AN IMPROVED PERFORMANCE SUPER HIGH STRENGTH COPPER NICKEL ALLOY FOR USE IN OFFSHORE OIL & GAS AND OTHER MARINE ENVIRONMENTS

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ABSTRACT

Although resistant to environmental degradation due to hydrogen, super high strength Cu-Ni-Mn-Al cupronickels (typical proof stress 730 N/mm^2) without cathodic protection have been shown to be susceptible to stress corrosion phenomena, when stressed to levels which cause significant plastic deformation, in ammoniacal environments or those in which saline solutions are present at temperatures above 50°C. Stress corrosion of Cu-Ni-Mn-Al is principally manifested by the occurrence of a brittle intergranular fracture morphology which is probably due to the operation of an anodic dissolution mechanism. The presence of large grains in some Cu-Ni-Mn-Al alloys appears to be associated with a greater susceptibility to environmental degradation. Improvements in the manufacturing methods used for alloy production have demonstrated that resistance to these phenomena can be achieved for a Cu-Ni-Mn-Al alloy when used in environments encountered by marine fasteners.

Keywords: Copper-nickel, seawater corrosion, stress corrosion, marine corrosion, hydrogen embrittlement, ammoniacal, Ammonia, amines, high strength, marine fastener, slow strain rate testing.

INTRODUCTION

Since the discovery that the addition of aluminium to a solid solution of Cu-Ni produces a strengthening effect[1], a series of engineering alloys based on Cu-Ni-Al have been developed. At the present time, super high strength Cu-Ni-Mn-Al cupronickels (typical proof stress 730 N/mm^2) have become established for widespread applications in the offshore oil and gas industry due to their good seawater corrosion resistance coupled with mechanical properties similar to ASTM A193 Grade B7 carbon steel. Principal applications have included high strength fasteners, high integrity connectors and a wide variety of actuator devices. Over 250 tonnes of the principal alloy of this type[2] have been used in marine engineering applications with demonstrated resistance to hydrogen embrittlement[3,4]. However, evidence has been found (through failures which have been reported[5]) that, if these alloys are tensioned to levels significantly above the recommended engineering stress regime, intergranular stress corrosion cracking can result when particular environments are present. Slow strain rate testing[5] has suggested that such deleterious environments include aqueous solutions containing ammonia, organic amines or certain concentrations of chloride ions at elevated temperature. This type of phenomenon has been rarely reported for cupronickel alloys, which are regarded as being highly resistant to stress corrosion[6] cracking. However, it has previously been observed in standard cupronickels when exposed to high levels of ammonia[6] or sulphide[7] . In most published work it has been suggested that crack growth involves the selective loss of copper at the grain boundaries, and this mechanism has been supported by electron microprobe analysis and electrochemical studies[7,8,9].

Of principal concern to offshore engineers is the possibility that lack of abuse tolerance in fastener alloys could lead to catastrophic failure which may be assisted by stress corrosion effects. The present paper describes results achieved with the Cu-Ni-Mn-Al MARINEL✚ [(1)], which shows resistance to stress corrosion cracking and a substantial degree of ductility.

EXPERIMENTAL PROCEDURE

Slow strain rate testing (SSRT) and C-ring testing was performed on Cu-Ni-Mn-Al alloy specimens. Four of the alloys tested (designated by batch numbers B3735, Y5110, Y5111 and Y5112) are of the super high strength type and possess mechanical properties similar to ASTM A193 B7 carbon steel. Another Cu-Ni-Mn-Al alloy investigated, designated B8873, was of slightly different composition but similar in strength to the other alloys, although with lower ductility. The compositions and properties of these materials are given in Table 1.

For slow strain testing of alloy Y5111, SSRT machines (manufactured by Fritz Fackert KG, Duisdurg) were employed and these were suitably equipped with data acquisition computer cards and software for efficient data collection. The tensile specimens had a gauge length of 20mm and a gauge diameter of 2.5mm and the surface was prepared in accordance with EN ISO 7539[10]. The SSRT machines were designed to give a minimum strain rate of 6.25×10^{-6} s^{-1} for the specimen geometry used. In order to carry out testing in a number of different aqueous environments with a temperature range of up to 82°C, cylindrical testing containers were constructed from heat resistant polymers. These were designed to fit around the tensile specimen and functioned as electrolyte containers. Heating of the aqueous electrolytes contained within them was applied by means of an electrically-controlled heating foil immersed in the solution. The insertion of a platinum electrode in the solution allowed the tensile specimen to be cathodically polarised versus a saturated calomel

