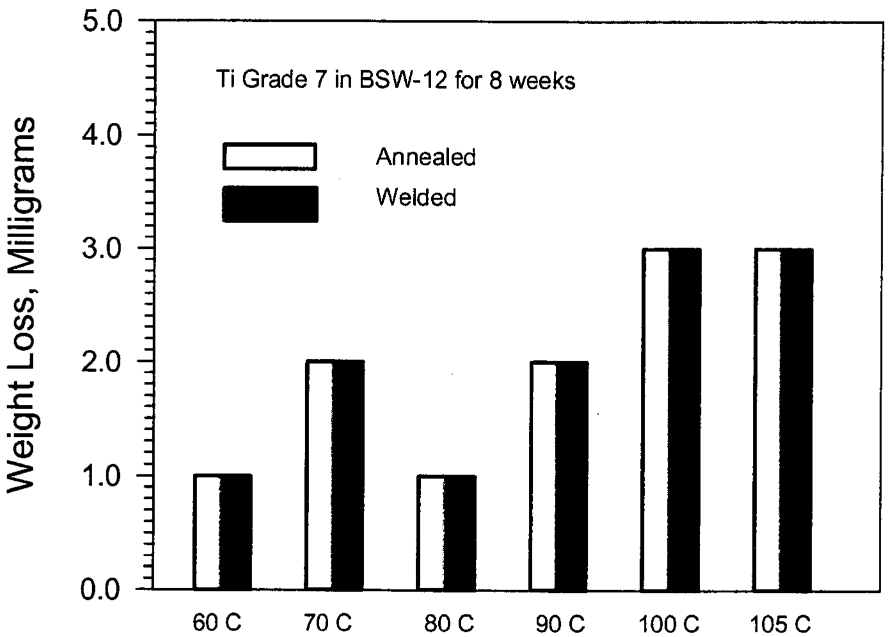
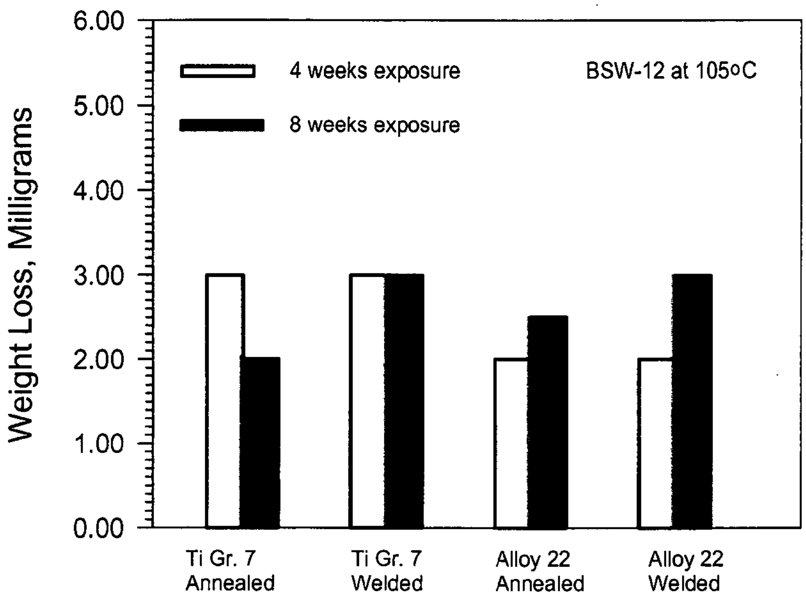
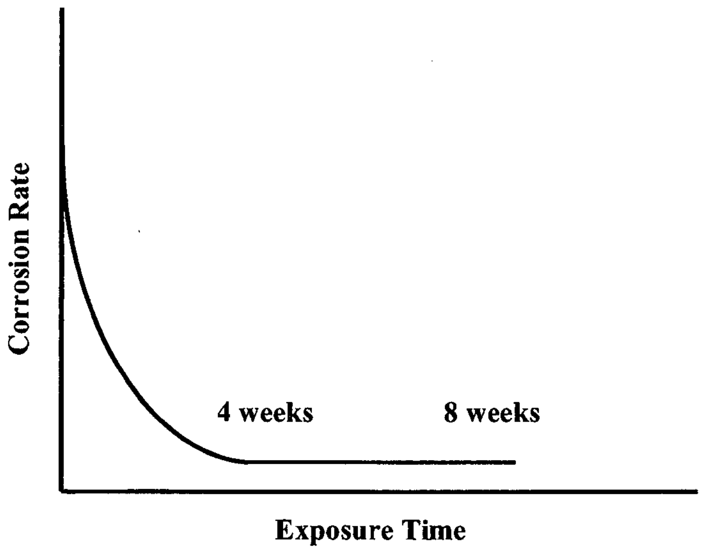


Figure 3 Descaled weight loss of annealed and welded Titanium Grade 7 as a function of the exposure temperature

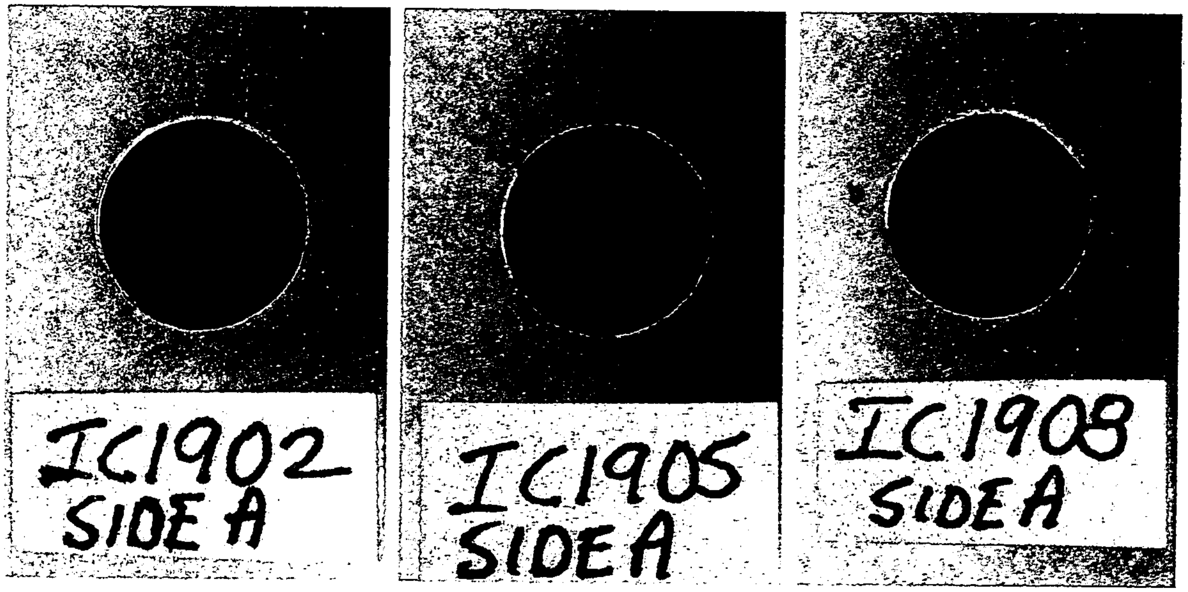


(a)

