



CORROSION TESTING IN LOW OXYGEN CONTENT BRINE

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1. INTRODUCTION

CAPCIS Ltd conducted corrosion and stress corrosion cracking tests on five materials in a simulated brine with three dissolved oxygen levels.

2. WORKSCOPE

2.1 TEST MATERIALS

The following free-issued materials were tested:

- Hastelloy C276
- Alloy 625 (cast)
- Alloy 625 (weld overlay)
- Zeron 100 superduplex stainless steel
- 6% Mo superaustenitic stainless steel

2.2 TEST CONDITIONS

Three test conditions were employed in this work.

Brine: Seawater made up to 360 g/l NaCl

[This was achieved by making up "Substitute Ocean Water" (ASTM D 1141), but using 360 g/L NaCl in place of 24.53 g/L NaCl. This represents a concentration factor of approximately 14.7 over typical seawater.]

Temperature: 65°C

Dissolved oxygen content: 20, 100 & 500 ppb (µg/l)

[This was achieved using oxygen in nitrogen gas mixes of 0.44%, 2.21% & 11% respectively.]

2.3 CORROSION TESTS

For each material (apart from the Zeron 100 superduplex stainless steel) four coupons were machined: two 30x30 mm and two 30x15 mm, all approximately 3 mm thick. A hole was drilled in the centre of each coupon and pairs of coupons (one 30x30 mm coupon and one 30x15 mm coupon) were bolted together in order to create metal to metal crevice assemblies. For the Zeron 100 superduplex stainless steel, four circular coupons were machined 50 mm in diameter and approximately 5 mm thick. For each pair of coupons a hole was drilled centrally in one of the coupons and 15 mm from the centre in the other coupon. The pair of coupons were bolted together in order to create metal to metal crevice assemblies. Plastic to metal crevices were present on the rear faces of the coupons; PEEK 'top hat' washers were used to insulate the titanium alloy bolts from the test coupons. Two such assemblies of each of the five test materials were used in each test condition.

The surface condition of each coupon was prepared to the equivalent of a 1200 grit finish.

The crevice assemblies were exposed in the test conditions described in section 2.2 for 720 hours, after which they were disassembled and photographed. Weight loss determination was carried out after corrosion products were removed using nitric acid, in accordance with ASTM G1. Note that hydrochloric acid was required to remove the corrosion products from the Hastelloy C276.

The potentials of plain coupons of each test material were recorded daily, using a saturated calomel reference electrode connected via a salt bridge.

2.4 STRESS CORROSION CRACKING TESTS

U-bend coupons, to ASTM G30, were made from four of the test materials (not the 6% Mo superaustenitic). Duplicate coupons were exposed in each of the three test conditions described in section 2.2 of this report.

3. RESULTS

The results are presented in Table 1 and Figures 1-22.

3.1 CORROSION RATES

The general corrosion rates in Table 1 were calculated from weight loss measurements. The general metal loss was very low. This coupled with difficulty in removing all the corrosion product meant that for some coupons general corrosion rates could not be determined.

3.2 LOCALISED CORROSION

Crevice and pitting effects were present on many of the coupons as indicated in Table 1. Illustrations are presented in Figures 2-22 attached.

3.3 POTENTIAL MEASUREMENTS

Potential measurements are presented in Figure 1. Note that an unidentified fault prevented the correct recording of the potential of the welded Alloy 625 in 2.21% oxygen conditions.

3.4 STRESS CORROSION CRACKING

No stress corrosion cracking was found on any of the U-bend coupons by visual inspection at x20 magnification and dye penetrant inspection.

Table 1. Corrosion results.

Material	20 ppb O ₂ DO			100 ppb O ₂ DO			500 ppb O ₂ DO		
	Corrosion rate (µm/year)	Crevice corrosion	Pitting corrosion	Corrosion rate (µm/year)	Crevice corrosion	Pitting corrosion	Corrosion rate (µm/year)	Crevice corrosion	Pitting corrosion
Hastelloy C276	NC	10 µm	10 µm	NC	10-40 µm	10-40 µm	NC	10 µm	10 µm
	0			NC			NC		
	0	10 µm		0.13	10-40 µm	10-40 µm	0.13	10 µm	10 µm
	NC			NC			NC		
Alloy 625 cast	0	<5 µm	10 µm	1.0	DP	<5 µm	2.7	DP	<5 µm
	1.3			2.9			4.5		
	0	<5 µm	<5 µm	1.0	DP	<5 µm	4.8	200 µm	shallow
	NC			4.2			4.8		
Alloy 625 welded	19.2			1.4	shallow		2.9		
	9.3			1.3			11.9	shallow	
	2.1	[69-135]	[69-135]	1.4	DP		10.7	[>200]	[>200]
	4.0			2.7			10.6		
Zeron 100	NC			NC			0.6	DP	
	NC			1.9	[16 µm]		9.7	100 µm	
	NC			NC	DP		NC	DP	
	NC			NC			3.2	80 µm	
6%Mo	1.4			0.4	DP	<5 µm	1.4		
	NC			1.3			22.5		
	1.4	10 µm	10 µm	NC	DP		7.1	400 µm	<5 µm
	NC			NC			14.6		

Notes: NC denotes weight increase on coupon, due to adherent corrosion product, preventing calculation of corrosion rate.
 DP denotes depassivation with no measurable depth of attack.
 DO denotes dissolved oxygen content.

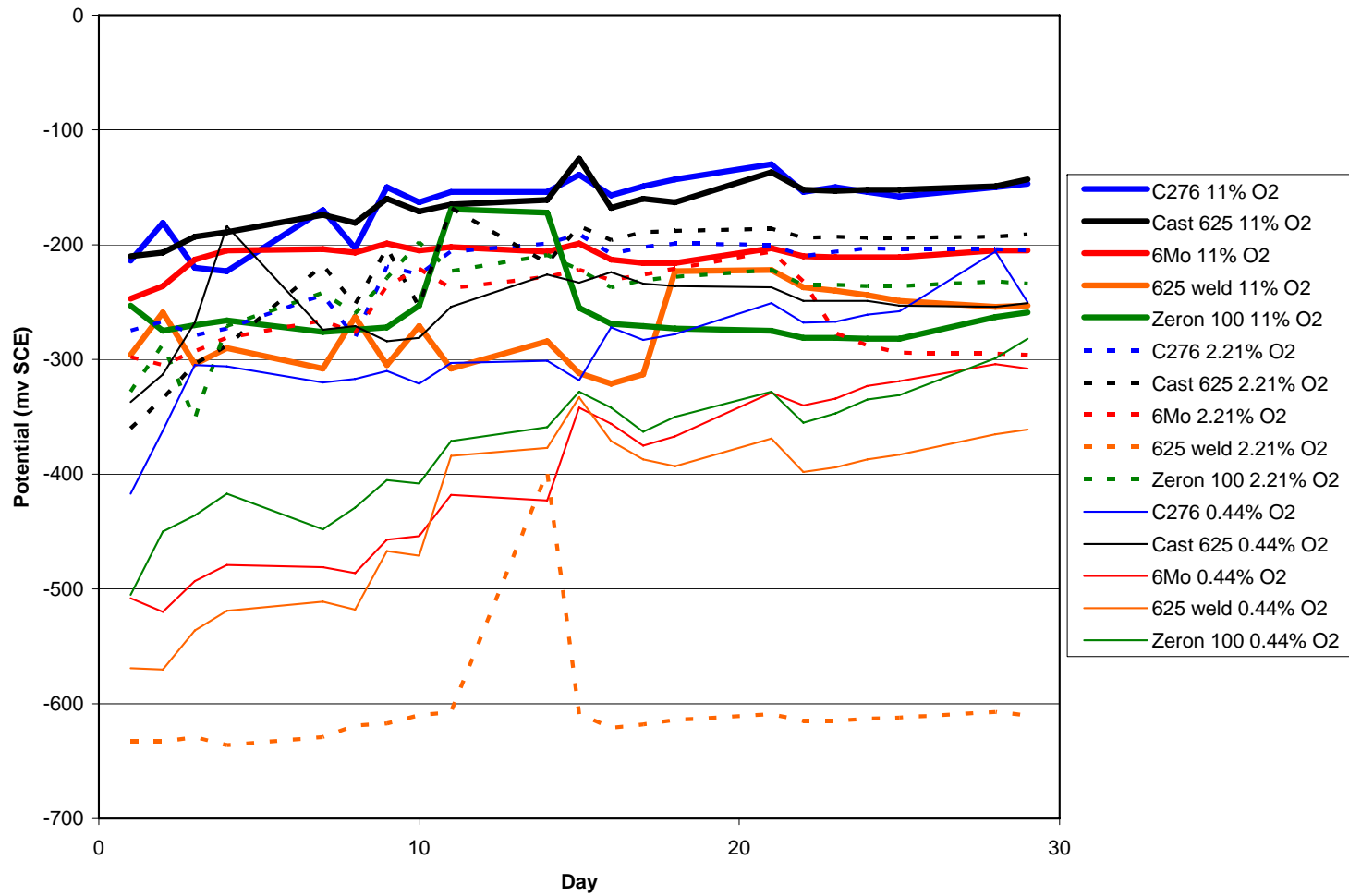


Figure 1. Potential measurements vs. SCE.