[1] MARINEL is a Registered Trade Mark of Meighs Ltd

electrode (SCE) through the use of a potentiostat (Jaissle Model 1031A). In this arrangement, the reference electrode was placed in a small beaker containing the test solution at room temperature and connected to the actual test solution through a Luggin capillary. The cathodic polarisation voltage used was chosen to match that of Andersen *et al*[5] at -1050mV vs SCE, as this voltage is taken to represent standard cathodic protection conditions.

The slow strain rate testing of Y5110 was carried out at Cortest Laboratories, Sheffield using the practice of NACE standard TM-01-98. In this case, tensile specimens had a gauge length of 25.4mm and a gauge diameter of 3.81mm (± 0.127mm).

The strain rates adopted in this work were designed to match, where possible, the strain rates cited in the work of Andersen *et al*[5], allowing facility of comparison. The particular strain rates which they report are 2×10^{-6} and 4×10^{-6}, these being used for experiments in saline solutions and ammonium chloride solutions respectively. These values of strain rate are adopted in the present work for these same environments except in the case of experiments utilising the Fackert slow strain rate machine. With these instruments, the nearest comparable strain rate possible was 6.25×10^{-6}, thus this was the strain rate adopted for all the SSRT work with alloy Y5111.

For each slow strain rate test, the time to failure was recorded and the reduction of area of each half of the fracture face was measured. Ratios between time to failure (TF) in the environment and TF in air under the same SSRT conditions were calculated and these ratios were termed the TF ratios. Similarly, the ratios of the reduction of area (RA) values from the environmental slow strain rate test and room temperature air tests were termed RA ratios. Both the RA ratios and TF ratios were used as an indication of the effect of the environment on alloy ductility. It has been reported[5] that, if these ratios fall below 0.8, a degree of embrittlement has probably occurred. After each test, the fracture surface and surrounding necked gauge length was examined on a x 40 stereo optical microscope. Some specimens were prepared as sections for metallographic investigation or further examination in a Scanning Electron Microscope (SEM). The majority of the environments and strain rates used in the present slow strain rate testing programme, together with the method of analysing the results derive from the publication of Andersen *et al*[5] on Cu-Ni-Mn-Al as it was deemed important to produce results which were directly comparable. Thus, the particular environments chosen for slow strain rate testing were 10% ammonium chloride (NH_4Cl) and saline solutions, both being maintained at elevated temperatures. All tensile testing was carried out under open circuit conditions apart from an experiment on alloy Y5111 in 10% sodium chloride at 50°C, which was conducted under cathodic polarisation of -1050mV vs SCE. This particular test was undertaken as a comparison with Andersen *et al*[5]'s experiment in seawater under the same conditions, the higher sodium chloride concentration of the present work being used to try to determine the possibility of any increased detrimental effects with greater chloride concentration.

Static load testing was carried out using the C-ring method EN ISO 7539[11] with threaded rods and nuts being made from the same super high strength Cu-Ni-Mn-Al alloy to ensure galvanic compatibility. The applied stress was initially measured using strain gauges and compared to the calculation given by EN ISO 7539. Very good correlation was found between calculated stress and measured stress which enabled accurate stressing of the C-rings to be carried out. C-ring testing of Y5111 was determined in 3.5% sodium chloride, in the more severe environment represented by 20% sodium chloride as well as under ammoniacal conditions (10% ammonium chloride at 80°C), stressing in all cases being maintained at 110% of the 0.2% proof stress. This stress regime was selected as it represents a stress level approximately 35% above recommended engineering stress maximum and is thus comparable with severe overstressing, as with an extreme case of abuse on a marine fastener. C-rings of alloy B3735 were also stressed at 110% of $R_{P,0.2}$ and these were tested in

3.5% sodium chloride solution at 50°C. All these C-ring tests were all of 60 days duration after which they were examined under a stereo optical microscope for evidence of cracking.