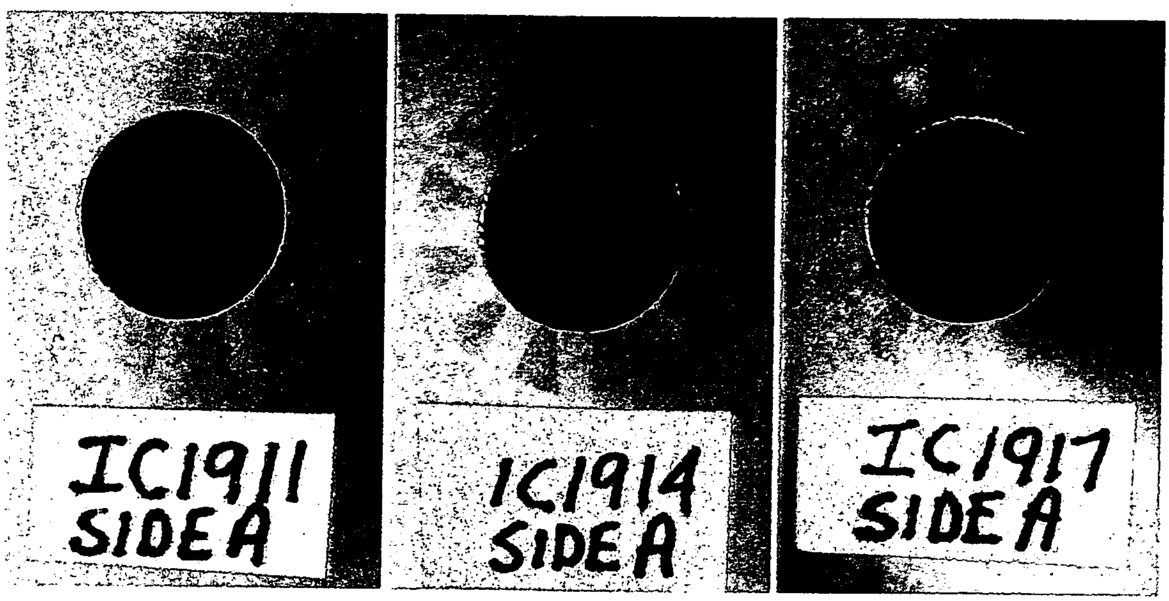


(b)

Figure 4 Comparison of the descaled weight loss of annealed and welded Ti Grade 7 and annealed and welded Alloy 22 after 4 weeks and 8 weeks exposure (a) and the schematic illustration for a possible explanation (b).

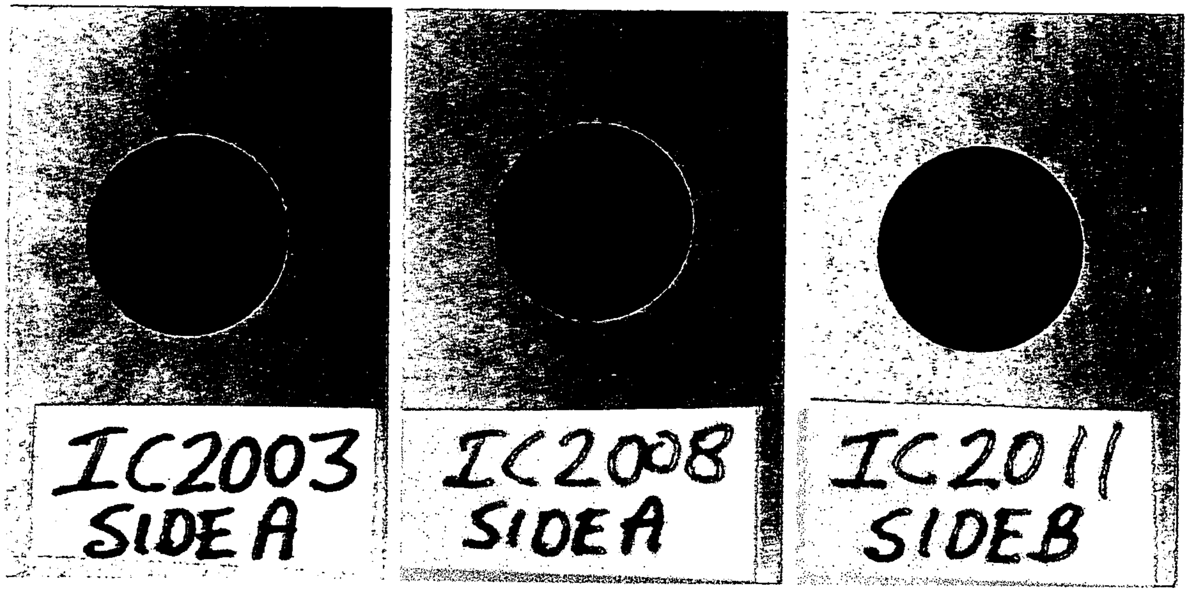


Welded Alloy 22, 60°C, 8 weeks Welded Alloy 22, 70°C, 8 weeks Welded Alloy 22, 80°C, 8 weeks

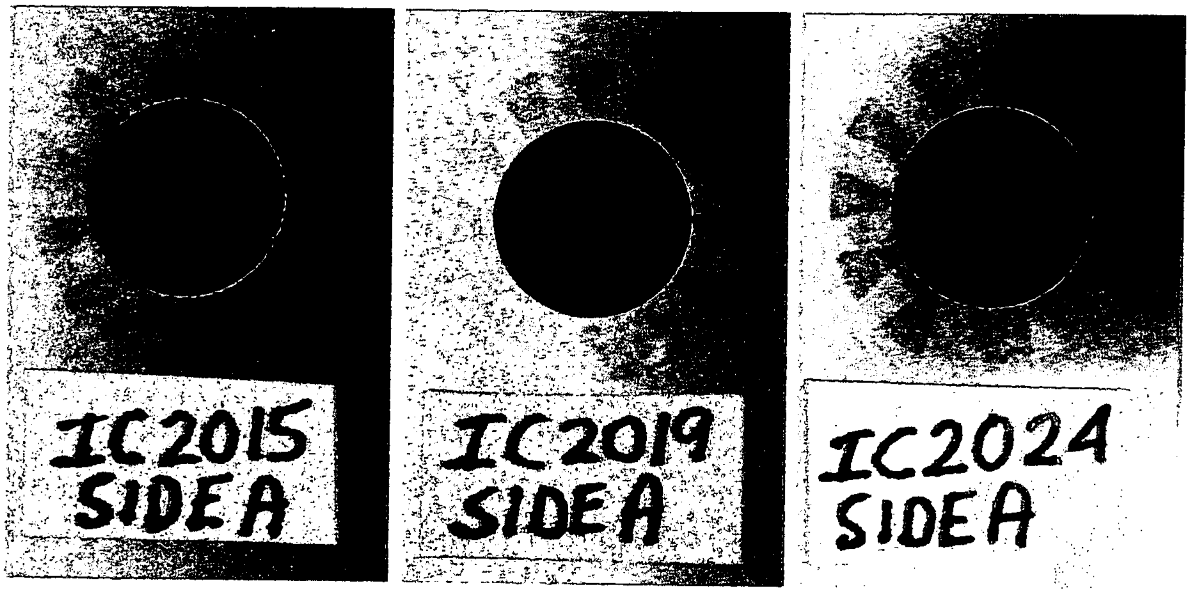


Welded Alloy 22, 90°C, 8 weeks Welded Alloy 22, 100°C, 8 weeks Welded Alloy 22, 105°C, 8 weeks

Figure 5 Microscopic morphologies of welded Alloy 22 MCA specimens after exposed at temperatures 60° ~ 105°C for 8 weeks, showing the evolution of discoloration underneath the crevice former with increasing temperature.