4. DISCUSSION

Meaningful general corrosion rates could not be calculated for some of the test coupons because of the difficulty in removing corrosion product without damaging the coupons. However, the general corrosion rate was not significant.

4.1 HASTELLOY C276

General corrosion rates of nil and 0.13 $\mu\text{m}/\text{y}$ were calculated. This indicates that the bulk of the surface of this material was in the passive condition.

Slight corrosion attack had occurred within and away from the crevices. This was limited to $\sim 10 \mu\text{m}$ in the 20 and 500 ppb DO brines but was up to $\sim 40 \mu\text{m}$ in the 100 ppb DO brine. This ordering is not expected, but note that there is some degree of scatter in pitting and crevice corrosion processes.

No SCC was detected.

4.2 CAST ALLOY 625

General corrosion rates averaged over each set of four coupons were 0.4, 3.0 and 5.6 $\mu\text{m}/\text{y}$ for the 20 ppb, 100 ppb and 500 ppb dissolved oxygen contents respectively. While increasing the DO content of the water would be expected to increase its corrosivity, this should not result in general corrosion. The bulk of the surface of Alloy 625 would be expected to remain in the passive condition corrosion with localised corrosion occurring at crevices or in pits.

Localised corrosion was typically $< 5 \mu\text{m}$ in depth, but at the edge of the crevice in the 500 ppb containing oxygen test, an area of crevice corrosion to approximately 200 μm was identified.

No SCC was detected.

4.3 ZERON 100

No weight loss corrosion rates could be calculated for the 20 ppb DO test. 1.9 $\mu\text{m}/\text{y}$ was recorded for one of the 100 ppb DO coupons and an average of 4.5 $\mu\text{m}/\text{y}$ for three of the 500 ppb DO coupons.

One area of crevice corrosion was identified on the rear of one coupon (at the PEEK contact point) in the 100 ppb DO test and depassivation had occurred on the other large coupon. Crevice corrosion had occurred in the 500 ppb DO test.

This is consistent with the increase in corrosivity with oxygen content, although no measurable localised corrosion was found on the coupons.

No SCC was detected.

4.4 6%MO SUPERAUSTENITIC

General corrosion rates averaged over each set of four coupons were 1.4, 0.9 and 11.4 $\mu\text{m}/\text{y}$ for the 20 ppb, 100 ppb and 500 ppb dissolved oxygen contents respectively.

Localised corrosion occurred to one coupon at each temperature. At 20 ppb DO the depth of attack was limited to 10 μm within and away from crevices. At

100 ppb DO attack was limited to a visual indication of depassivation at crevice sites plus pitting to <math><5\ \mu\text{m}</math> away from the crevices. At 500 ppb DO the depth of attack was approximately 400 μm within a crevice and pitting to a depth of <math><5\ \mu\text{m}</math> away from crevices.

No SCC was detected.

4.5 WELDED ALLOY 625

Corrosion rates calculated from weight loss averaged over each set of four coupons were 11.5, 2.3 and 12 $\mu\text{m}/\text{y}$ for the 20 ppb, 100 ppb and 500 ppb dissolved oxygen contents respectively. However, most or all of the weight loss was due to some form of defect in the overlay as discussed below.

Cavities were present on one coupon at each temperature. These cavities appeared to be porosity or other weld-related features, and did not have the characteristics of localised corrosion attack. At 20 ppb DO the depth of the cavities ranged from 69-135 μm and were randomly distributed within and away from crevices. At 100 ppb DO attack was limited to a visual indication of depassivation at crevice sites plus shallow propagation. At 500 ppb DO the depth of cavities was in excess of 200 μm within and away from crevices and slight indications of crevice corrosion were also evident.

The pattern of the cavities suggested their origin was related to the deposition of the second layer of weld metal, but no metallurgical investigation was conducted to properly characterise them.

No SCC was detected.

4.6 GENERAL

In general, the corrosivity of the brine increased with increasing dissolved oxygen content, as would be expected. However, some results were obtained that were not fully in accordance with this trend. Pitting and crevice corrosion are stochastic processes and there can be significant scatter in the results of such tests. Additionally, it has been particularly difficult to remove the corrosion products from some of these test coupons without damaging them.

The Hastelloy C276 showed only shallow indications in all the test conditions. Note that it is often the case that pitting corrosion initiates to a depth of ~5-10 μm within the first few days of a test, then propagates slowly or even completely ceases to propagate. It is not valid to annualise pit penetration rates (which in this case would be 120 $\mu\text{m}/\text{y}$ for pits that are 10 μm deep after 30 days) because propagation rates invariably fall significantly within days or weeks.

The Zeron 100, 6%Mo superaustenitic and the cast Alloy 625 exhibit very low corrosion rates computed from weight loss and little or no localised corrosion at 20 and 100 ppb DO. However, there does appear to be a change in behaviour between the 100 and 500 ppb dissolved oxygen level conditions. These alloys exhibit similar critical pitting and crevice temperatures in seawater. Note that crevice corrosion has been reported for wrought Alloy 625 in fully oxygenated seawater at temperatures as low as 30°C and cast materials typically exhibit slightly lower corrosion resistance than wrought materials. Oil industry guideline document Norsok M-001 places the same operational limits on 6%Mo superaustenitics as they do on the 25%Cr superduplex grades (such as Zeron 100).

It must be noted that there are a number of factors that are involved, such as the exact composition of the steel (their specifications allow for significant variations of Cr, Mo and N contents), surface finish, the development of the protective oxide film over time, etc.

The welded Alloy 625 suffered significant weight loss, but the bulk of this was clearly related to the presence (or formation) of cavities. These cavities had the appearance of weld metal porosity, or perhaps slag inclusions dissolved during the exposure period. The cavities were present in only some of the coupons tested. The true extent of localised corrosion was limited to a few microns in depth, as would be expected in these test environments. Note that welding can significantly reduce the corrosion resistance of corrosion resistant alloys; this can occur simply due to alloying element segregation within the weld metal, it can be caused by loss of alloying elements (particularly Cr) during welding (especially if inert gas shielding is ineffective) and it can be caused by incorrect selection of welding consumable. However, the reason for the high weight losses recorded in these tests was the quality of the weld metal overlay; correctly deposited Alloy 625 would be expected to exhibit good resistance, as was evident away from the areas where cavities developed.

Potentials measured in the course of these tests rose for the first 15 days or so. This increase in potential is termed 'ennobling'. It is commonly observed, and is thought to be related to changes that occur to the oxide film that is present on the surface of stainless steels and other CRAs. In real seawater at ambient temperature (e.g. 20-30°C) the potentials of CRAs rise by a greater amount. This is due to microbiological action in the seawater (this effect is not possible in a sterile brine) and is the reason that real seawater is more corrosive than a brine of the same composition but which does not contain bacteria. Note that in seawater at temperatures above approximately 40°C the bacteria cease to proliferate and the ennobling effect becomes insignificant. Similarly, high salt content prevents the proliferation of bacteria, hence the ennobling effect is insignificant in stronger brines.

For each test material the trend was for the higher dissolved oxygen levels to produce higher potentials; this is to be expected.

In each test condition the trend was for C276 and cast Alloy 625 to adopt the highest potentials and welded Alloy 625 to adopt the lowest potential.

A sudden fall in potential can indicate the onset of localised corrosion. However, in the present work the extent of corrosion is so low that small anodic areas have not influenced the potentials of the coupons. CAPCIS therefore considers that the potential data should not be used to interpret the results of these tests.

No stress corrosion cracking occurred on any material in these tests, but 6%Mo was not tested. No cracking would be expected for any of these alloys at 65°C.

5. CONCLUSIONS

The results obtained in the course of these tests are consistent with information in the open literature. Extensive data exists for the corrosion behaviour of stainless steels and other corrosion resistant alloys in seawater, but less exists for brines.

- All five test materials showed high resistance to corrosion in the 20 and 100 ppb dissolved oxygen conditions.
- The 500 ppb dissolved oxygen test condition caused slight corrosion to the 6%Mo superaustenitic stainless steel, cast Alloy 625, welded Alloy 625 and Zeron 100.
- Hastelloy C276 was the only material that showed essentially nil crevice corrosion at 500 ppb dissolved oxygen.
- The welded Alloy 625 test material contained some form of defect.

