

Creep of Uncoated and Cu-Cr Coated NARloy-Z

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Abstract

Stress rupture creep tests were performed on uncoated and Cu-30vol%Cr coated NARloy-Z copper alloy specimens exposed to air at 482°C to 704°C. The results showed that creep failure in air of unprotected NARloy-Z was precipitated by brittle intergranular surface cracking produced by strain assisted grain boundary oxidation (SAGBO) which in turn caused early onset of tertiary creep. For the protected specimens, the Cu-Cr coating remained adherent throughout the tests and was effective in slowing down the rate of oxygen absorption, particularly at the higher temperatures, by formation of a continuous chromium oxide scale. As the result of reducing oxygen ingress, the coating prevented SAGBO initiated early creep failure, extended creep deformation and increased the creep rupture life of NARloy-Z over the entire 482°C to 704°C test temperature range.

Introduction

Although copper possesses corrosion resistance in most ambient temperature environments, it deteriorates rapidly in oxidizing environments at elevated temperatures because of formation of an unprotective oxide. Above 400°C, copper oxidation proceeds rapidly because of oxide decohesion and flaking leaving the surface unprotected for further oxidation. Leidheiser [1] found that copper oxide scales were non adherent from 400°C to 600°C. Above 600°C, the scales remained adherent while at temperature but exfoliated during cooling to ambient temperature.

Most attempts to provide oxidation protective coatings on copper have been frustrated because of thermal expansion mismatch. It has been recently shown [2] that an oxidation resistant coating with acceptable substrate-coating thermal expansion match can be achieved with a low temperature arc vapor deposited (LTAVD) coating of Cu-30vol.%Cr. The microstructure of the coating consists of finely dispersed Cr particles in a copper matrix. The copper matrix provides thermal expansion compatibility and chromium provides oxidation protection by formation of a protective Cr_2O_3 scale. This coating produced oxidation protection of Cu-15vol%Nb under static air exposure conditions over the 500-700°C temperature range. At 650°C, oxidation was over 2 orders of magnitude slower than for uncoated copper as measured by weight gain.

Most hardware applications, however, involve cyclic and/or static loading which can crack coatings and reduce coating adherence. This paper addresses the effectiveness of the Cu-30vol.%Cr coating for protecting a copper alloy under creep-stress rupture, air environment conditions. The substrate material was NARloy-Z which is an age hardened, high conductivity copper alloy and is used as the combustor liner in the space shuttle main engines. For this

application, the NARloy-Z liner is exposed to H₂-O₂ oxidizing environments in static stress rupture loading conditions.

Experimental Details

Smooth specimens with 5 mm wide by 38 mm long reduced sections were fabricated from 3.25 mm NARloy-Z sheet with a nominal composition of 3.0 Ag, 0.5 Zr and Bal Cu in wt %. Stress rupture creep tests were performed in laboratory air on uncoated specimens and specimens coated with 0.05 mm thick Cu-30vol.%Cr. As presented in [2], the coating was applied by LTAVD utilizing a nonplanar consumable cathode for evaporation. The nature of the process produces virtually identical composition transfer from the cathode to the substrate. Oxygen and nitrogen analysis were performed on material taken near the fractures using a LECO Oxygen/Nitrogen Determinator.

Results

Table 1 is a tabulation of creep durations separated into 1st, 2nd and 3rd stage creep segments and stress rupture life. Most of the tests showed no measurable 1st stage creep. That is 2nd stage creep began at the start of the test.

The major effect of the coating was delaying the onset of 3rd stage creep. For every test condition, the sum of 1st and 2nd stage creep was longer for the coated specimens than for the uncoated specimens. The coated specimens also had longer 3rd stage creep durations than the uncoated specimens tested under the same conditions.

The creep strains and strain rates are listed for each stage in Table 2. For most of the tests, the coated specimens had total creep strains 50% to 100% greater than the uncoated specimens. The 2nd stage creep strain rates, on the other hand, were about the same for the coated and uncoated specimens between 538°C and 649°C. At 482°C, the uncoated specimen appeared to have faster 2nd stage creep rate than the coated specimen. But the 2nd stage creep life was comparatively short, and the measured creep rate was probably a combination of 1st and 2nd stage creep. At 704°C, both the coated specimens had faster creep rates than the uncoated specimens. Creep plots at 482°C and 704°C are shown in Figure 1. Despite the faster creep rate at 704°C, the coating extended creep deformation and increased the creep rupture life.