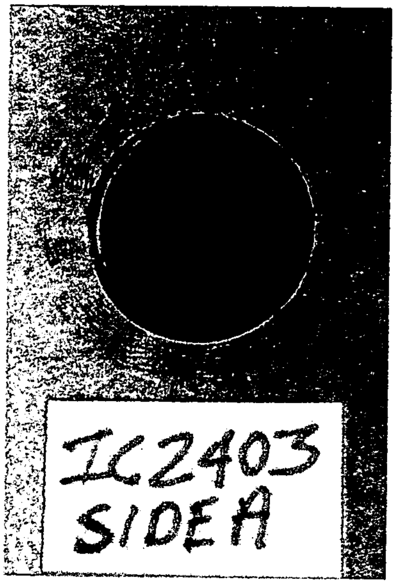


Annealed Alloy 22, 60°C, 8 weeks   Annealed Alloy 22, 70°C, 8 weeks   Annealed Alloy 22, 80°C, 8 weeks

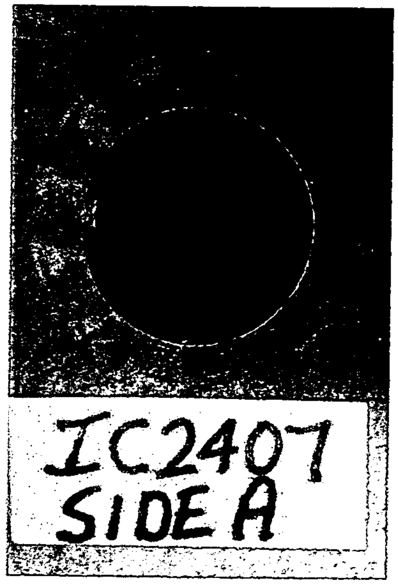


Annealed Alloy 22, 60°C, 8 weeks   Annealed Alloy 22, 70°C, 8 weeks   Annealed Alloy 22, 80°C, 8 weeks

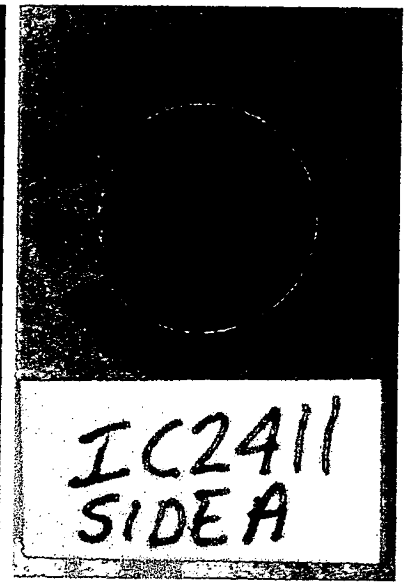
Figure 6 Microscopic morphologies of annealed Alloy 22 MCA specimens after exposed at temperatures 60° ~ 105°C for 8 weeks, showing the evolution of discoloration underneath the crevice former with increasing temperature



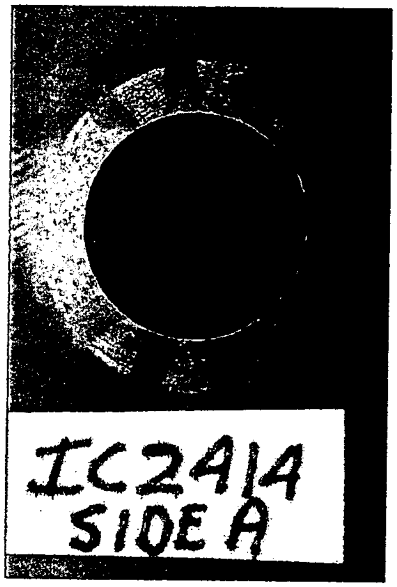
Welded Ti Gr. 7, 60°C, 8 weeks



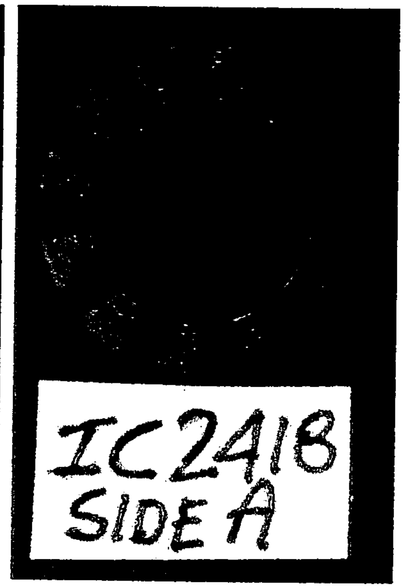
Welded Ti Gr. 7, 70°C, 8 weeks



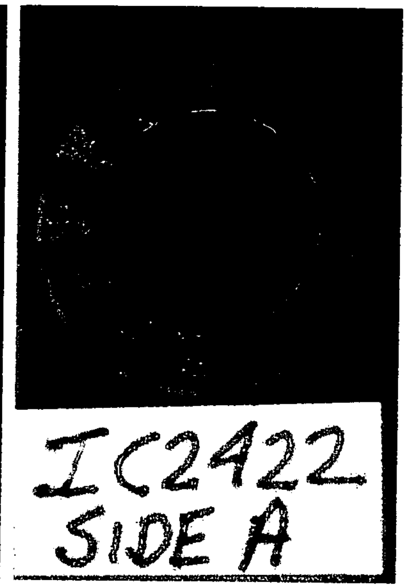
Welded Ti Gr. 7, 80°C, 8 weeks



Welded Ti Gr. 7, 90°C, 8 weeks

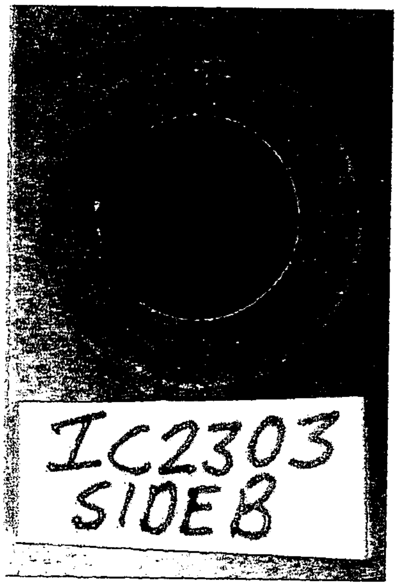


Welded Ti Gr. 7, 100°C, 8 weeks

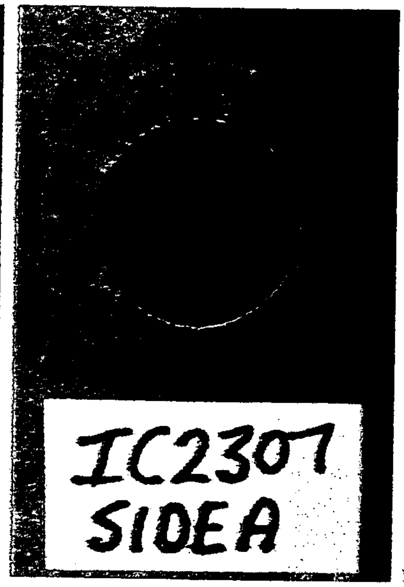


Welded Ti Gr. 7, 105°C, 8 weeks

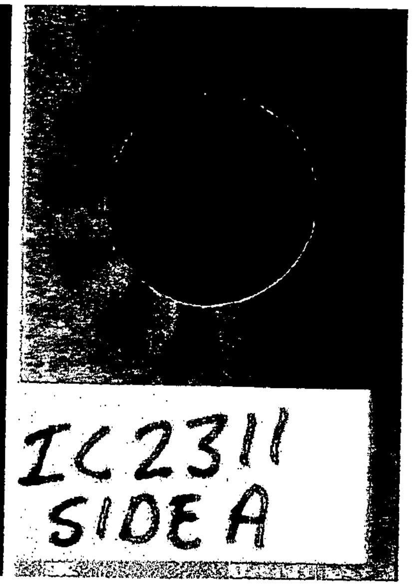
Figure 7 Microscopic morphologies of welded Ti Grade 7 MCA specimens after exposed at temperatures 60° ~ 105°C for 8 weeks, showing the evolution of the discoloration underneath the crevice former with increasing temperature