With alloy Y5112 a different set of tests were conducted in order to determine effects of various substances which are applied to (or come into close proximity with) practical marine fasteners. Such substances are known to include amine-cured epoxy paints and coatings, locking adhesives, coal tar based epoxy coatings and glass-reinforced plastics (GRP). In these experiments, the C-ring stress level was 80% of $R_{P,0.2}$, chosen to represent a value slightly above the recommended maximum for fasteners. Immediately after stressing each C-ring, one of the following coatings was applied: an amine-cured epoxy, a locking adhesive (two varieties were investigated), a gel coat epoxide or a coal tar epoxy. After allowing the C-rings to fully cure for seven days at ambient temperature the specimens were immersed in a 3.5% concentration of sea salt at ambient temperature for 90 days. In order to determine any possible effect of GRP on the mechanical properties of Cu-Ni-Mn-Al, one C-ring was left uncoated and placed such that its region of maximum stress was rested inside a close-fitting U-shaped groove cut in a block of GRP material. This arrangement attempted to simulate the use of Cu-Ni-Mn-Al fasteners with GRP. Once in this position, both C-ring and block were immersed in the sea salt solution in a similar manner to the other samples. After 90 days' exposure, all the C-rings were examined under a stereo optical microscope for evidence of cracking. They were also examined after being further deformed by continued tightening of the tensioning screws; this action tended to cause some of the coating to crack and spall. Alloy B3735 was also tested as a coated C-ring in sea salt solution for 90 days but the single coating investigated was that of amine-cured epoxy.

RESULTS

To allow direct comparison of slow strain rate test data from the present work with that of Andersen *et al*[5], their results are reported in the initial rows of Table 2, Table 3 and Table 4 in this paper. Table 2 shows SSRT results on specimens tested in elevated temperature saline solutions under cathodic polarisation conditions and demonstrate that there was no indication of significant loss of ductility under these conditions, which included testing in a chloride concentration significantly above that of seawater. Observation of the fracture morphology showed that it was completely ductile in nature with no secondary cracking evident along the gauge length.

Slow strain rate test results for the 10% NH_4Cl solution at elevated temperature are shown in Table 3. In this electrolyte, the previous results[5] and those for alloy B8873 in the present case, both indicate the occurrence of stress corrosion cracking. Secondary cracks observed in B8873 were of a brittle intergranular nature; an optical micrograph of a section through a cracked region is shown in Figure 1. However, both Y5111 and Y5110 were found to fracture in a ductile manner in 10%NH_4Cl above 60°C, with no secondary cracking along the gauge length, as is demonstrated by scanning electron micrograph in Figure 2. The fracture surface in this case is somewhat obscured by artefacts produced by deposited corrosion products but the micrograph gives evidence of typical ductile cup-and-cone fractography.

Results shown in Table 4 indicate that the Cu-Ni-Mn-Al alloy used in the work of Andersen *et al*[5] and alloy B8873 of the present work suffered from stress corrosion cracking in seawater at 50°C when no cathodic protection was applied. In the case of alloy B8873 the cracking was of a brittle intergranular nature similar to that seen in Figure 1 for B8873 in 10%NH_4Cl. This result differs somewhat from that of Anderson *et al*[5] in that they reported the occurrence of transgranular brittle cracking for their Cu-Ni-Mn-Al alloy when it was tested in seawater at 50°C. For alloys

Y5110 and Y5111 tested in this medium there was no indication of environmental degradation at 50°C or 60°C.

Dynamically-loaded slow strain rate tensile test results reported above were found to correlate well with results of the statically-loaded C-ring tests. Table 5 summarises the results of testing in elevated temperature ammonium chloride and saline environments and indicates that the less highly-developed Cu-Ni-Mn-Al alloys, B8873 and B3735, show evidence of brittle intergranular cracking whereas Y5111 indicates freedom from stress corrosion. Figure 3 shows an SEM micrograph exhibiting the intergranular nature of the crack morphology of B3735 in 3.5% NaCl at 50°C and this alloy also produced evidence of stress corrosion cracking susceptibility when exposed to amine-cured epoxy adhesive, as is shown in Table 6. This detrimental behaviour produced by organic amine curing agents was not evident for the more advanced Cu-Ni-Mn-Al alloy Y5112, either after coating with this agent or in association with the other marine fastener compounds tested.

DISCUSSION

The differences apparent in the cracking susceptibility demonstrated by the slow strain rate testing of Cu-Ni-Mn-Al under cathodic polarisation conditions to those obtained without applied potential (Table 2 and Table 4), as well as indicating that the alloy does not suffer from hydrogen embrittlement, strongly suggest that the stress corrosion mechanism involves an anodic dissolution reaction at the grain boundaries.