Table 3 lists the post test oxygen and nitrogen contents. Prior to testing the uncoated specimens contained 44 ppm oxygen and 2 ppm nitrogen, and the coated specimens contained 46 ppm oxygen and 3 ppm nitrogen. Both oxygen and nitrogen absorption occurred during the creep tests, but oxygen absorption was at least a factor of ten greater than nitrogen. Table 3 includes the rate of oxygen absorption which, except for the lowest temperature tests, was considerably higher for the uncoated specimens than for the coated specimens. In general, the uncoated/coated specimen absorption ratio increased with increasing temperature which infers increasing coating effectiveness with increasing temperature.

Metallography examination showed that unprotected NARloy Z failed predominately from intergranular cracking originating at the surface. On the other hand, the coated specimens failed predominately by creep cavitation. Figure 2 shows the microstructures of uncoated and coated specimens tested at 704°C. Surface cracking was present to a much greater degree in the uncoated specimen while grain boundary creep cavitation was much more predominant in the coated specimen. Figure 3 shows higher magnification metallography of the fractures. Intergranular surface cracking extended about 6.5 mm or ~40% of the distance to the center of the uncoated specimen. On the other hand, the coated specimen fracture was almost entirely creep cavitation.

Figure 4 shows cracking and self healing of the coating of the specimen tested at 3.4 MPa and 704°C without final specimen failure. Chromium migrated to the surface and formed a continuous Cr_2O_3 layer around the oxidized region and inhibited further oxygen penetration into the coating. Figure 5 shows the final break down of the coating at the lowest and highest test temperatures. At the lower temperature, 482°C, the Cr_2O_3 band was not resolved by optical microscopy. Copper oxide formed along the substrate surface followed by penetration into the metal. At 704°C, breakup of the Cr_2O_3 band was readily observed by optical metallography examination. For temperatures $\geq 538^\circ\text{C}$, oxidation of the NARloy-Z substrate appeared to be limited to areas in the immediate vicinity of the Cr_2O_3 band ruptures.

Discussion

The results showed that the NARloy Z failed by intergranular surface cracking when not protected by the Cu-Cr coating. The role of the coating was to inhibit intergranular oxidation of the NARloy Z specimens. Appleby and Tylecote [3] showed that copper oxidation proceeds by copper ion diffusion into the oxide with vacancy migration into the metal to balance the stresses. The vacancies accumulated at the grain boundaries initiating grain boundary cracking. This opened the grain boundary to intergranular oxide.

Stress can increase grain boundary oxidation (SAGBO) by further prying open the grain boundaries. Stress assisted grain boundary oxidation (SAGBO) was originally observed [4-6] in the high temperature nickel base alloys and can increase the creep rate by a factor of 2-3 in these alloys. Hayes and coworkers [6] have shown that moisture in air can be as important as O_2 in promoting SAGBO in nickel base alloy and postulated that water vapor accelerated the kinetics of oxide grain boundary embrittlement.

Literature on grain boundary fracture in copper and copper alloys is mainly restricted to near threshold fatigue. Higo et al. [7] observed that fracture initiation and propagation near the fatigue thresholds in copper alloys were intergranular while fast fatigue crack growth and failure was transgranular. Marchand et al. [8] showed that the fatigue lives of copper and alpha brass in N_2 and CO_2 environments were dependent on the ($\text{O}_2 + \text{H}_2\text{O}$) partial pressures. The closer to the fatigue threshold, the greater the accelerating effect of these gaseous impurities. In this region, crack growth was intergranular and 44 times faster than in vacuum. At higher growth rates where oxidation could not keep up with the crack front, fatigue fractures were transgranular.

The authors interpreted these results as hydrogen embrittlement from strain induced hydrogen migration to the copper grain boundaries. Dislocation transportation of surface-adsorbed hydrogen into metals was originally proposed by Tien [9] to account for plastic deformation increasing the rate of hydrogen permeation. Using Tien's dislocation relationship, Marchand showed a consistent relationship between the lower bound for intergranular cracking and the kinetics of grain boundary hydrogen enrichment. The upper bound for intergranular cracking was consistent with the threshold rate for water adsorption.

Thromas and Sun [10] performed cyclic crack growth measurements on copper while immersed in an aqueous solution and polarized to promote either oxidizing or reducing conditions. By this means they were able to determine the relative roles of oxidation and hydrogen embrittlement in accelerating cyclic crack growth in copper. Their results showed that it was only under oxidizing conditions that crack growth was both accelerated and accompanied by intergranular fracture. Cathodic polarization, which promoted hydrogen absorption, slowed crack growth and produced transgranular fracture. Their interpretation was that brittle intergranular cracking in copper was strictly the result of oxidation with hydrogen embrittlement not playing a role.