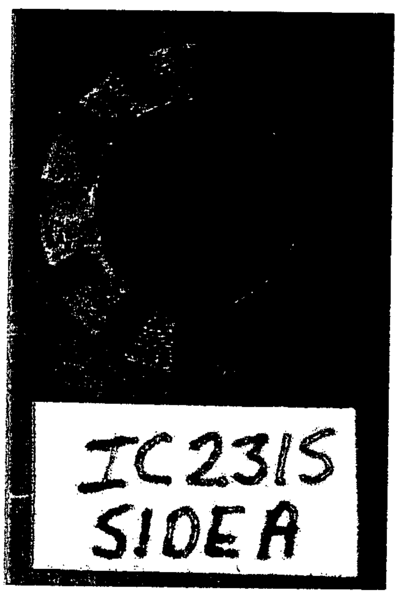
Annealed Ti Gr. 7, 60°C, 8 weeks



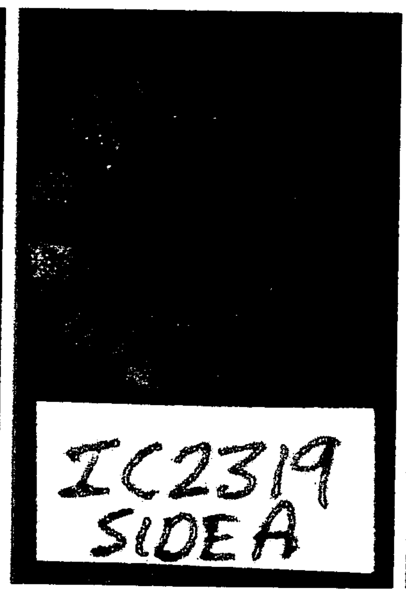
Annealed Ti Gr. 7, 70°C, 8 weeks



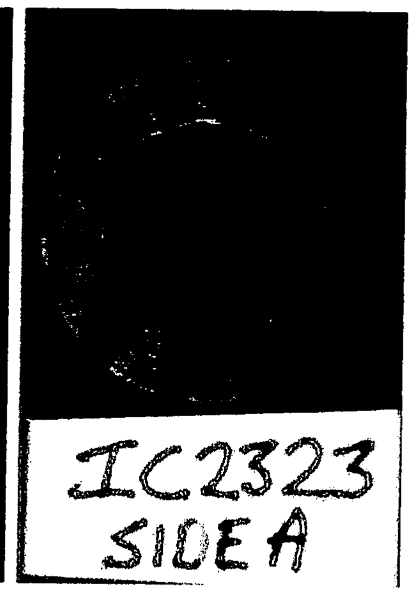
Annealed Ti Gr. 7, 80°C, 8 weeks



Annealed Ti Gr. 7, 90°C, 8 weeks



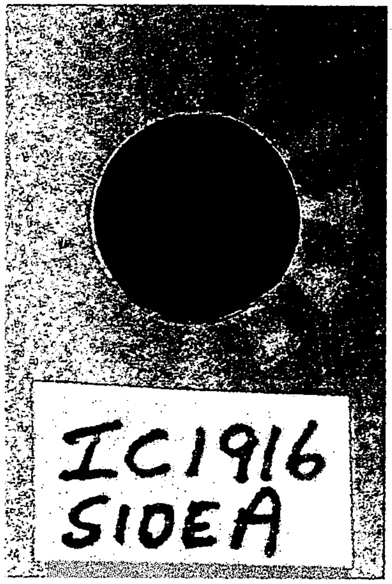
Annealed Ti Gr. 7, 100°C, 8 weeks



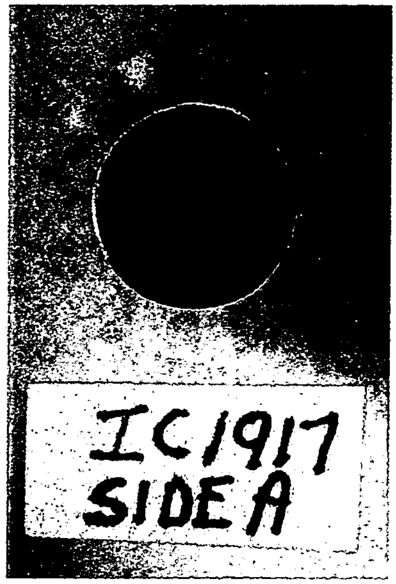
Annealed Ti Gr. 7, 105°C, 8 weeks

(b)

Figure 8 Microscopic morphologies of annealed Ti Grade 7 MCA specimens after exposed at temperatures 60° ~ 105°C for 8 weeks, showing the evolution of the discoloration underneath the crevice former with increasing temperature

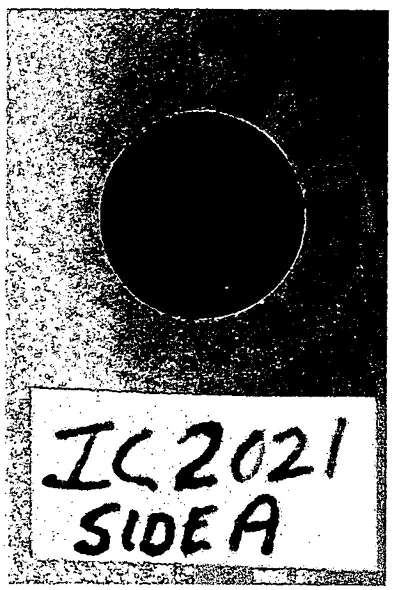


Welded ALLOY 22, 105°C, 4 weeks

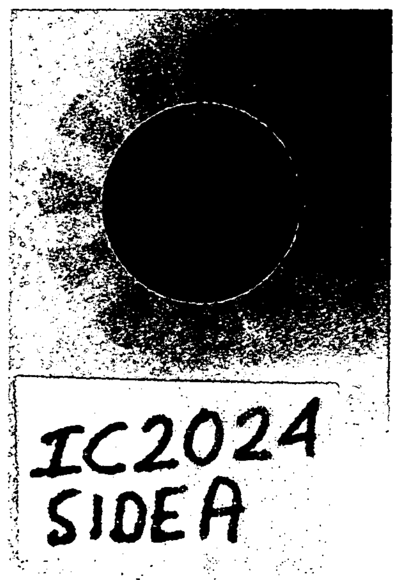


Welded ALLOY 22, 105°C, 8 weeks

(a)



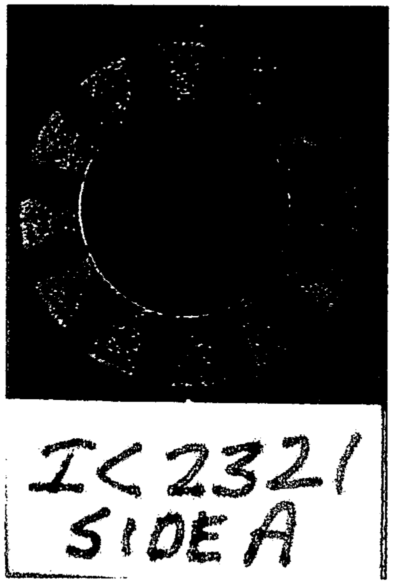
Annealed ALLOY 22, 105°C, 4 weeks



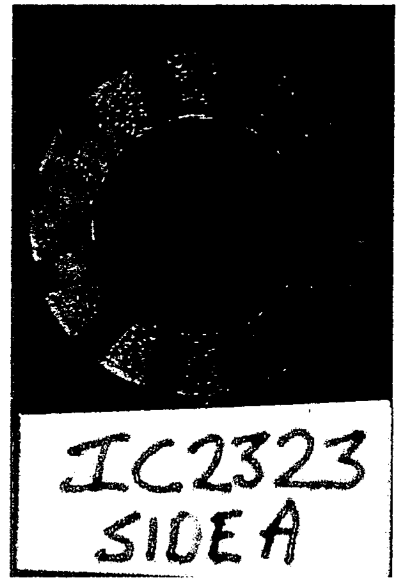
Annealed ALLOY 22, 105°C, 8 weeks

(b)

Figure 9 Macroscopic morphologies of welded (a) and annealed Alloy 22 MCA specimens after 4 weeks and 8 weeks of exposure time at 105°C, showing no significant difference in the degree of discoloration underneath the crevice former