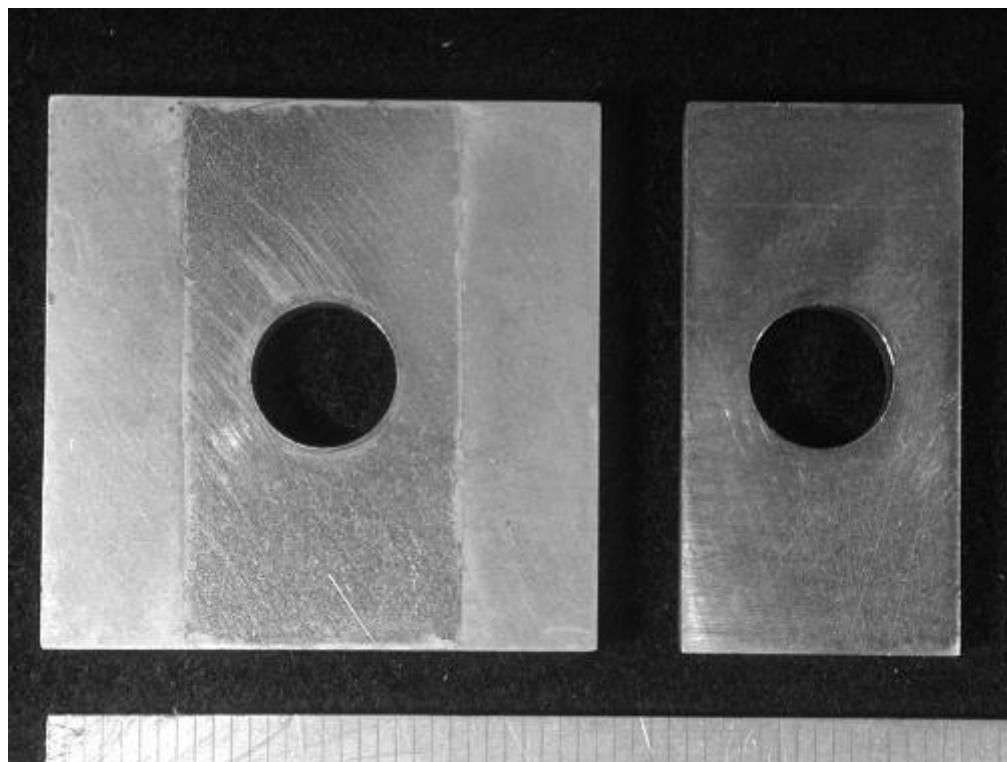


Figure 2. Hastelloy C276 coupons after test in 20 ppb O₂, before cleaning.

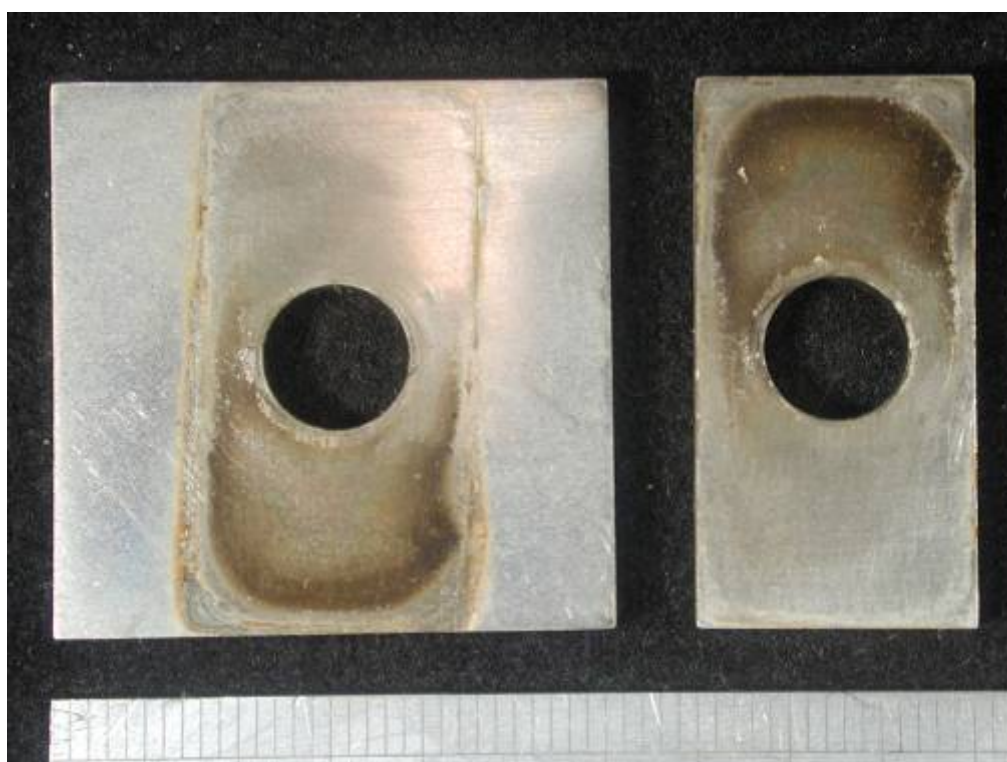


Figure 3. Hastelloy C276 coupons after test in 500 ppb O₂, before cleaning.

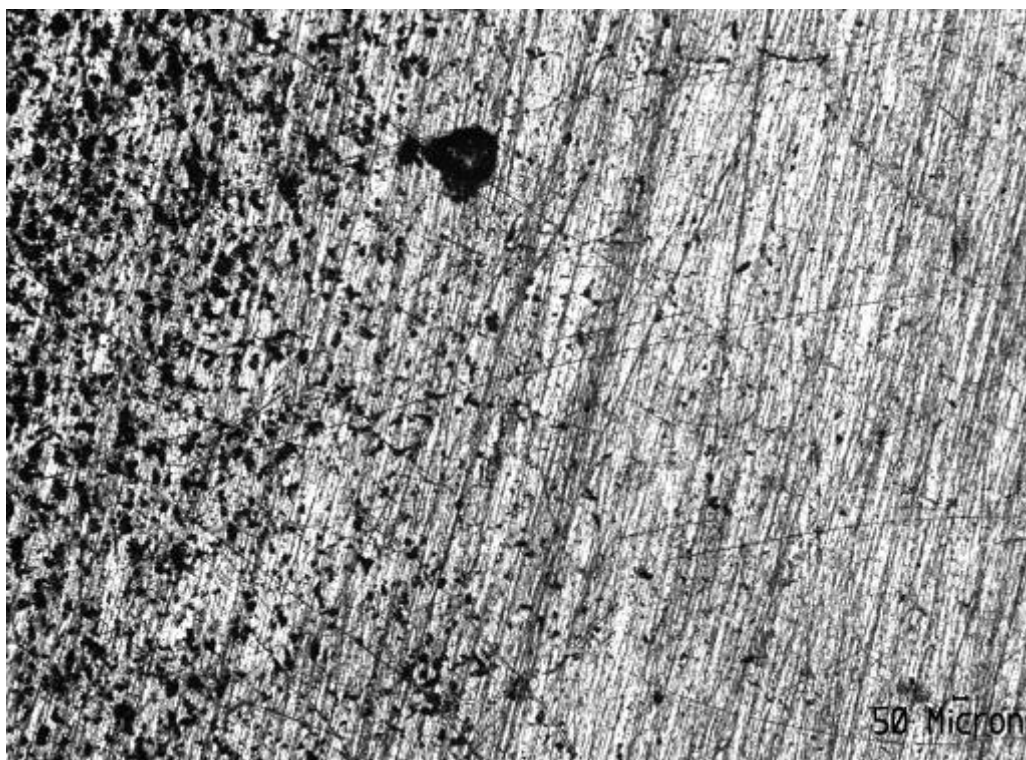


Figure 4. Edge of creviced area on Hastelloy C276 coupon after cleaning.