Such an anodic process would be expected to be hindered when a strongly negative potential is being imposed at the alloy/electrolyte interface. Although no previously published detailed work on the corrosion behaviour or environmental degradation characteristics of Cu-Ni-Mn-Al alloys is known, stress corrosion been reported for standard Cu-Ni alloys in ammoniacal[6,8] and sulphide[7] solutions. This phenomenon is principally manifested by brittle intergranular cracking by and the most feasible operating mechanism is proposed to involve selective dealloying of the copper matrix at the grain boundaries[7,9]. Selective corrosion attack at the grain boundaries is linked to intergranular corrosion, and this is usually explained by the operation of a higher electrochemical activity at the grain boundaries caused by small differences in chemistry from that of the grains. Such a situation can result in accelerated corrosion at the grain boundaries due to the production of a galvanic couple which consists of a small anodic grain boundary area and large adjacent cathodic grain surface area. Relating this to the present work, it is interesting to compare the grain structure of B8873 with that of Y5110, and etched structures of these are displayed in Figure 4a and Figure 4b, respectively. It can be seen that the B8873 grain morphology of Figure 4a is very inhomogeneous, and it consists of a proportion of grains of ASTM E117 Size 7 together with evidence of secondary recrystallised grains of Size 1-2. In contrast alloy Y5110 exhibits homogeneous, fine, recrystalline twinned grains as shown in Figure 4b. Consideration of the likely effect of this disparity of grain structure on localised corrosion of these alloys at the grain boundaries would lead to the suggestion that the relative grain boundary area in Y5110 is at least five times greater than that of B8873, thus the corrosion current density (and therefore the corrosion rate) at the grain boundaries of B8873 will be higher than that at the grain boundaries of Y5110. This is one factor which may explain the observed preferential occurrence of anodic intergranular stress corrosion effects in B8873.

With regard to grain boundary chemistry, Y5110, Y5111 and Y5112 have been manufactured using high purity raw materials as well as undergoing a very strict processing procedure at all stages of manufacturing. As well as the use of high purity raw materials, this includes restrictive melt chemistry, a well-controlled intermediate forging process and carefully adjusted hot rolling and ageing practice. This manufacturing method represents a differentiating factor for these alloys

which is designed to have a direct influence on the dispersion of elements within the material. Further work is ongoing to determine the exact relationship between the improved manufacturing method and alloy micro-chemistry as this will lead to a full explanation of the observed improved stress corrosion cracking resistance properties achieved. To summarise the overall results, they indicate that the more highly developed Cu-Ni-Mn-Al alloys Y5110, Y5111 and Y5112 show resistance to stress corrosion in ammoniacal and elevated temperature saline environments.

CONCLUSIONS

Cu-Ni-Mn-Al alloys under extreme mechanical stressing and with imposed cathodic polarisation are resistant to hydrogen embrittlement and stress corrosion cracking in elevated temperature chloride solutions.

Cu-Ni-Mn-Al alloys under severe mechanical stress conditions with no applied cathodic polarisation can be susceptible to stress corrosion cracking when exposed to environments containing ammonium compounds, organic amines or saline solutions at temperatures above 50°C.

Stress corrosion cracking of Cu-Ni-Mn-Al is manifested by the occurrence of brittle intergranular fracture morphology which is probably due to the operation of an anodic dissolution mechanism. The presence of large grains in some Cu-Ni-Mn-Al alloys appears to be associated with a greater susceptibility to environmental cracking.

Control of raw materials, chemical composition limits and the complete manufacturing process can enable Cu-Ni-Mn-Al alloys to be produced which show resistance to stress corrosion cracking when under states of high mechanical stress in environments containing ammonia, organic amines, and elevated temperature saline solutions.