Hydrogen can, however, damage copper in previously oxidized material. Nieh and Nix [11] showed that intergranular microstructural bubbles were produced in copper by first annealing in air at 800°C to absorb oxygen and then in hydrogen at 600°C for hydrogen absorption. Intergranular water vapor bubbles were produced from the combined absorption of oxygen and hydrogen. Auger analysis showed that oxygen absorption was almost entirely intergranular—about 80,000 ppm in the grain boundaries compared to about 13 ppm lattice solubility. Thus a potential mechanism for the combined role of ($O_2 + H_2O$) in promoting brittle intergranular cracking in copper would be by O_2 - H_2 grain boundary bubble formation.

With respect to environmental effects on copper during creep deformation, Sklenicka [12] reported intergranular surface cracking during creep testing in air. Biner and Spitzig [13] showed only ductile grain boundary cavitation in argon environment creep. Hayes [14] found that “reduced creep life in air takes the form of a reduction in the strain to the onset of tertiary creep in air as opposed to in argon”.

The results of the present study are clearly consistent with stress assisted grain boundary oxidation (SAGBO). In the nickel base superalloys, SAGBO effects are manifested by brittle intergranular crack growth during slow strain rate tensile testing and creep. The NARloy-Z creep tests on the uncoated specimens duplicated these results. Early onset of tertiary creep occurred because of cross section reduction of the test specimens which for the test conducted at 704°C amounted to about 40% cross section reduction at the point of failure.

The point at which cracking initiated was quite likely at the upward change in the second stage creep rate. For the 482°C creep test (Fig. 1), cracking initiated at about 50 hours into the test. For the 704°C creep test, cracking of the uncoated specimen initiated at about 250 hours into the test. There was, therefore, an incubation period preceding surface crack initiation. This was the period for oxygen absorption into the material which according to Nieh and Nix [11] was almost entirely intergranular. Cracking began after a critical accumulation of oxygen was reached. The

interstitial analysis performed on the specimens showed increased concentrations of nitrogen as well as oxygen. The experiments conducted by Marchand et al. [Ref. 8], however, showed that the absorbed nitrogen did not contribute to surface cracking.

Moisture in the air environment may, however, have played a role. A moisture effect would be manifested by intergranular bubble or blistering ahead of the surface cracks. Close microscopy examination of the uncoated specimen tested at 704°C suggests that this could have taken place, but it was not definitive. Similar blistering was not observed in the coated specimen creep tested at 704°C.

Besides producing early 3rd stage creep by SAGBO, there was strong indication of material strengthening during the 704°C test where the largest amount of oxygen absorption occurred. In both series of tests, the 2nd stage creep rate was slower for the uncoated specimens than for the similarly tested coated specimens. This is consistent with the 2-3 fold hardening effect obtained by Nieh and Nix (Ref. 12) in 800°C oxygen saturated copper. The remaining creep tests were performed at lower temperatures, and the 2nd stage creep rates were similar for both the uncoated and coated specimens.

The Cu-Cr coating was effective in slowing down the rate of oxygen absorption particularly at the higher temperatures where the formation of a continuous chromium oxide scale was most evident. Chiang et al [15] showed that the protective Cr₂O₃ layer formed by chromium migration to the oxide surface and acted as a barrier to oxygen ingress. Protection was greater at the higher temperatures because of the increased chromium diffusivity. The Cr₂O₃ film slowed down and in most cases effectively prevented significant SAGBO induced surface cracking. Metallographic examination of the coated specimens showed formation of short intergranular surface cracks, but in none of the specimens was there significant penetration, and the fracture surfaces were almost entirely creep cavitation.

Conclusions

The following conclusions can be drawn from this study:

1. Creep failure in air of unprotected NARloy-Z was precipitated by brittle intergranular surface cracking produced by strain assisted grain boundary oxidation (SAGBO) which in turn caused early onset of tertiary creep.
2. At temperatures between 482°C to 704°C in air, the Cu-30vol.%Cr coating extended creep deformation and increased the creep rupture life of NARloy-Z by forming a protective Cr₂O₃ scale which acted as a barrier for oxygen ingress. The Cu-30vol.%Cr coating remained adherent throughout the tests and prevented SAGBO initiated early creep failure.

