

Effect of Tempering on Corrosion Resistance of Cast Aluminium Bronzes

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INTRODUCTION

Aluminium bronzes are copper base alloys containing aluminium up to 12 % with additions of nickel, iron and manganese. Because of their good mechanical properties and corrosion resistance these materials are mainly used in components operating in contact with sea water. In power plant applications these materials have been used e.g. in sea water pumps and valves. The major corrosion problem encountered in aluminium bronze castings in sea water applications is dealloying in crevices.

The microstructures of these alloys at low temperatures are products of β -phase transformation, which also enables heat treatment. The regions of the high temperature β -phase and the transformation products formed during slow cooling can be seen from the equilibrium diagrams of these alloys (Fig. 1). The decomposition sequence of the β -phase during slow cooling is presented in Fig. 2. The chemical compositions of the different equilibrium phases after slow cooling are presented in Table 1.

Martensitic and bainitic transformations occur in Cu-Al alloys. After quenching the microstructure is martensitic or bainitic depending on the cooling rate and the chemical composition of the alloy. Tempering heat treatments can be used to improve the mechanical properties, corrosion and wear resistance as well as other properties.

Generally these alloys are used in the as-cast condition. In the literature there are heat treatment recommendations for Cu-Al-Fe-Mn alloy in the range of 600...700 °C and for Cu-Al-Fe-Ni alloy in the range of 650...675 °C for 6 to 8 hours /1, 3, 4/. In this study two aluminium bronzes were investigated by microstructural study, corrosion testing as well as by electrochemical measurements in as-cast and in heat treated conditions. The main emphasis was to examine if it is possible to overcome dealloying corrosion in sea water conditions.

EXPERIMENTAL METHODS

The test materials were a nickel aluminium bronze (Cu-Al-Fe-Ni) and an aluminium bronze with iron and manganese additions (Cu-Al-Fe-Mn). The chemical compositions of these materials are shown in Table 2.

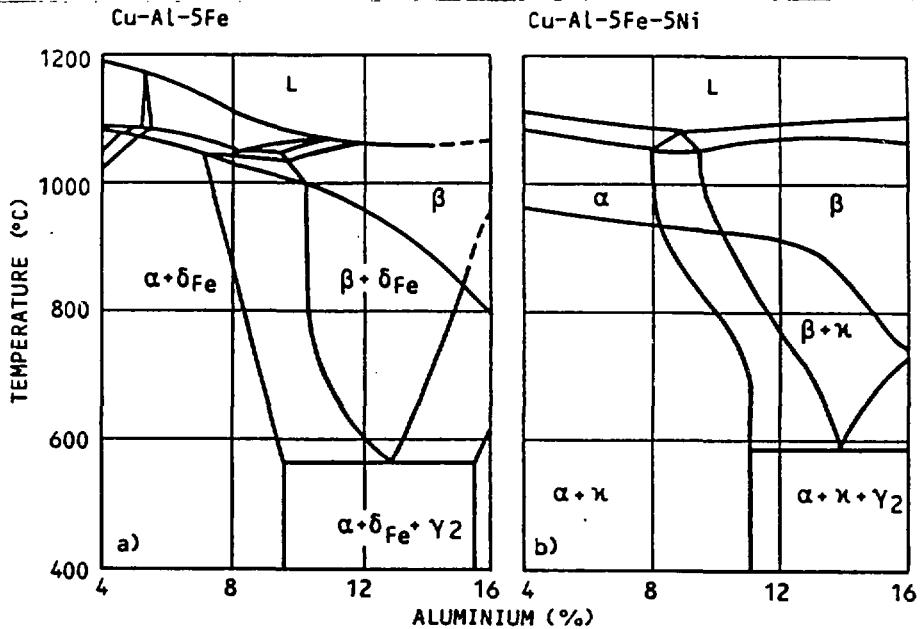


Fig. 1. Equilibrium diagrams of (a) aluminium bronze with iron additions (Cu-Al-Fe) and (b) nickel aluminium bronze (Cu-Al-Fe-Ni). /1/.

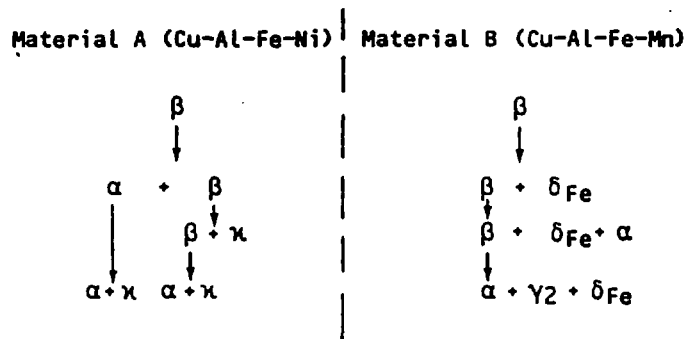


Fig. 2. Decomposition of β -phase during slow cooling /1, 2/.