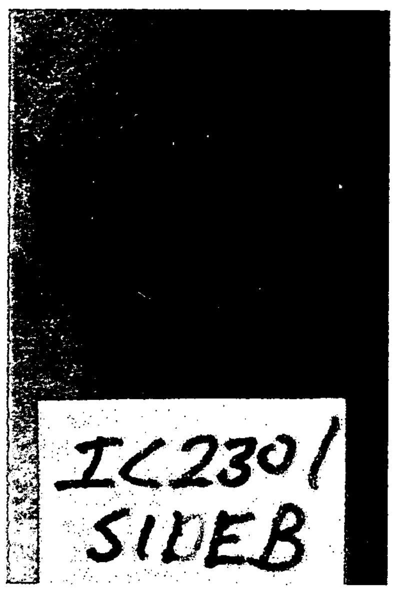


Annealed Ti Gr. 7, 105°C, 4 weeks

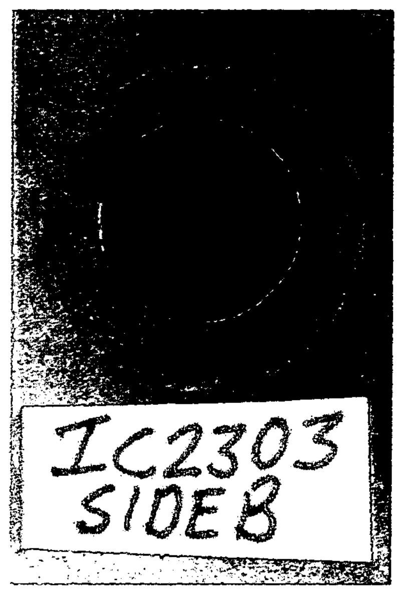


Annealed Ti Gr. 7, 105°C, 8 weeks

(a)



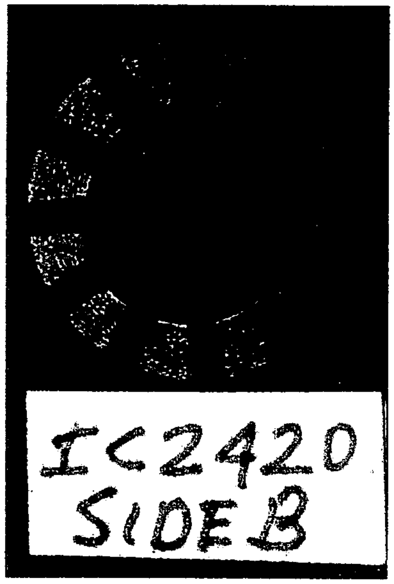
Annealed Ti Gr. 7, 60°C, 4 weeks



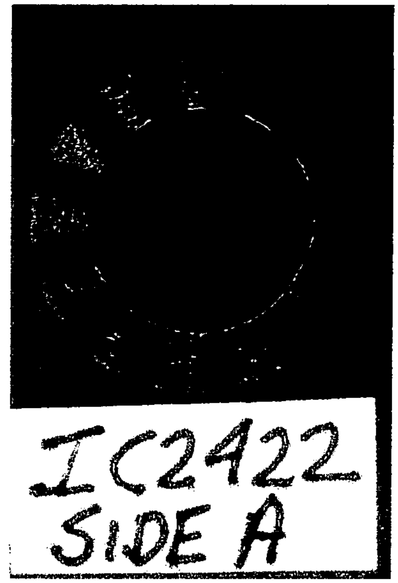
Annealed Ti Gr. 7, 60°C, 8 weeks

(b)

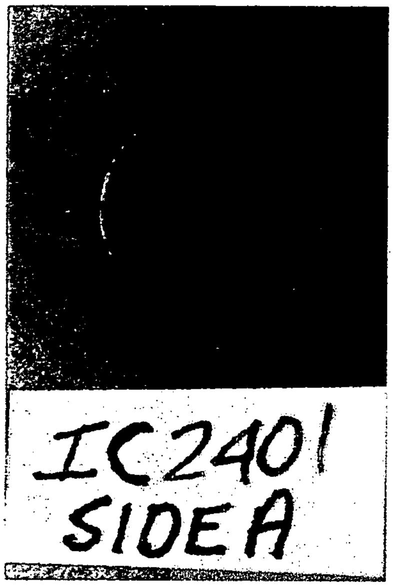
Figure 10 Macroscopic morphologies of annealed Ti Grade 7 MCA specimens after 4 weeks and 8 weeks of exposure time at (a) 105°C and (b) 60°C, showing no significant difference in the degree of discoloration underneath the crevice former



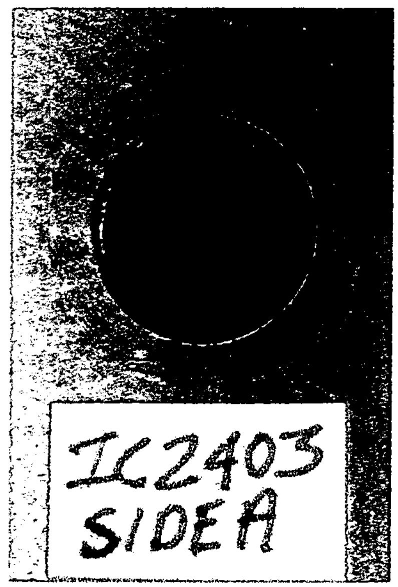
Welded Ti Gr. 7, 105°C, 4 weeks



Welded Ti Gr. 7, 105°C, 8 weeks

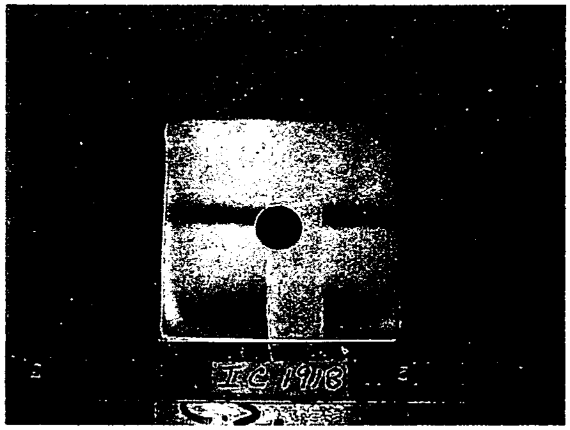


Welded Ti Gr. 7, 60°C, 4 weeks



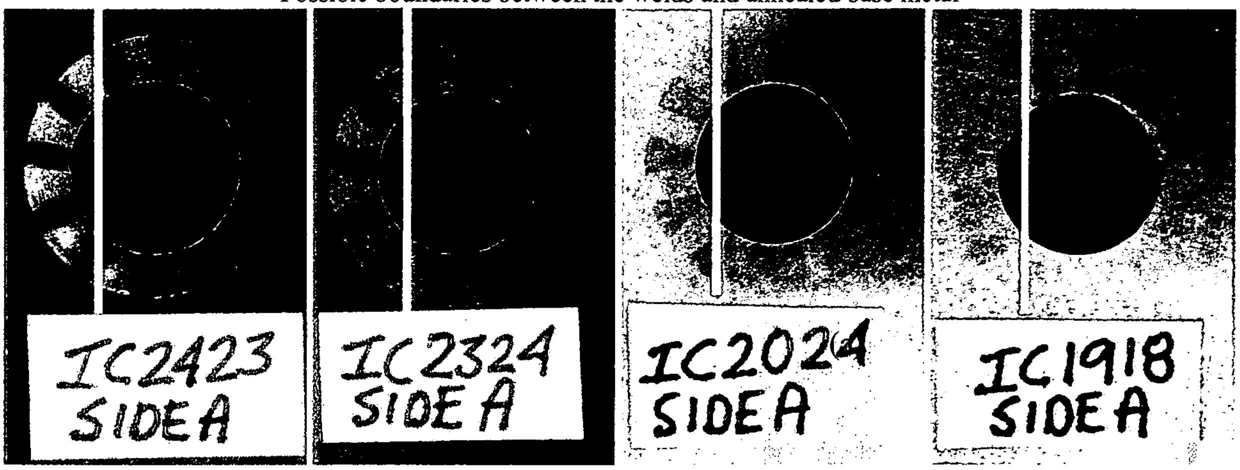
Welded Ti Gr. 7, 60°C, 8 weeks

Figure 11 Macroscopic morphologies of welded Ti Grade 7 MCA specimens after 4 weeks and 8 weeks of exposure time at (a) 105°C and (b) 60°C, showing no significant difference in the degree of discoloration underneath the crevice former