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TABLE 1

COMPOSITION (wt%) AND MECHANICAL PROPERTIES OF THE PRINCIPAL ALLOYS INVESTIGATED

Sample I.D	B8873	B3735	Y5110	Y5111	Y5112
Ni	13.96	19.00	19.70	18.92	19.00
Mn	0.30	4.43	4.43	4.52	4.32
Al	3.08	1.92	1.90	1.86	1.89
Fe	1.23	1.20	0.92	0.76	1.23
Cr	-	0.47	0.36	0.39	0.37
Nb	-	0.75	0.84	0.82	0.65
Cu	Bal	Bal	Bal	Bal	Bal
R_m (N/mm^2)	953	998	936	925	1002
$R_{P,0.2}$ (N/mm^2)	820	757	737	730	791
A_5 (%)	14	15	16	22	16
HB	269	255	269	269	285
Impact Toughness CVN [-46°C] (J)	-	15	28	31	30

TABLE 2

SLOW STRAIN RATE TENSILE TEST RESULTS IN ELEVATED TEMPERATURE SALINE SOLUTIONS UNDER CATHODIC POLARISATION OF -1050 mV vs SCE

Sample I.D	RA Ratio (%)	TF Ratio (%)	Observations
Cu-Ni-Mn-Al (tested in seawater at 50°C)[5]	1.22†	0.99†	Ductile fracture. No secondary cracking
Y5111 (tested in 10% NaCl, 50°C)	0.90*	0.89*	Ductile fracture. No secondary cracking

† Strain rate 2 x 10^{-6} s^{-1} * Strain rate 6.25 x 10^{-6} s^{-1}

TABLE 3

RESULTS OF SLOW STRAIN RATE TESTS IN 10% AMMONIUM CHLORIDE ENVIRONMENTS AT ELEVATED TEMPERATURES

Sample I.D	RA Ratio (%)	TF Ratio (%)	Observations
Cu-Ni-Mn-Al [1994][5] (tested at 82°C)	0.19†	0.25†	Stress corrosion cracking.
Y5111 (tested at 60°C)	0.98*	0.97*	Ductile fracture. No secondary cracking.
Y5110 (tested at 82°C)	0.93†	0.81†	Ductile fracture. No secondary cracking.
B8873 tested at 82°C	0.68†	0.85†	Intergranular cracking. Secondary crack depth: 3% of diameter

+ Strain rate 4 x 10^{-6} s^{-1} * Strain rate 6.25 x 10^{-6} s^{-1}

TABLE 4

RESULTS OF SLOW STRAIN RATE TESTS IN SALINE ENVIRONMENTS AT ELEVATED TEMPERATURE UNDER OPEN CIRCUIT CONDITIONS

Sample I.D	RA Ratio (%)	TF Ratio (%)	Observations
Cu-Ni-Mn-Al [Tested in Seawater, 50°C][5]	0.84†	0.87†	Transgranular cracking. Crack depth: 0.5% of diameter.
B8873 [Tested in 3.5% NaCl, 50°C]	0.95†	0.85†	Intergranular cracking. Secondary Crack Depth: 2.5% of diameter
Y5110 [Tested in 3.5% NaCl, 50°C)	0.84†	1.39†	Ductile fracture. No secondary cracking.
Y5111 [Tested in 3.5% NaCl, 60°C]	1.00*	1.26*	Ductile fracture. No secondary cracking.

† Strain rate 2×10^{-6} s^{-1} * Strain rate 6.25×10^{-6} s^{-1}

TABLE 5

RESULTS OF C-RING STRESS CORROSION TESTS (60-DAY DURATION) IN VARIOUS ENVIRONMENTS

Stress Level: 110% of $R_{P,\ 0.2}$

Sample I.D	Environment	Final Result
B8873	3.5% NaCl 50°C	Intergranular cracking
B3735	3.5% NaCl 50°C	Intergranular cracking
Y5111	3.5% NaCl 80°C	No evidence of crack initiation
Y5111	20% NaCl 80°C	No evidence of crack initiation
Y5111	10% NH_4Cl 80°C	No evidence of crack initiation

TABLE 6

RESULTS OF C-RING STRESS CORROSION TESTS (90-DAY DURATION) IN ENVIRONMENTS OFTEN ENCOUNTERED BY MARINE FASTENERS. SAMPLES STRESSED TO 80% OF $R_{P,0.2}$ AND IMMERSED IN A 3.5% SOLUTION OF SEA SALT AT AMBIENT TEMPERATURE.