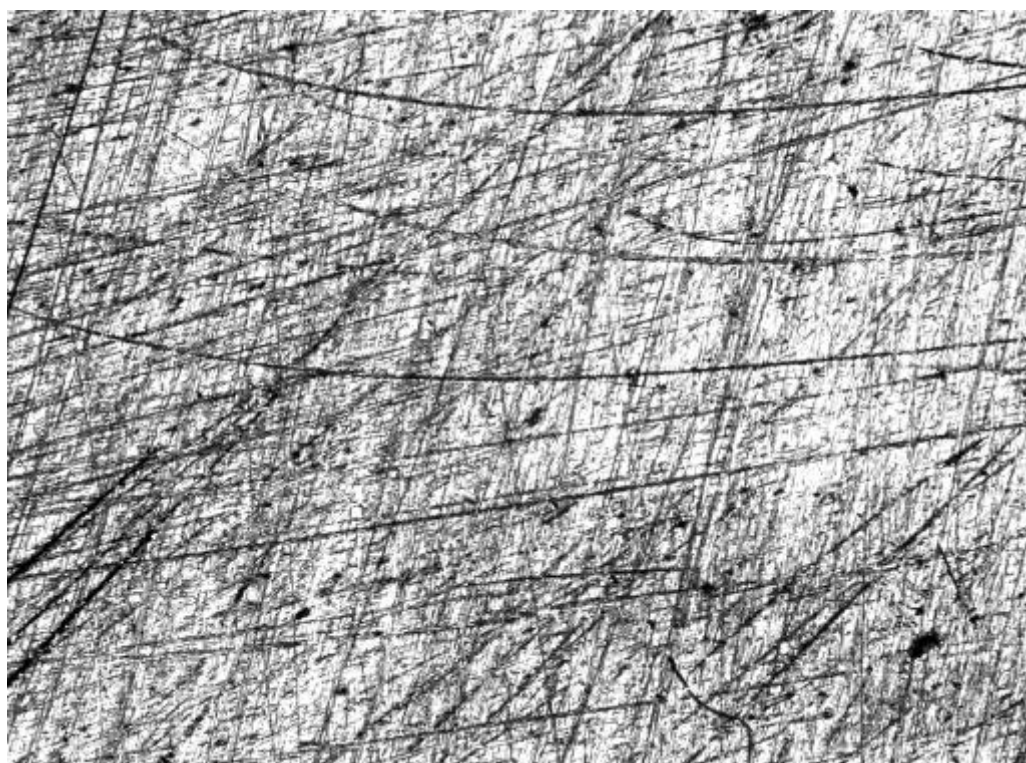


Figure 5. Non- creviced area on Hastelloy C276 coupon after cleaning.

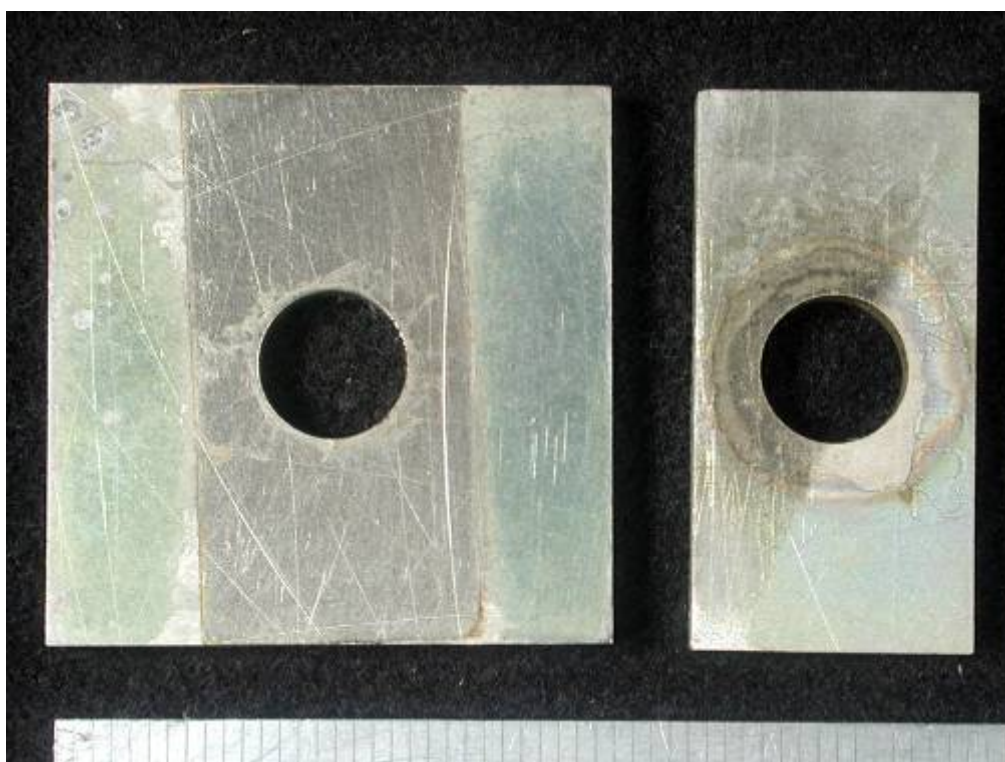


Figure 6. Cast Alloy 625 coupons after test in 20 ppb O₂, before cleaning.

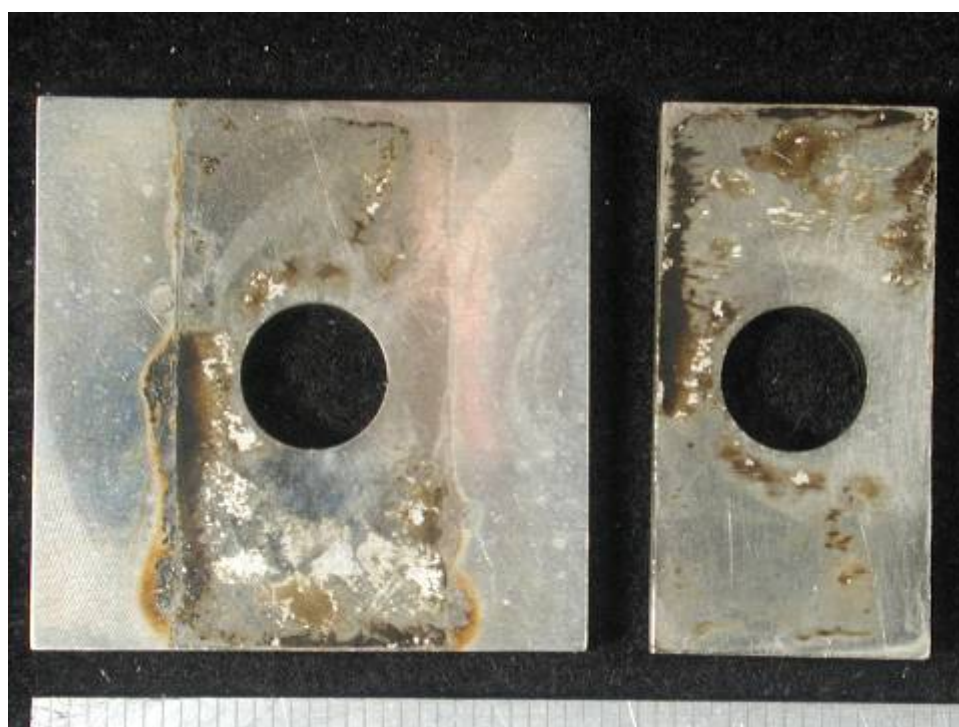


Figure 7. Cast Alloy 625 coupons after test in 500 ppb O₂, before cleaning.

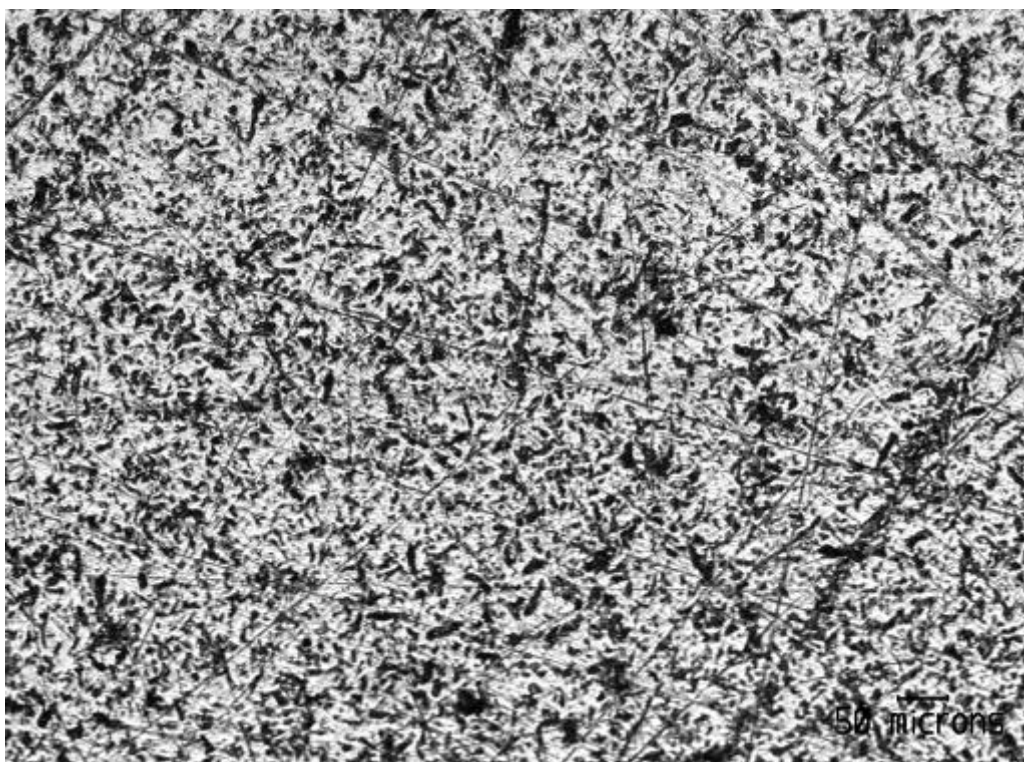


Figure 8. Creviced area on Alloy 625 coupon after cleaning.