(a)

Possible boundaries between the welds and annealed base metal



(b) (c) (d) (e)

(a) Location of weld metal in crevice corrosion specimen IC1918
(b) Welded Ti Gr. 7 after 8 weeks exposure at 105°C
(c) Annealed Ti Gr. 7 after 8 weeks exposure at 105°C
(d) Welded Alloy 22 after 8 weeks exposure at 105°C
(e) Annealed Alloy 22 after 8 weeks exposure at 105°C

Figure 12 Selected examples of the post-test welded specimens after 8 weeks exposure at 105°C, showing no noticeable difference in morphology across the welds/base metal boundaries

(a)

(b)

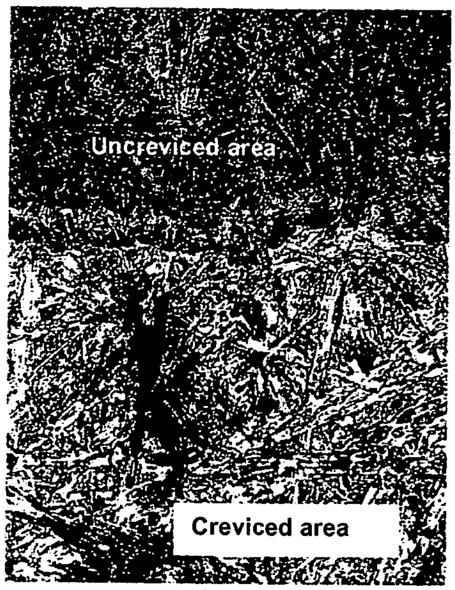
(c)

(d)

02529/~~24~~25 Lmm 11-16-2001

(e)

(f)



(g)

Figure 13 Micrographs of annealed Ti Grade 7 after exposed for 8 weeks at (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, (e) 100°C, (f) 105°C and (g) after exposed for 4 weeks at 105°C

(a)

(b)

(c)

(d)

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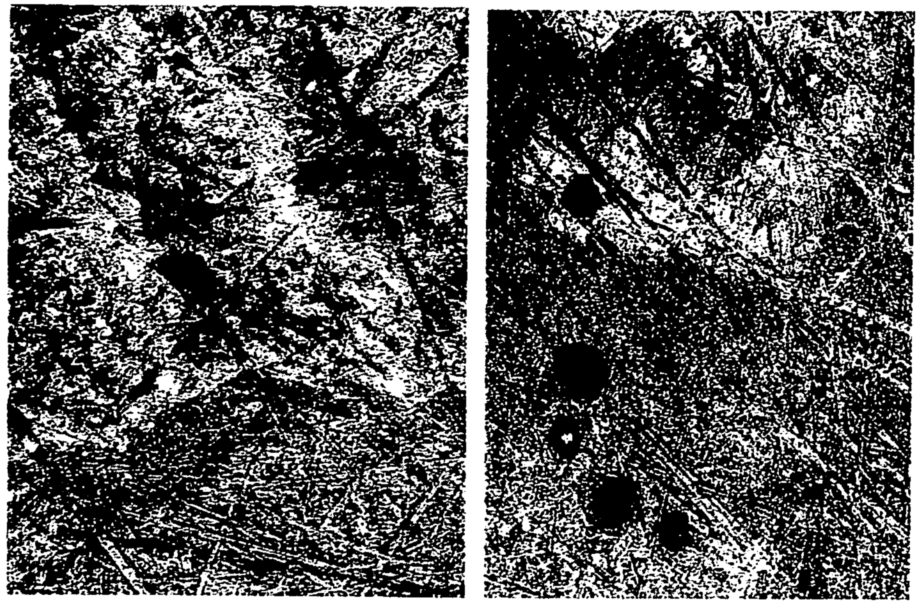
LMM 11-16-2001

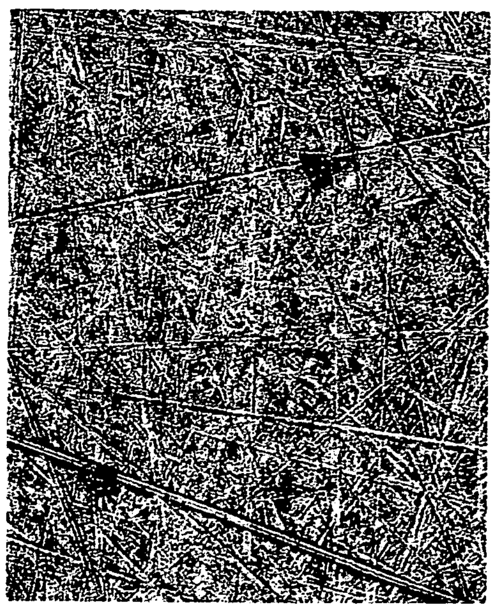


(e) (f)

Figure 14 Micrographs of welded Ti Grade 7 after exposed for 8 weeks at (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, (e) 100°C, and (f) 105°C (200×)

(a)

(b)



(c)

Figure 15 Optical micrographs of (a) annealed Alloy 22 after 4 weeks exposure at 60°C, (b) annealed Alloy 22 after 8 weeks exposure at 105°C and (c) untested annealed Alloy 22, 200×

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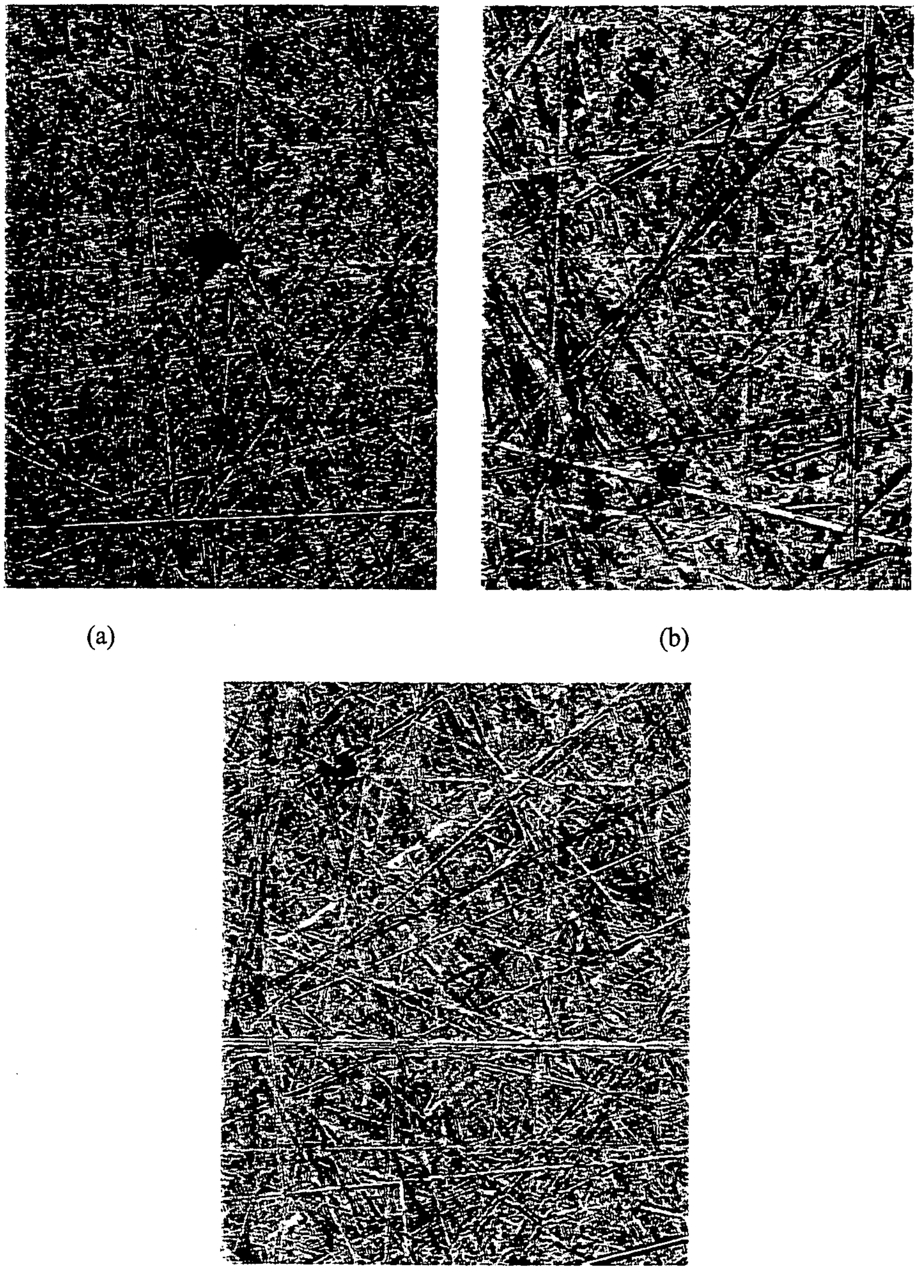