Sample I.D	Environment	Final Result
B3735	Amine - cured epoxy adhesive	Transgranular cracking
Y5112	Amine - cured epoxy adhesive	No evidence of crack initiation
Y5112	Locking adhesive 242	No evidence of crack initiation
Y5112	Locking adhesive 262	No evidence of crack initiation
Y5112	Gel-coat Epoxide Resin	No evidence of crack initiation
Y5112	Coal tar epoxy resin.	No evidence of crack initiation
Y5112	In contact with GRP Block.	No evidence of crack initiation

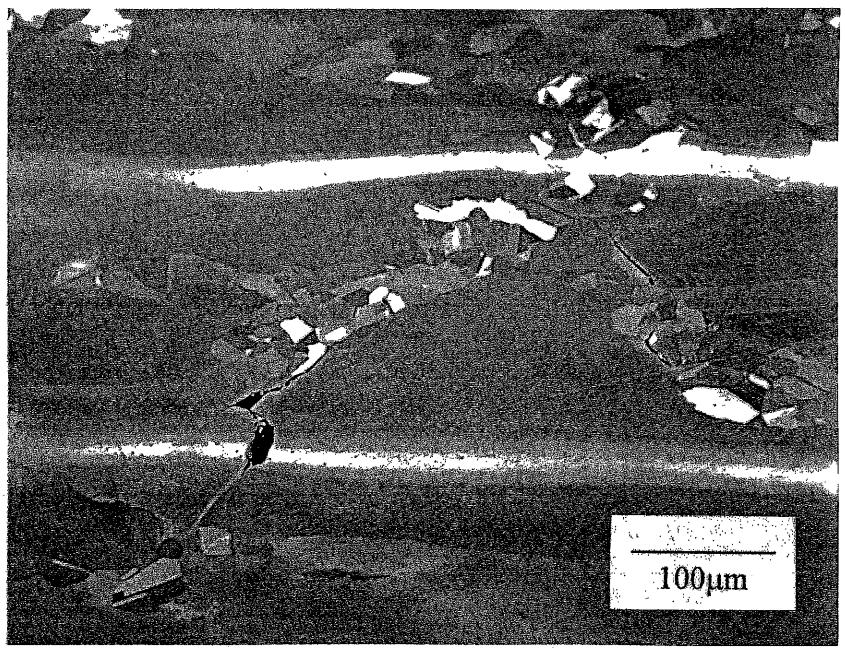

Figure 1. Optical micrograph of alloy B8873, after slow strain rate testing in 10% NH_4Cl at 82°C, showing a cross-section through a region adjacent to the fracture face.

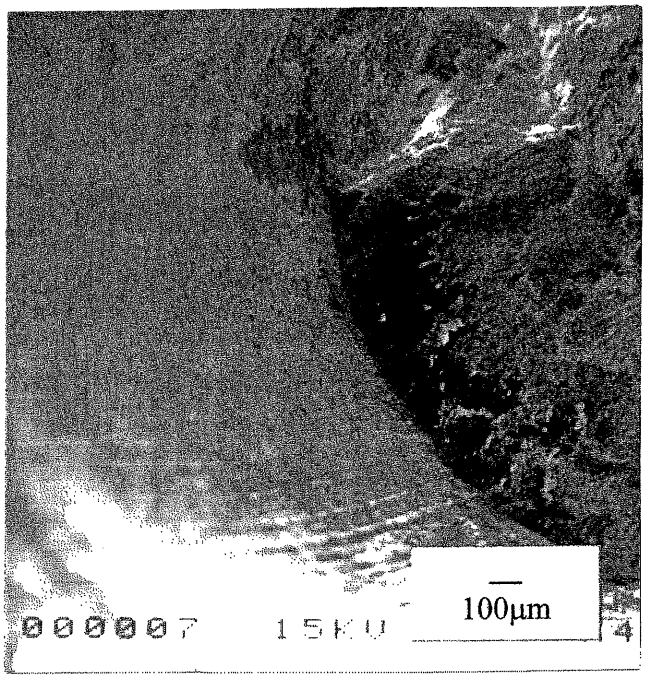

Figure 2. Scanning electron micrograph of the fracture face (right) and adjacent gauge length surface (left) of alloy Y5110 after slow strain rate testing in 10% NH_4Cl at 82°C.