Acknowledgments

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Table 1 NARloy-Z Creep Test Durations

Temp °C	Stress MPa	Coated or Uncoated	1st Stage Creep Hours	2 rd Stage Creep Hours	3 rd Stage Creep Hours	Stress Rupture Failure Hours	Comments
482	62	Uncoated	7	38	29	74	
		Coated	30	95	63	188	
538	41	Uncoated	10	34	39.2	73.2	
		Coated	10	95	51	156	
593	28	Uncoated	-	23	8.8	31.8	
		Coated	-	62	22.3	84.3	
649	17	Uncoated	-	16	8.5	24.5	
		Coated	-	29	15.4	44.4	
704	3.4	Uncoated	-	120	-	-	Did not fail
		Coated	-	265	-	-	Did not fail
	6.9	Uncoated	115	145	77	337.5	
		Coated	-	290	100	398	

Table 2 NARloy-Z Creep Strain Rates

Temp °C	Stress MPa	Coated or Uncoated	Total Strain %	2 nd Stage Creep Rate %/Hr	3 rd Stage Creep Rate %/Hr	Comments
482	62	Uncoated	2.9	0.022	0.07	
		Coated	5.16	0.014	0.05	
538	41	Uncoated	2.17	0.023	0.033	
		Coated	5.77	0.023	0.054	
593	28	Uncoated	5.2	0.14	0.23	
		Coated	7.55	0.052	0.17	
649	17	Uncoated	3.08	0.10	0.17	
		Coated	4.62	0.10	0.13	
704	3.4	Uncoated	-	0.0025	-	Did not fail
		Coated	-	0.004	-	Did not fail
	6.9	Uncoated	6.12	0.01	0.032	
Coated		11.95	0.022	0.038		

Table 3 Oxygen and Nitrogen Contents

Temp °C	Stress MPa	Coated or Uncoated	Oxygen ppm	Absorbed Oxygen/Test Duration Ratio (ppm/hr)	Uncoated/ Coated Absorbed Oxygen Ratio	ppm Nitrogen
-	-	Uncoated	44	-	-	2
		Coated	46	-		3
482	62	Uncoated	70	0.35	0.64	4
		Coated	150	0.55		10
538	41	Uncoated	160	1.58	2.92	10
		Coated	130	0.54		10
593	28	Uncoated	70	0.82	1.58	4
		Coated	90	0.52		3
649	17	Uncoated	780	30.0	3.99	50
		Coated	380	7.52		20
704	6.9	Uncoated	1480	4.25	3.22	80
		Coated	570	1.32		30