(a) (b)

(c)

Figure 16 Optical micrographs of (a) welded Alloy 22 after 4 weeks exposure at 60°C, (b) welded Alloy 22 after 8 weeks exposure at 105°C and (c) untested welded Alloy 22, 200×

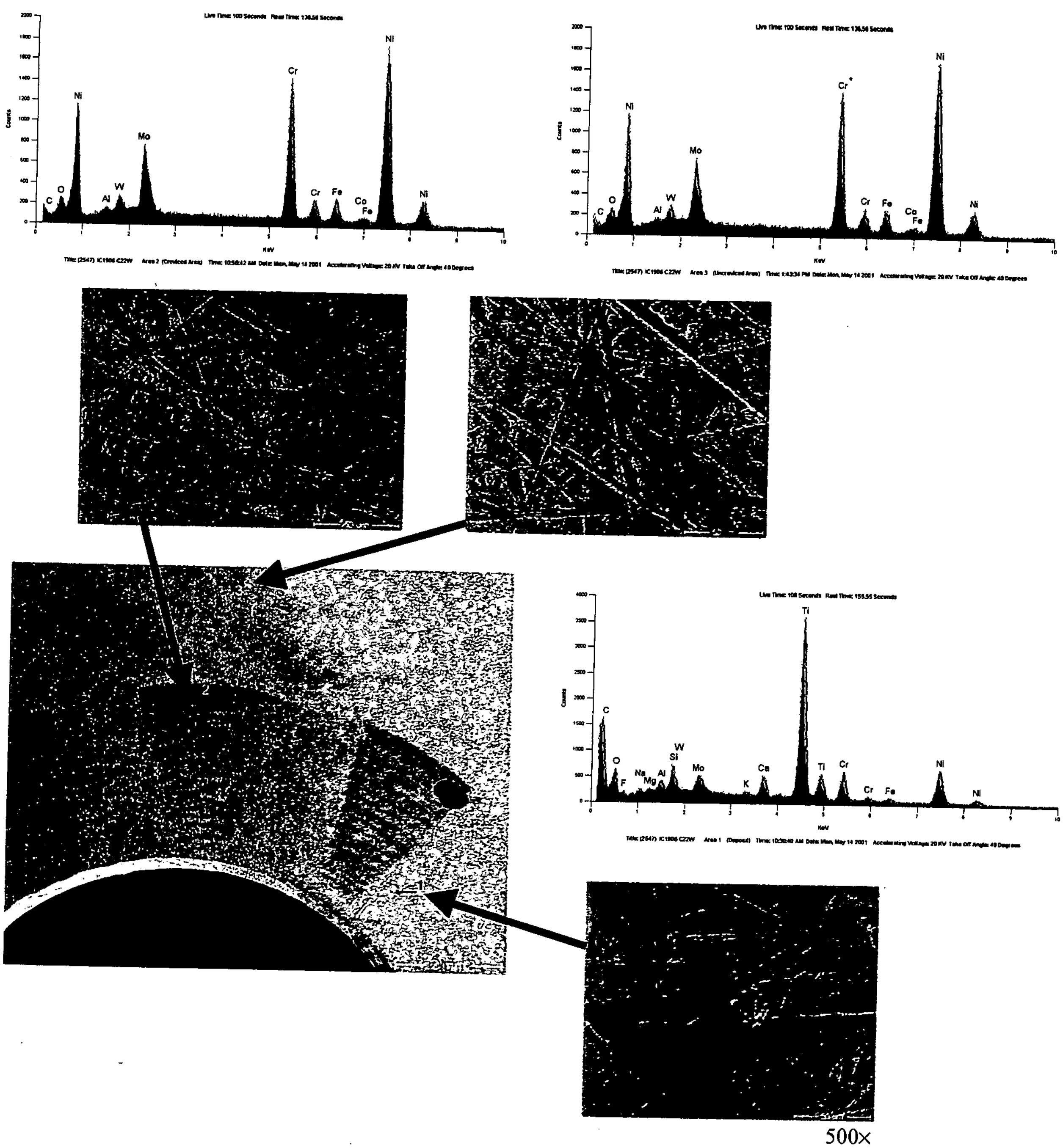

Figure 17 SEM images of a representative welded Alloy 22 specimen after 4 weeks exposure at 105°C (specimen IC 1906), showing the microscopic morphology outside of the creviced area (location 1, 500×) and the chemical compositions both at the creviced and uncreviced areas (locations 1, 2 and 3).