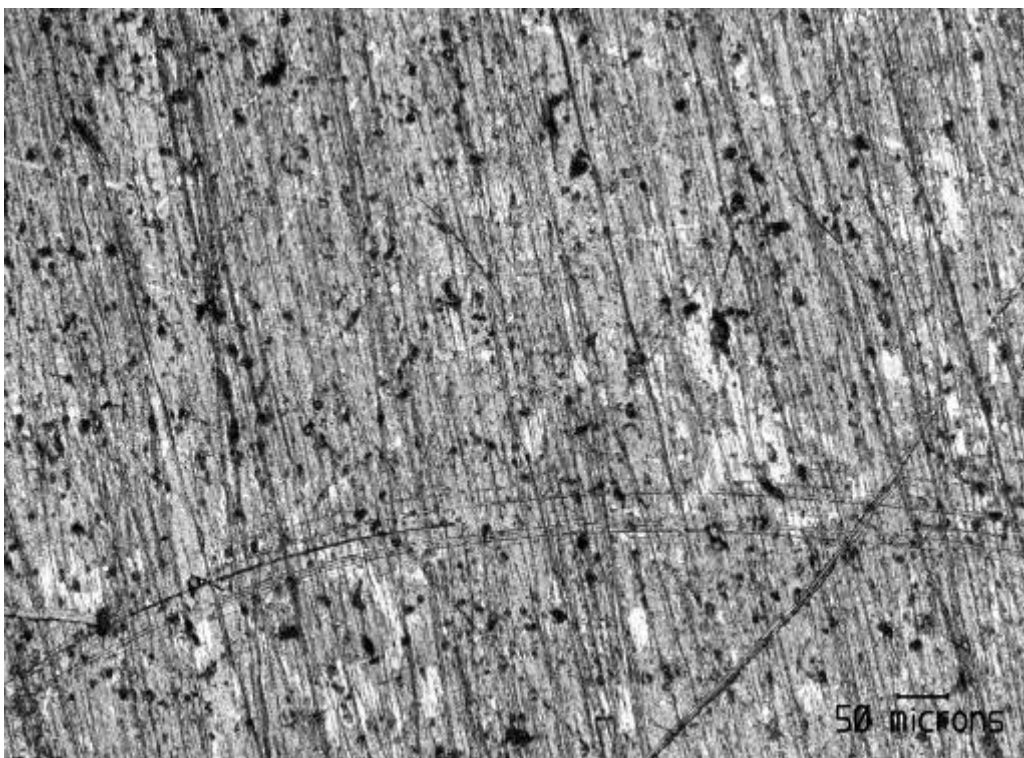


Figure 9. Non- creviced area on Alloy 625 coupon after cleaning.

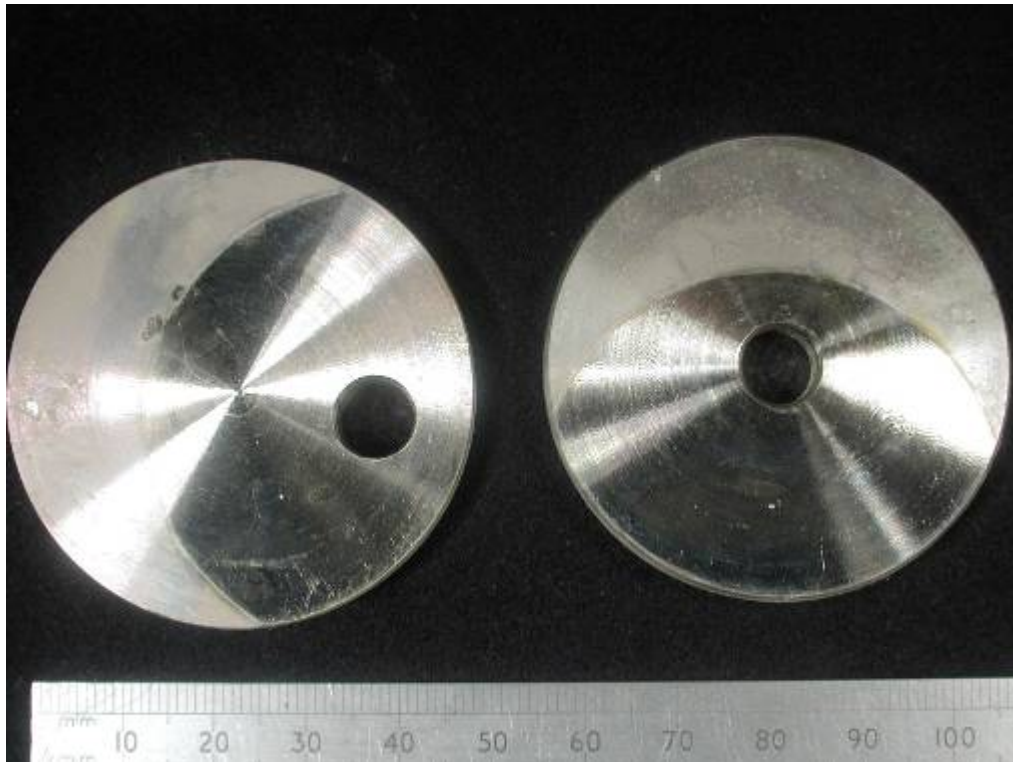


Figure 10. Zeron 100 coupons after test in 20 ppb O₂, before cleaning.



Figure 11. Zeron 100 coupons after test in 500 ppb O₂, before cleaning.

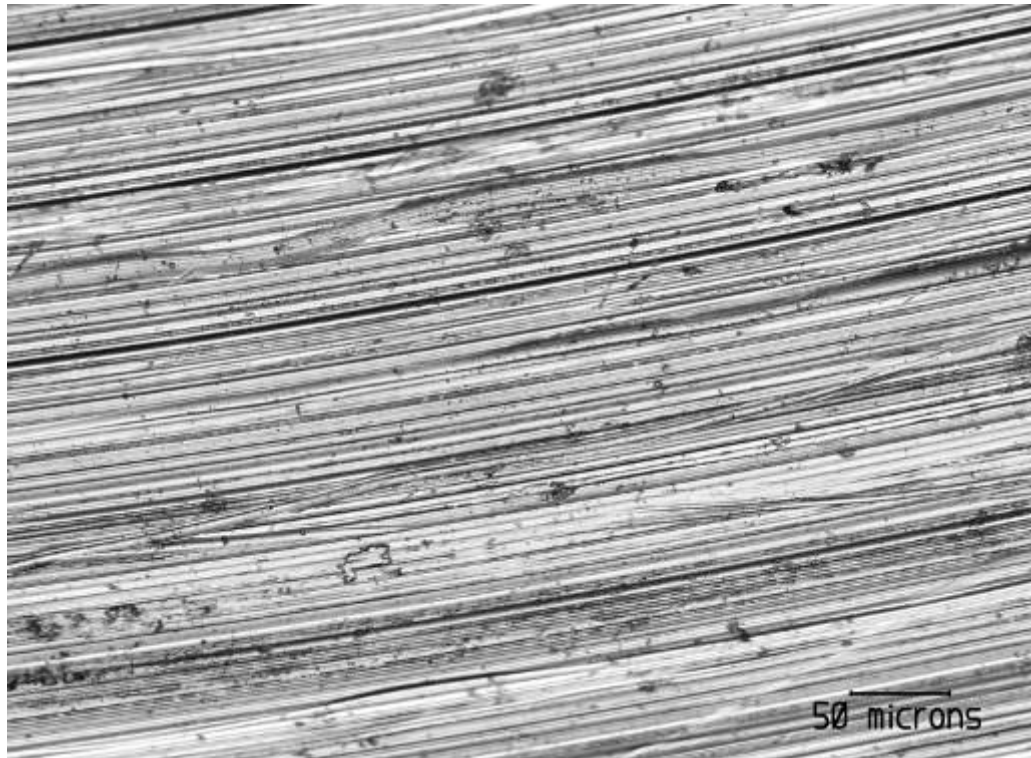


Figure 12. Creviced area on Zeron 100 coupon after cleaning.