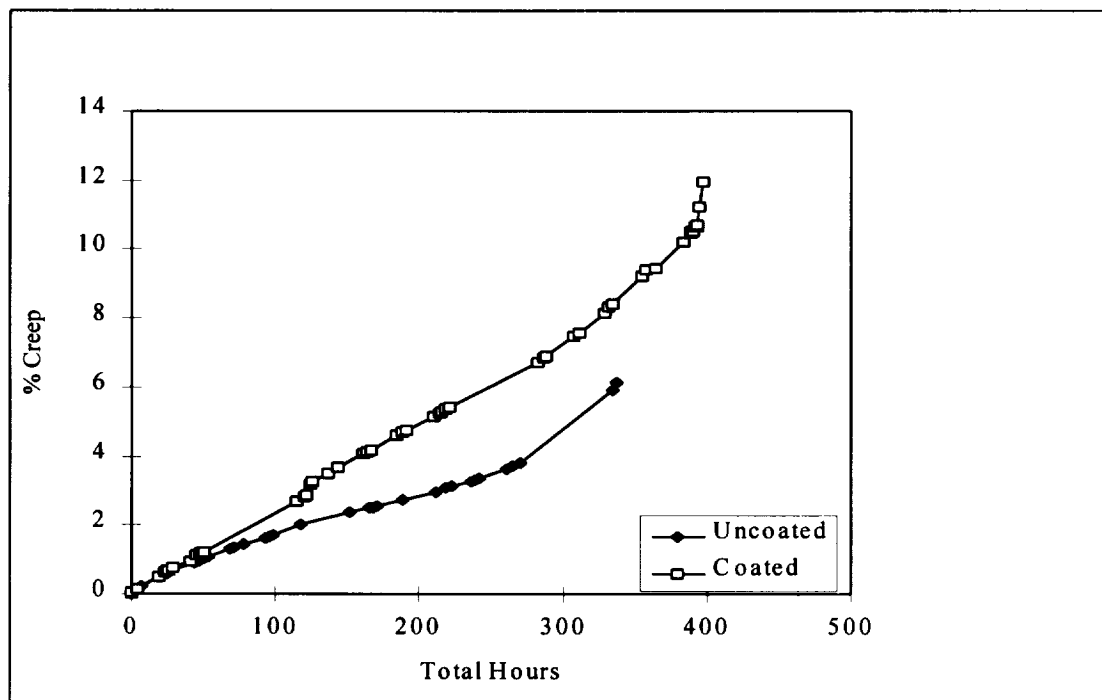
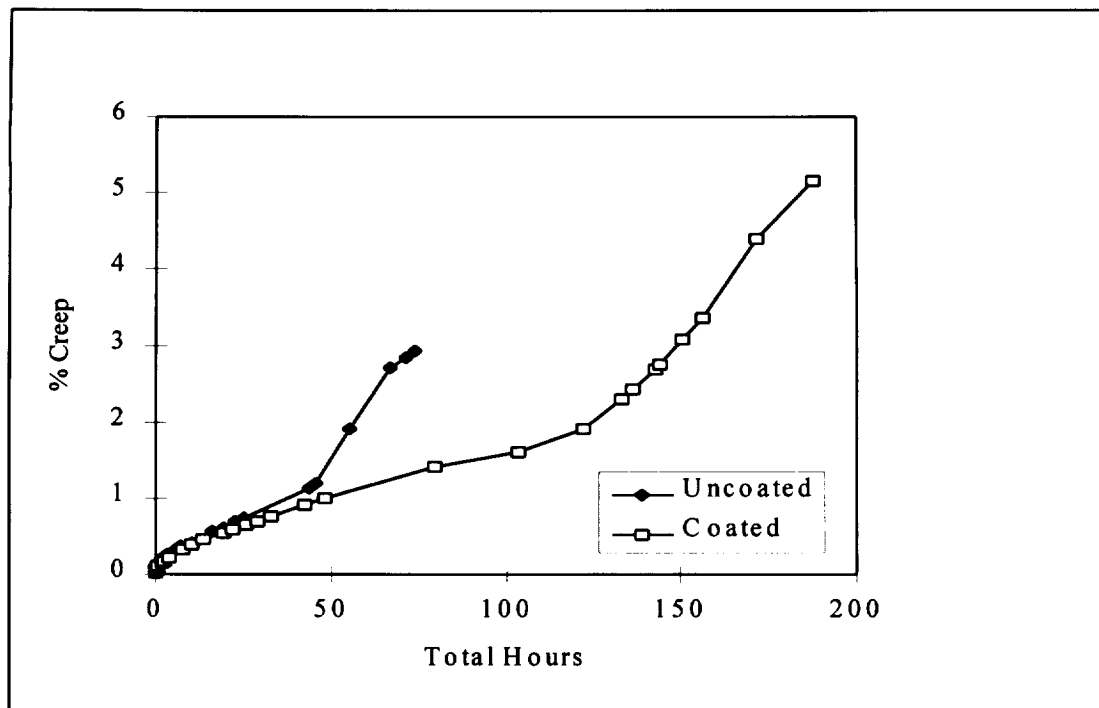


Figure 1 Creep rupture tests performed at:
Top: 482°C and 62 MPa
Bottom: 704°C and 6.9 MPa