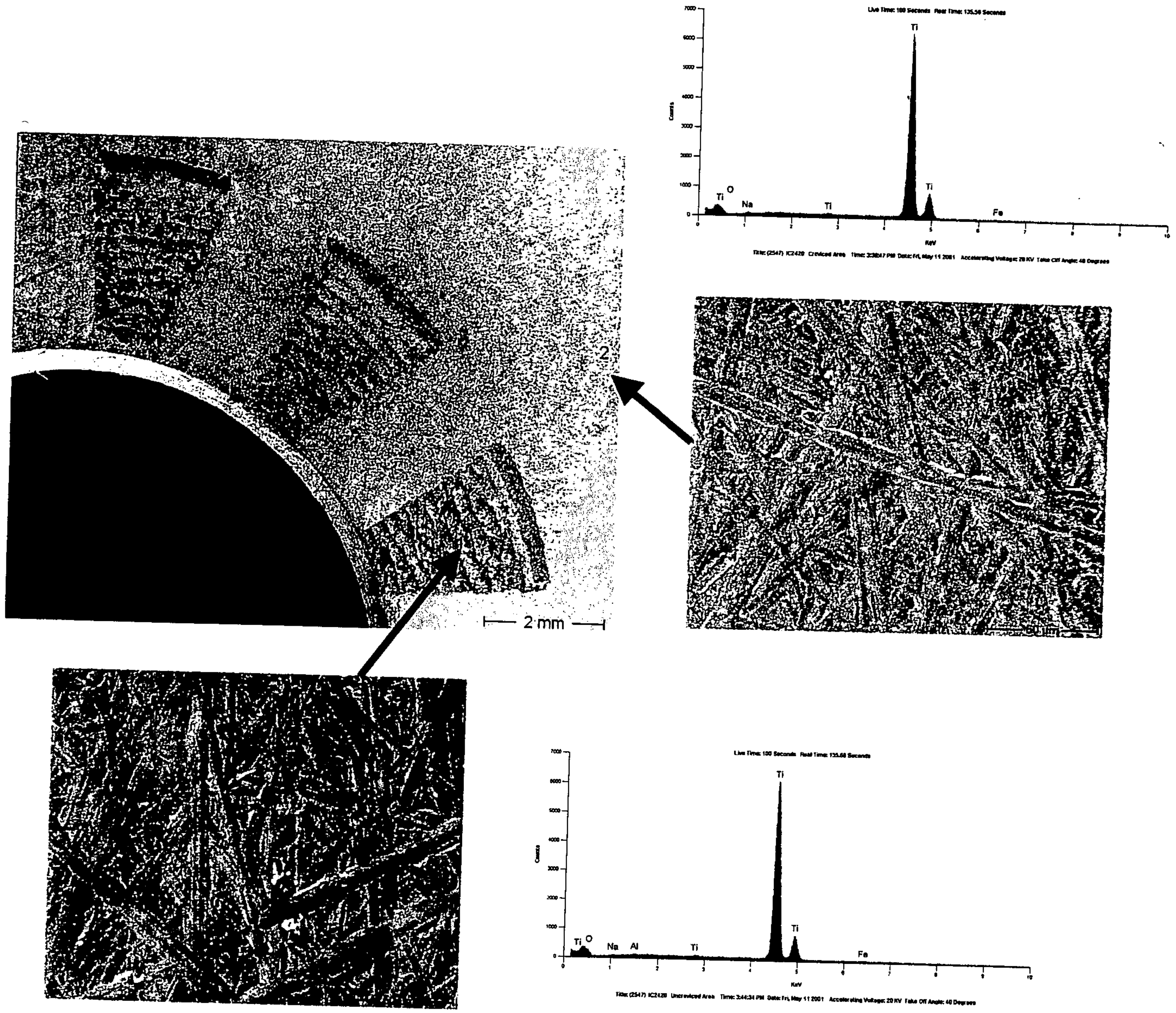

Figure 18 SEM images of a representative welded Ti Grade 7 specimen after 8 weeks exposure at 105°C (specimen IC 2420), showing the microscopic morphologies and chemical compositions of the areas both underneath the crevice former (location 1, 500×).) and outside of the creviced area (location 2, 500×).

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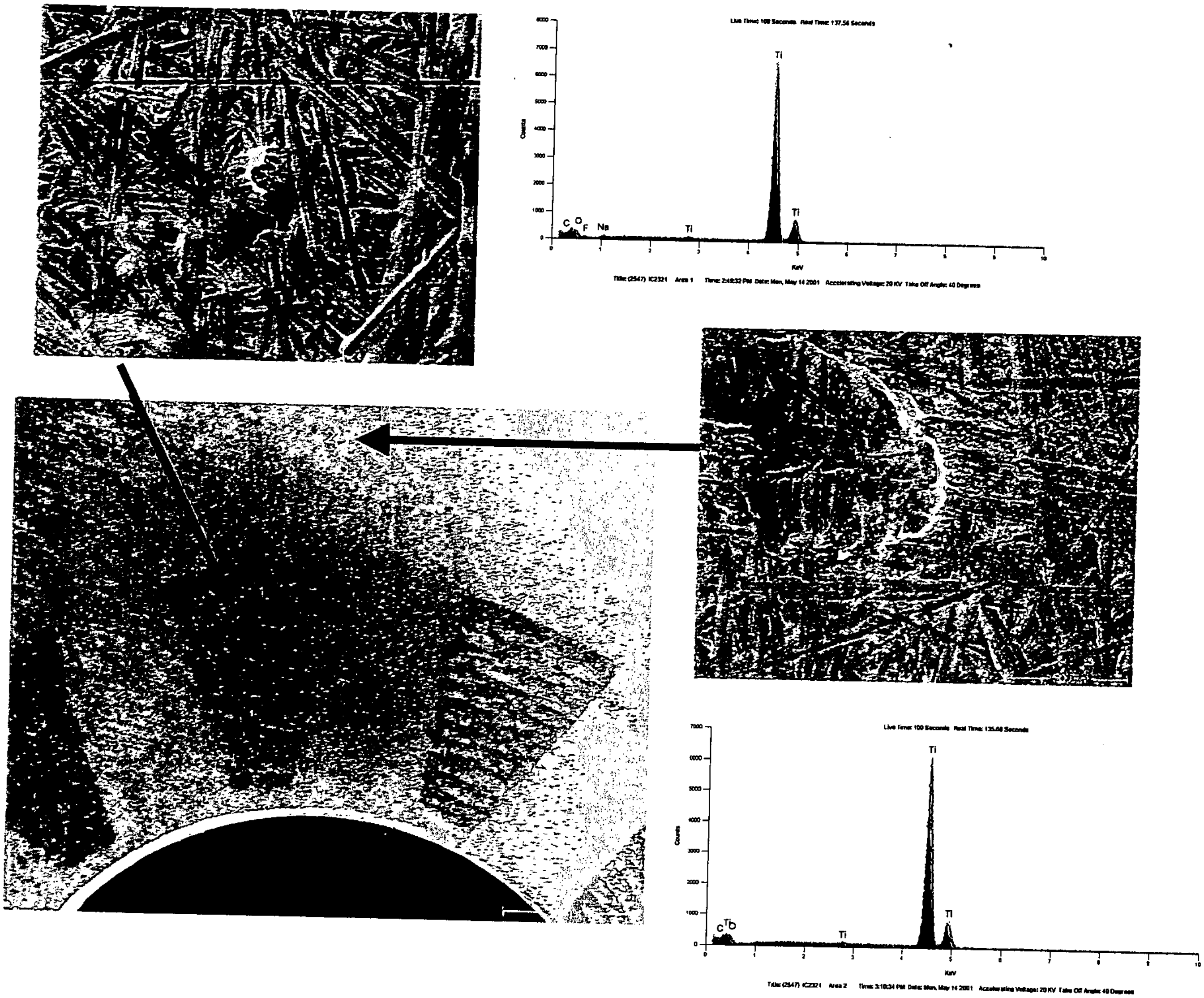
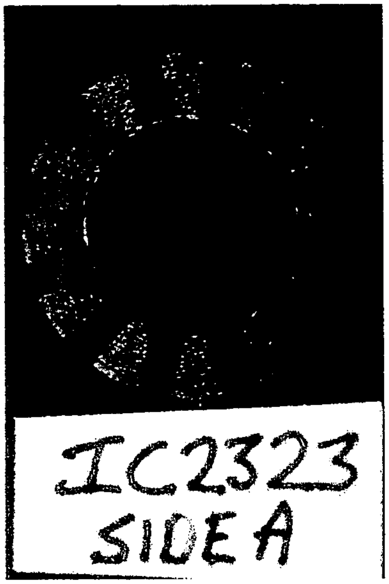
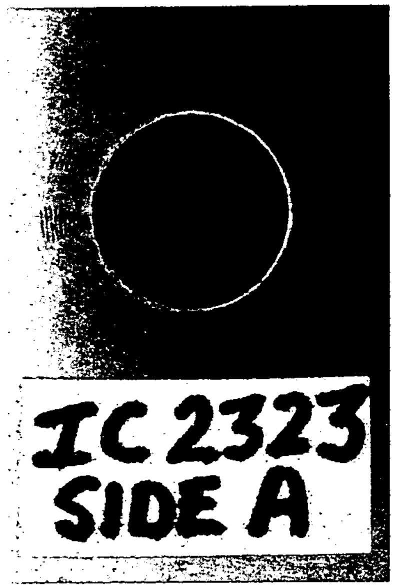


Figure 19 SEM images of a representative annealed Ti Grade 7 specimen after 4 weeks exposure at 105°C (specimen IC 2321), showing the microscopic morphologies and chemical compositions of the areas both underneath the crevice former (location 1, 500×) and outside of the creviced area (locations 2, 500×).



(a) Before descaling



(b) After descaling

(c) Uncreviced area 1,500×

(d) Creviced area 1,500×

Figure 20 Optical and SEM post-descaling morphologies of an annealed Ti Grade 7 specimen (IC 2323) tested in 105°C BSW-12 for 8 weeks, showing the macroscopic morphology of post-test specimen before descaling (a), the remaining "crevice pattern" on post-test post descaling specimen (b) and the similarity between the creviced and uncreviced areas on post-test post descaling specimen (c) and (d)

cmm
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