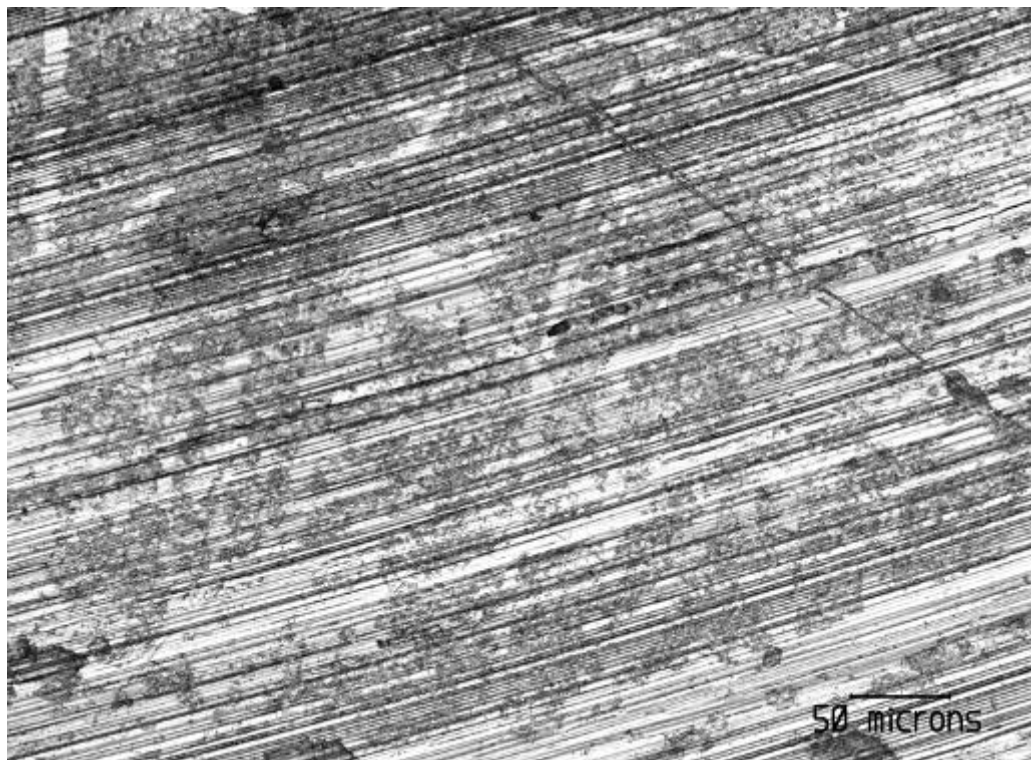


Figure 13. Non- creviced area on Zeron 100 coupon after cleaning.

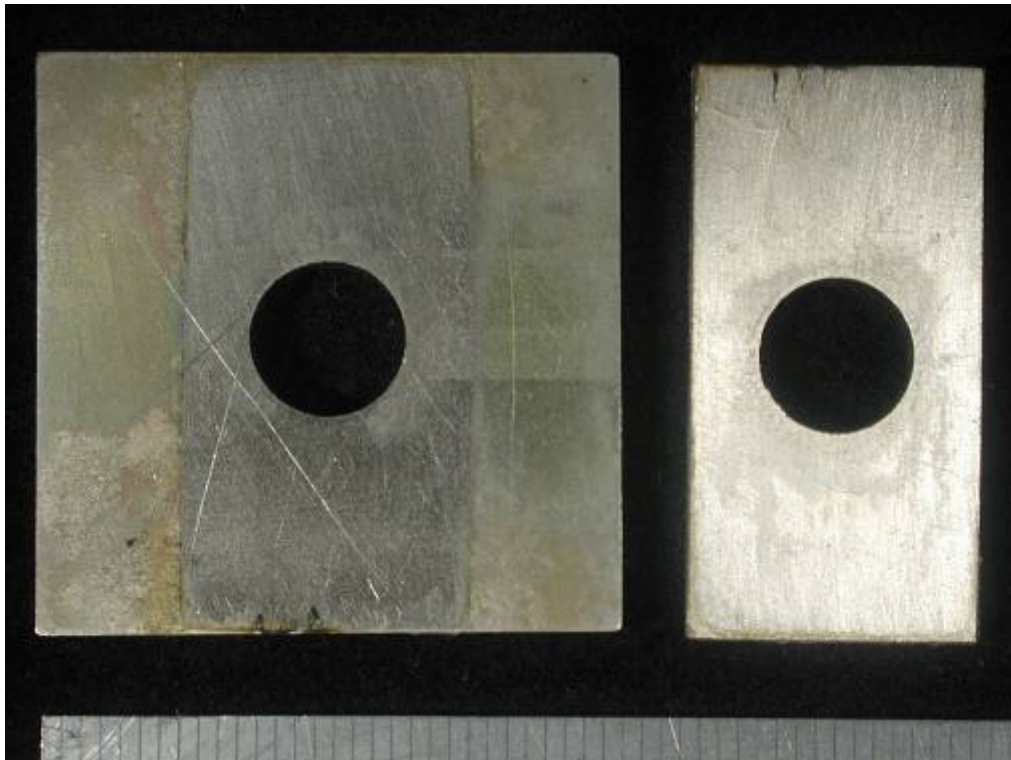


Figure 14. 6Mo coupons after test in 20 ppb O₂, before cleaning.

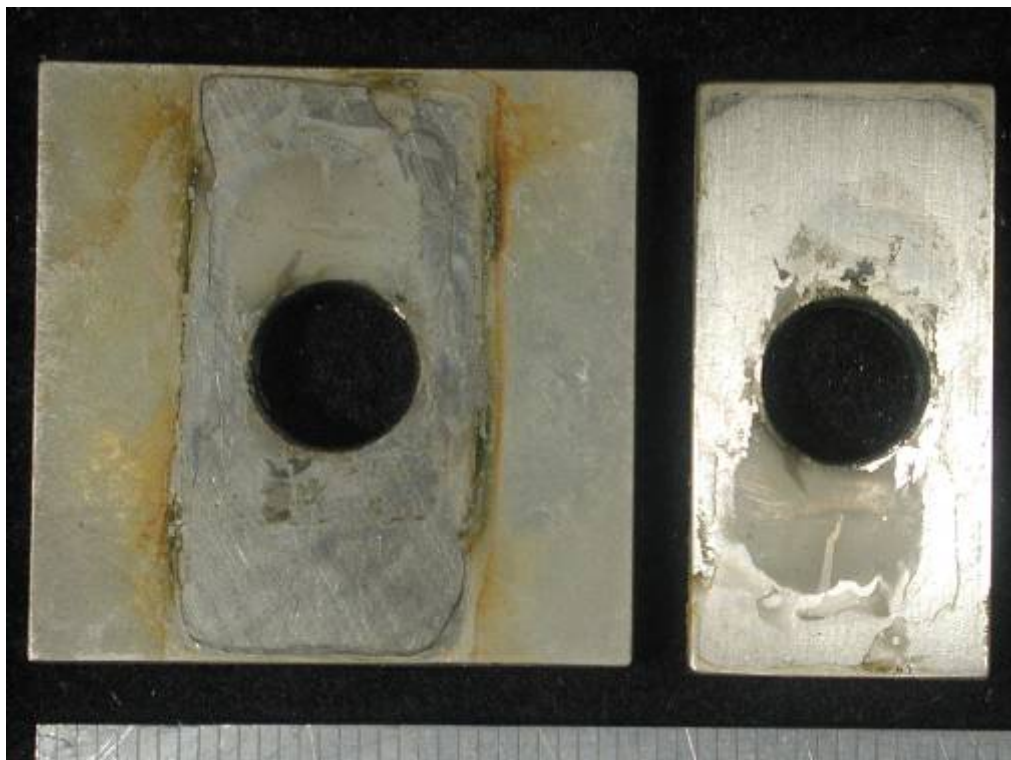


Figure 15. 6Mo coupons after test in 500 ppb O₂, before cleaning.