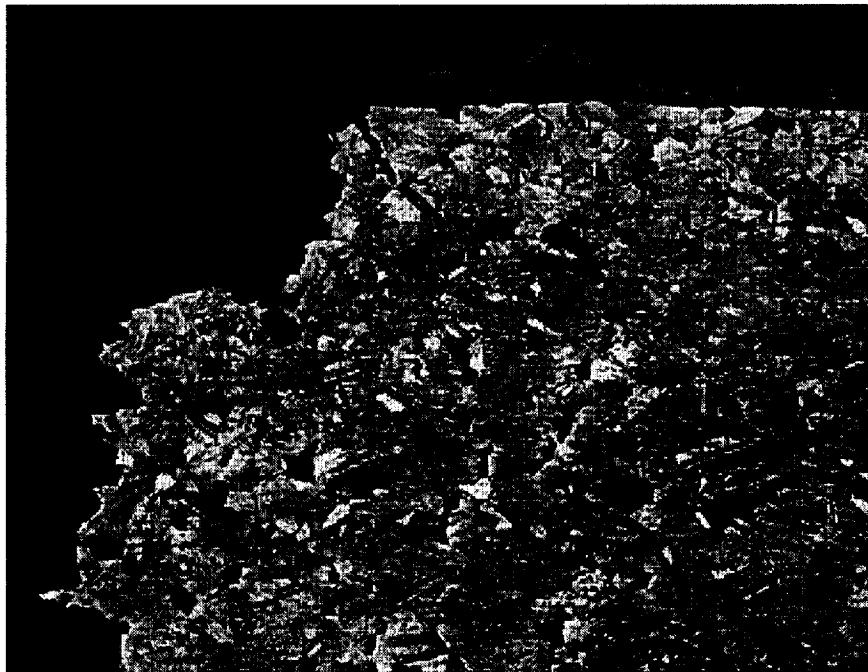
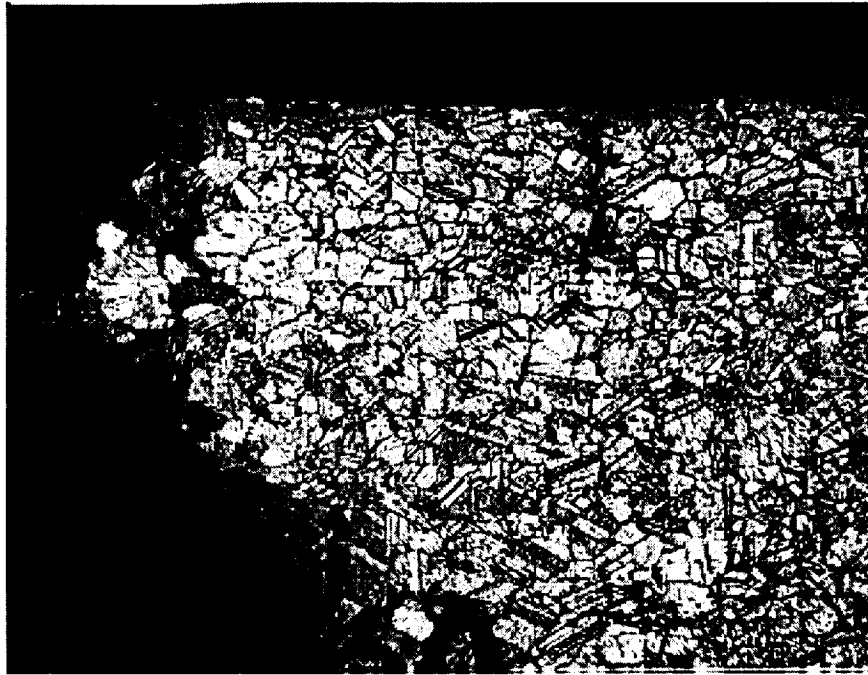


Figure 2 Photomicrographs showing microstructure overviews of uncoated (top) and coated (bottom) NARloy-Z specimens creep tested at 6.9 MPa and 704°C. (50X magnification)