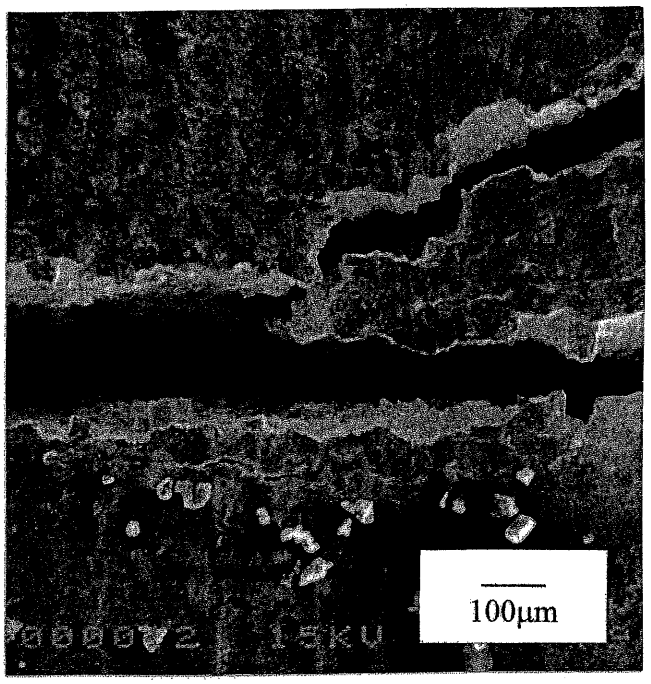

Figure 3. Scanning electron micrograph showing intergranular cracking in a C-ring specimen of alloy B3735 after testing for 60 days in 3.5% NaCl at 50°C.

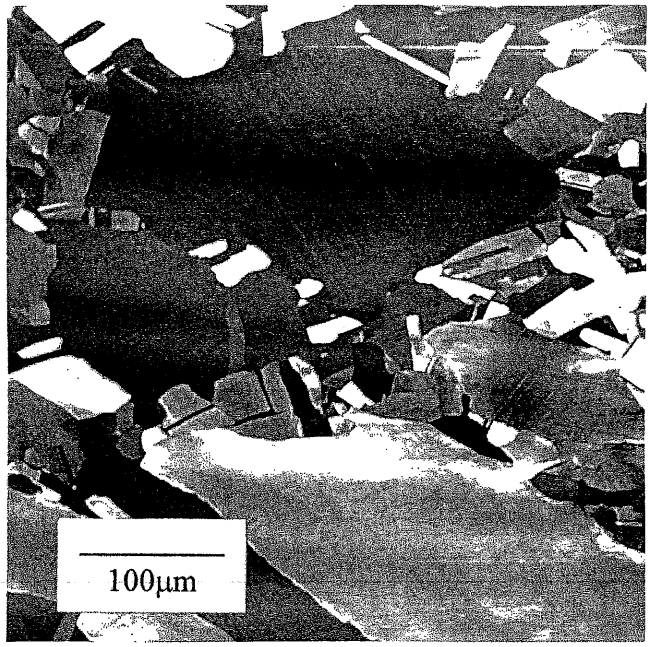

Figure 4a. Optical micrograph showing the grain structure of alloy B8873.

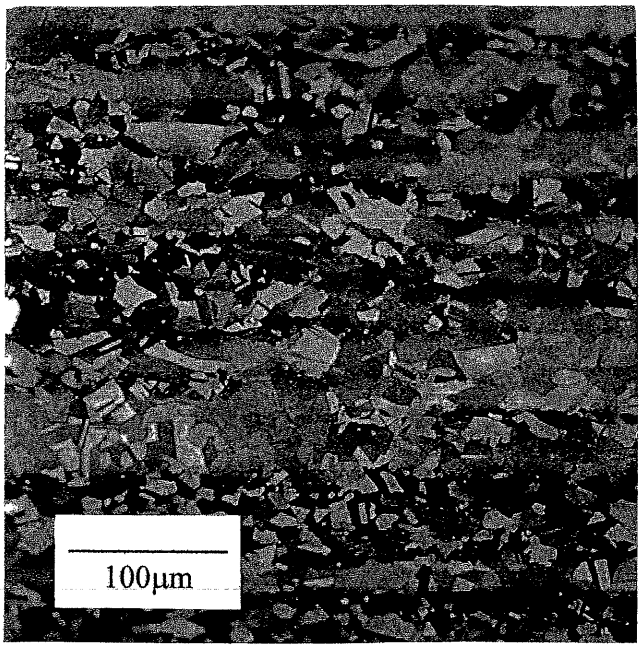

Figure 4b. Optical micrograph showing the grain structure of alloy Y5110.