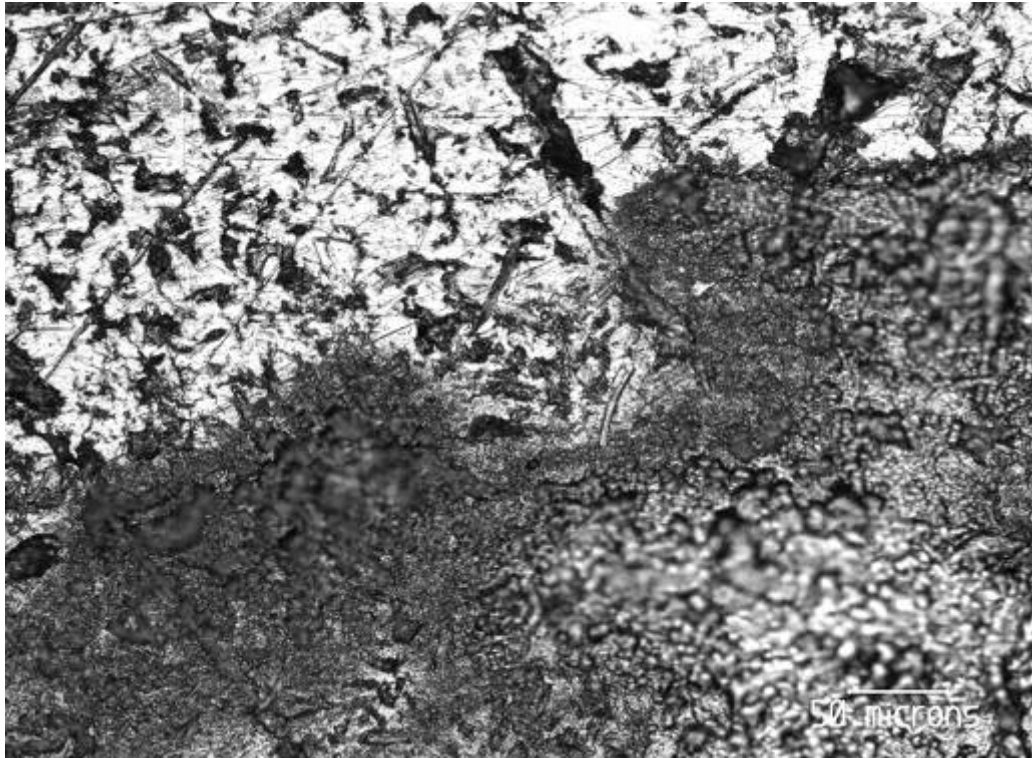


Figure 16. Creviced area on 6Mo coupon after cleaning.

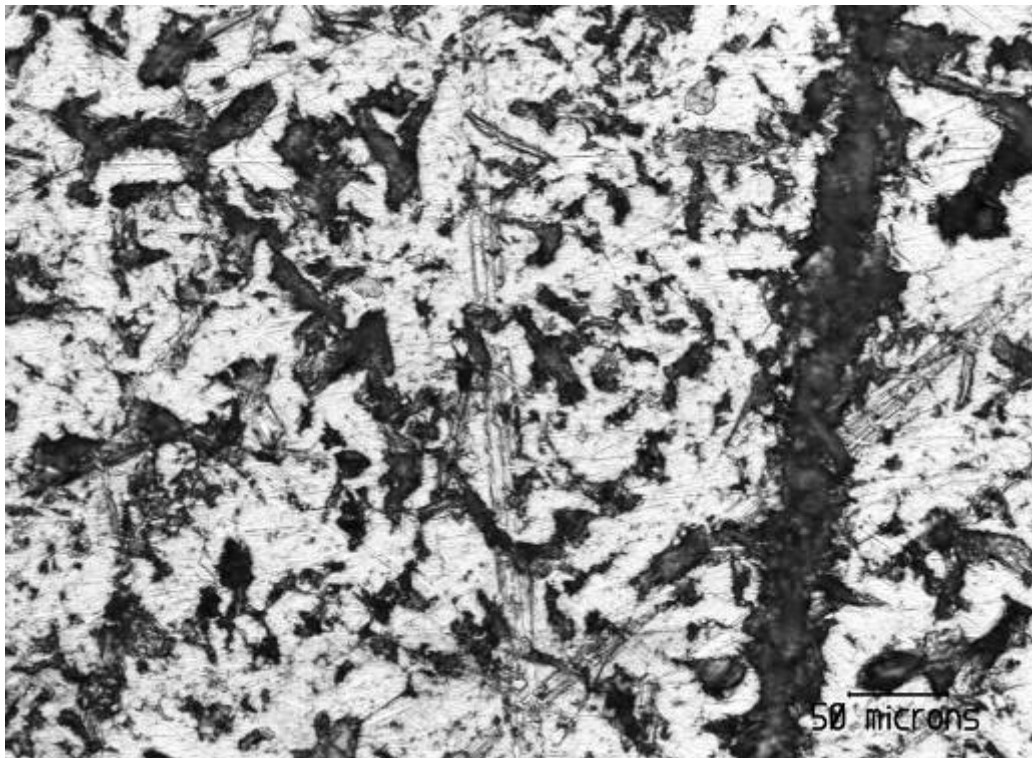


Figure 17. Non- creviced area on 6Mo coupon after cleaning.

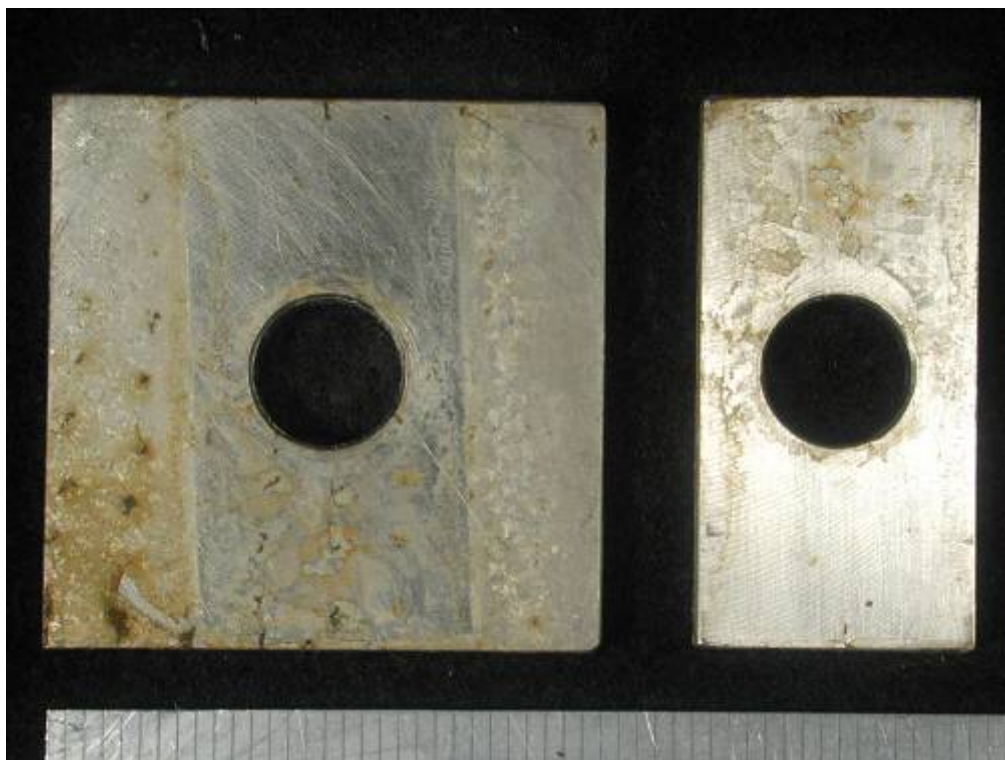


Figure 18. Welded Alloy 625 coupons after test in 20 ppb O₂, before cleaning.

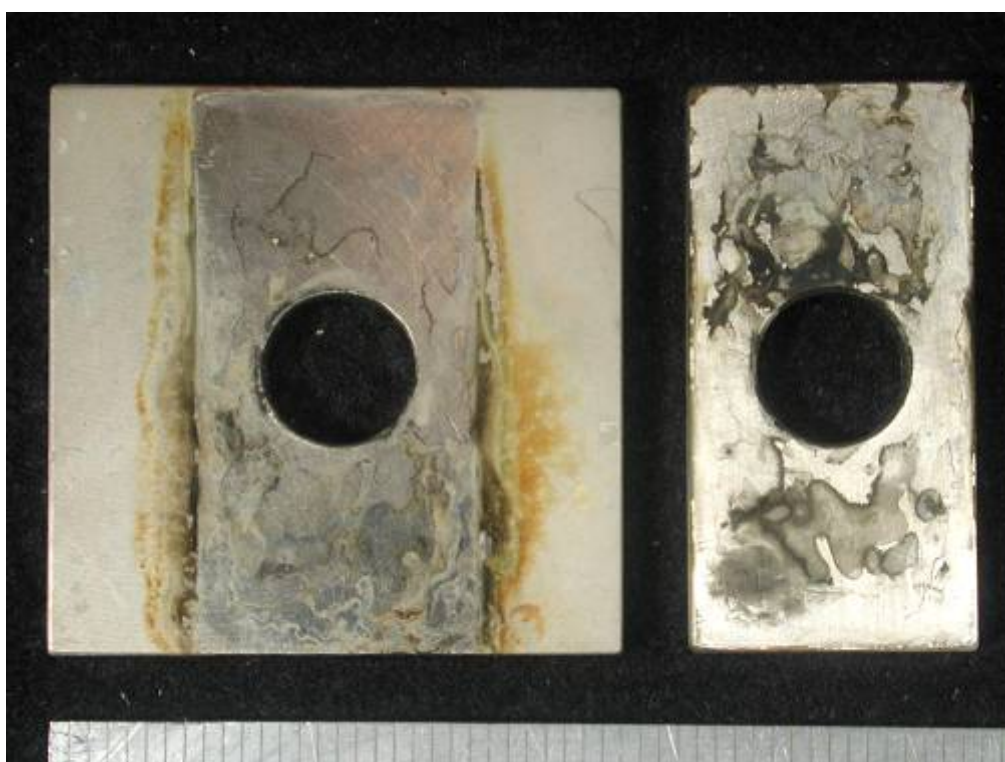


Figure 19. Welded Alloy 625 coupons after test in 500 ppb O₂, before cleaning.