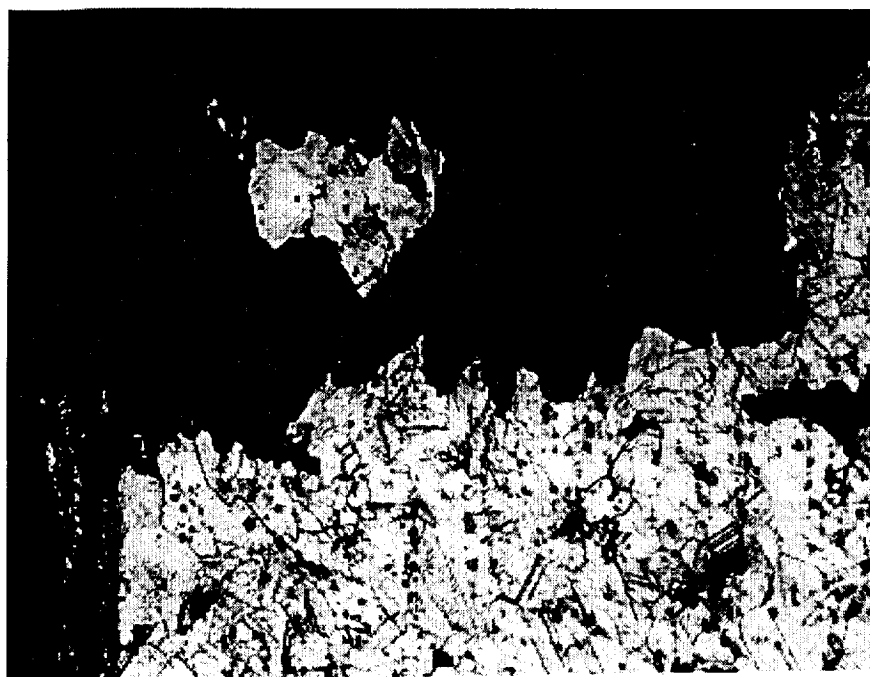
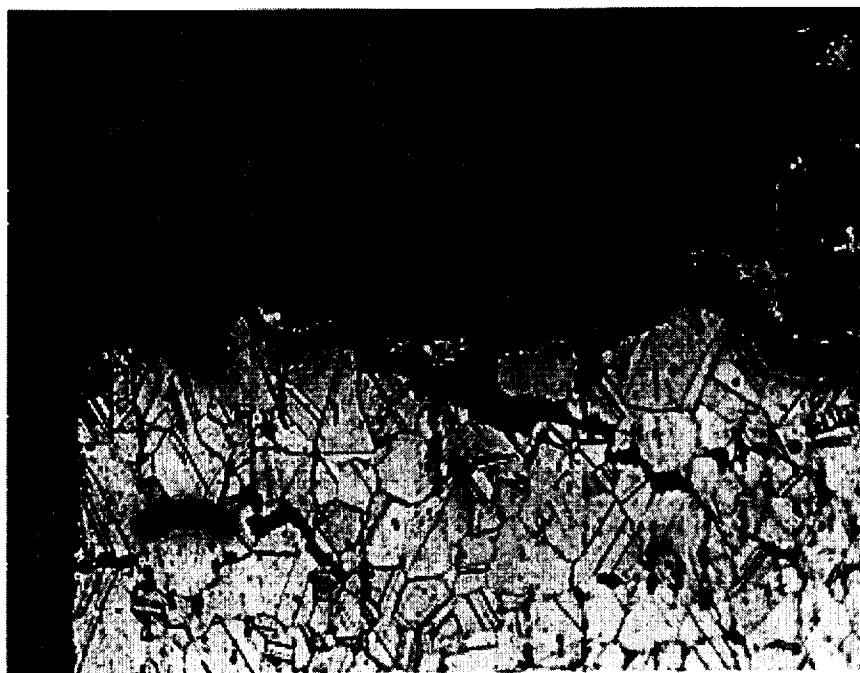


Figure 3 Photomicrographs intersecting the fractures of uncoated (top) and coated (bottom) NARloy-Z specimens creep tested at 6.9 MPa and 704°C (100X magnification)

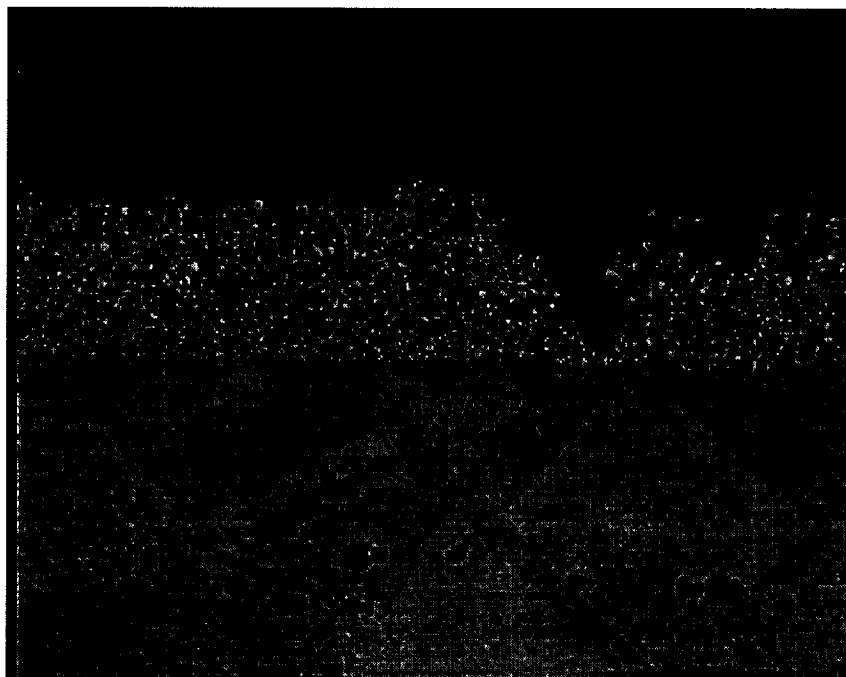


Figure 4 Photomicrograph showing formation of protective Cr₂O₃ film in a NARloy-Z coated specimen creep tested 265 hours at 3.4 MPa and 704°C. (400X magnification)