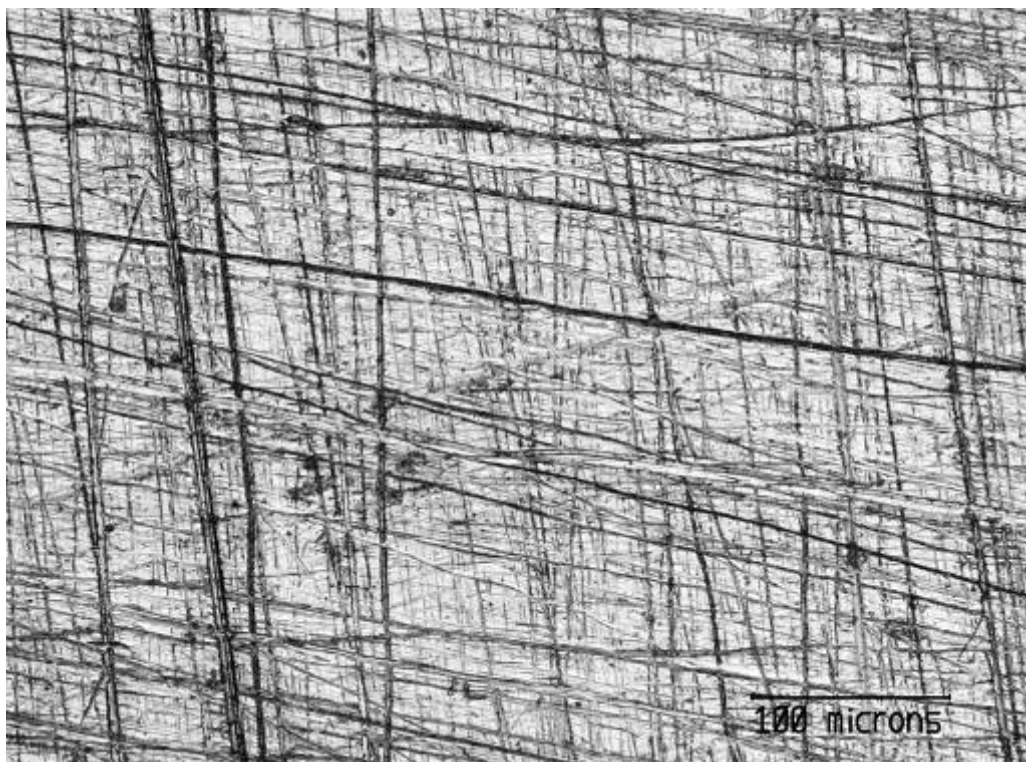


Figure 20. Creviced area on welded Alloy 625 coupon after cleaning.

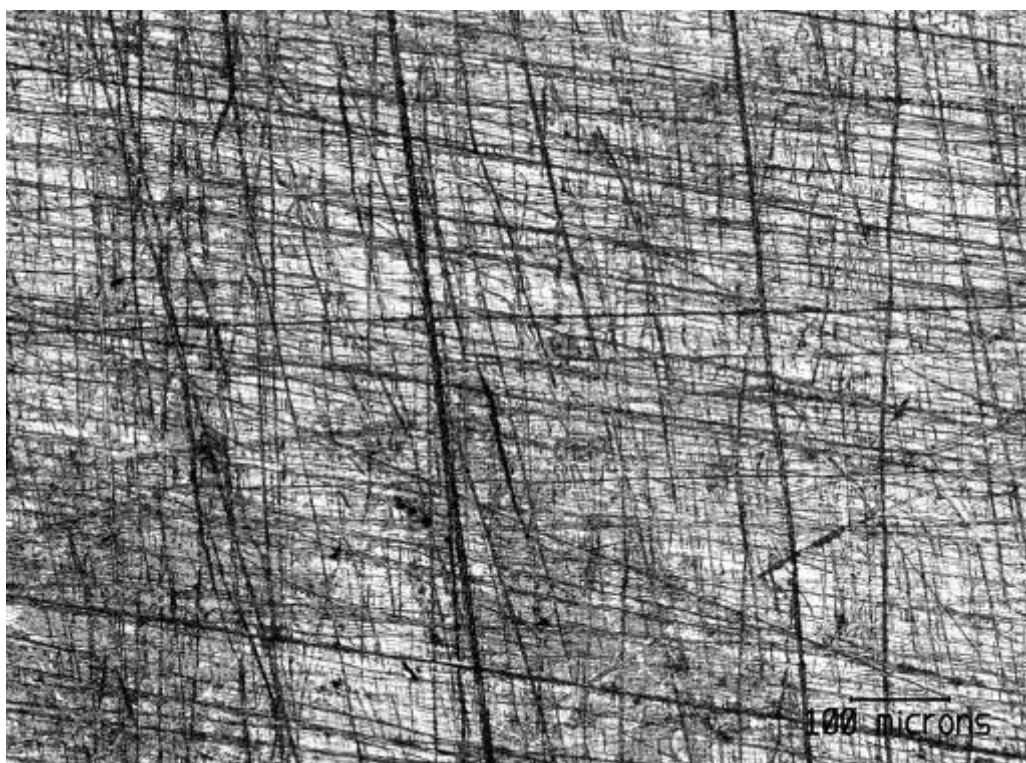


Figure 21. Non- creviced area on welded Alloy 625 coupon after cleaning.

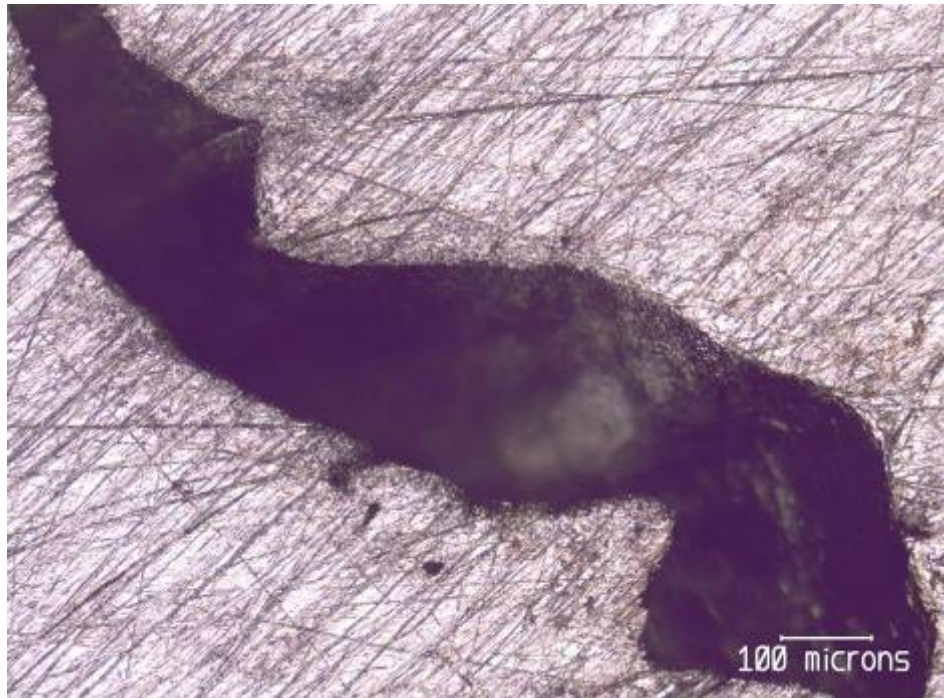


Figure 22. Cavity in welded Alloy 625 coupon.