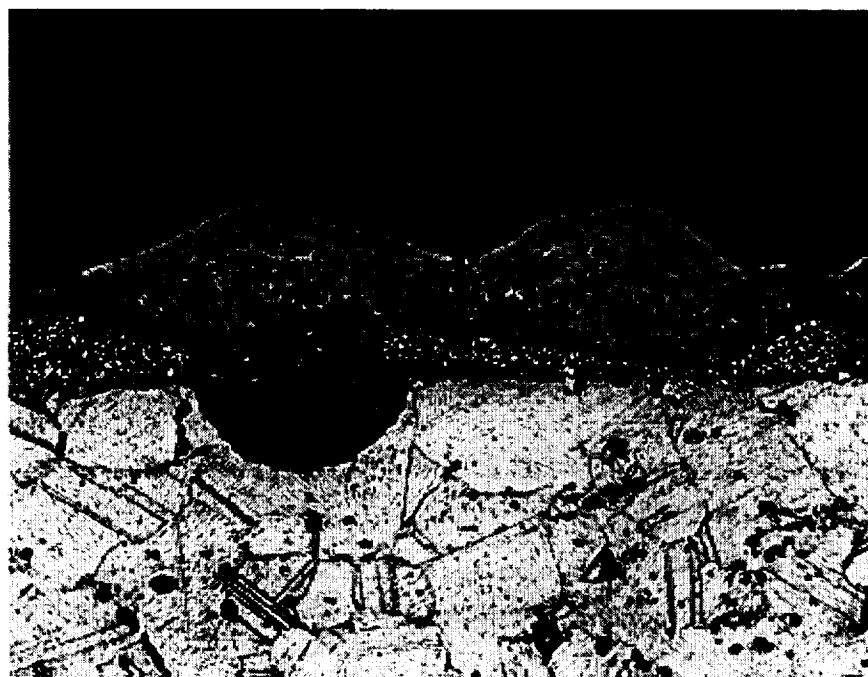
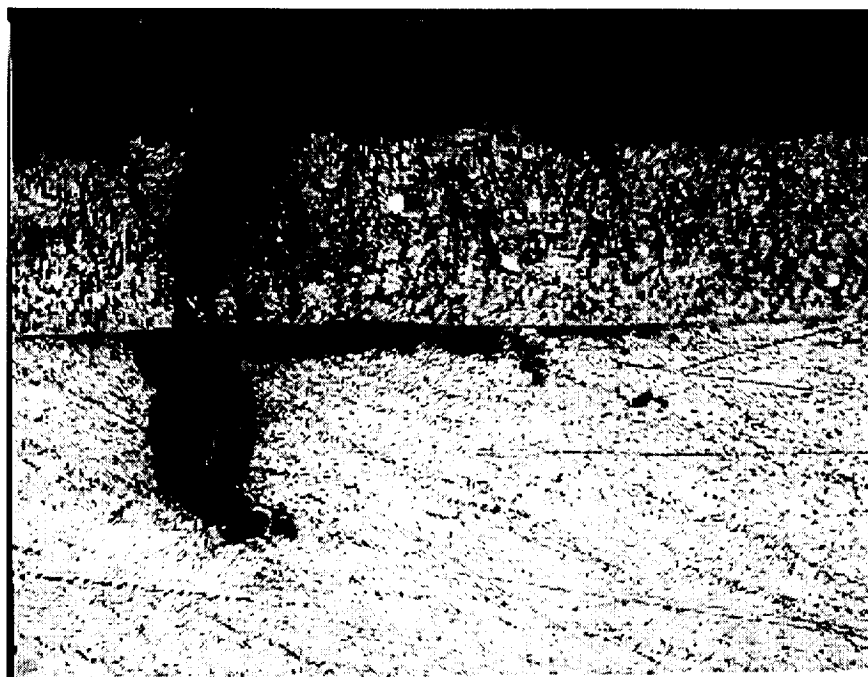


Figure 5 Photomicrograph of coating breakdown
 Top: specimen creep tested at 482°C (400X)
 Bottom: specimen creep tested at 704°C (200X)

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