Table 1. The average chemical compositions of β -decomposition products /1, 2/.

Material	Phase	Cu	Al	Fe	Ni
(Cu-Al-Fe-Ni) /1/	α	86	8	3	3
	κ	26	23	23	28
(Cu-Al-Fe-Mn) /2/	α	92	7.5	0.5	
	δ -Fe	11	17	72	
	γ_2	82	17	1	

Table 2. Chemical compositions of the test materials.

Material	Cu	Al	Fe	Mn	Ni
A (Cu-Al-Fe-Ni)	79.0	10.3	5.1	0.4	5.2
B (Cu-Al-Fe-Mn)	83.0	10.0	3.4	3.0	0.6

The heat treatments were selected on the basis of equilibrium diagrams. The various heat treatments that were studied are schematically shown in Fig. 3.

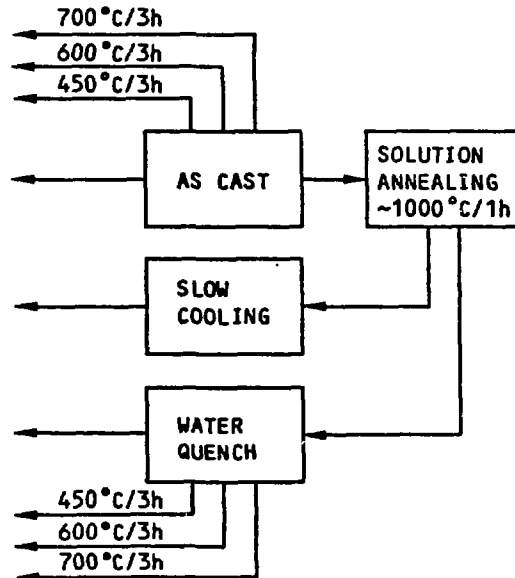


Fig. 3. Heat treatments of the test materials.

Based on the microstructure test materials were received in the as-cast condition, Figs. 4a and 4c. Polished specimens of each condition were etched in a FeCl_3 - solution for optical and scanning electron microscopy. The dealloying resistance of the materials in different solutions was studied according to the SFS 3873 standard test for dealloying of brasses /5/. The test consists of a microscopical study of the dealloyed layer after 24 hours' exposure to 1 % CuCl_2 solution at 75 °C.

The anodic polarization behaviour of the test materials was studied in neutral (pH ~ 8) and in acid (pH ~ 3) simulated sea water (0.005 N NaSO_4 + 0.09 N NaCl). The pH was adjusted with NaOH and HCl additions. The polarization curves were measured before and after the dealloying tests. The solution was deaerated with N_2 -purging for 10 min before the measurements. The scan rate was 20 mV/min. The corrosion potentials of some specimens were also measured for a longer time period in the solutions mentioned above.

RESULTS

Microstructures

The micrographs of the test materials in as-cast and water quenched conditions are shown in Figs. 4a - d. The microstructure of material A (Cu-Al-Fe-Ni) (Fig. 4a) in the as-cast condition consists of light-coloured α -grains surrounded by $\alpha+\kappa$ eutectoid and separate κ precipitates. Respectively, the microstructure of material B (Cu-Al-Fe-Mn) in as-cast condition (Figs. 4c and 5a) consists of α -grains surrounded by $\alpha + \text{bainite} + \gamma_2$ eutectoid and separate δ -Fe precipitates. After water quenching the microstructures of both materials have a Widmanstätten structure which consists of bainite and pro-eutectoid κ or δ -Fe phases (Figs. 4b and 4d). Thus, the microstructure of material A is basically similar to material B. The grain sizes of both materials are visible after water quenching and it can be seen that the grain size of material B is coarser than that of material A. The microstructures of material B after different tempering heat treatments are shown in Fig. 5. During tempering at 450 °C for 3 hours (Fig. 5b) the bainite of as-cast microstructure decomposes to α and γ_2 corresponding the equilibrium microstructure at temperatures below the eutectic temperature, 565 °C, and the amount of γ_2 -phase increases. Tempering above the eutectic temperature transforms the bainitic phase of as-cast microstructure to α and γ_1 , and γ_1 decomposes again to bainite during cooling (Figs. 5c and 5d). The microstructure obtained after tempering heat treatments (600...700 °C) is more homogeneous than after casting, when also γ_2 -phase is present.

DEALLOYING CORROSION

The results of the dealloying tests are presented in Fig. 6. The depth of dealloying of material A is in general smaller than that of material B. The microstructures and dealloyed zones of some specimens are shown in Figs. 7 - 9. The dealloying resistance of material A in the as-cast condition is good whereas that of material B is

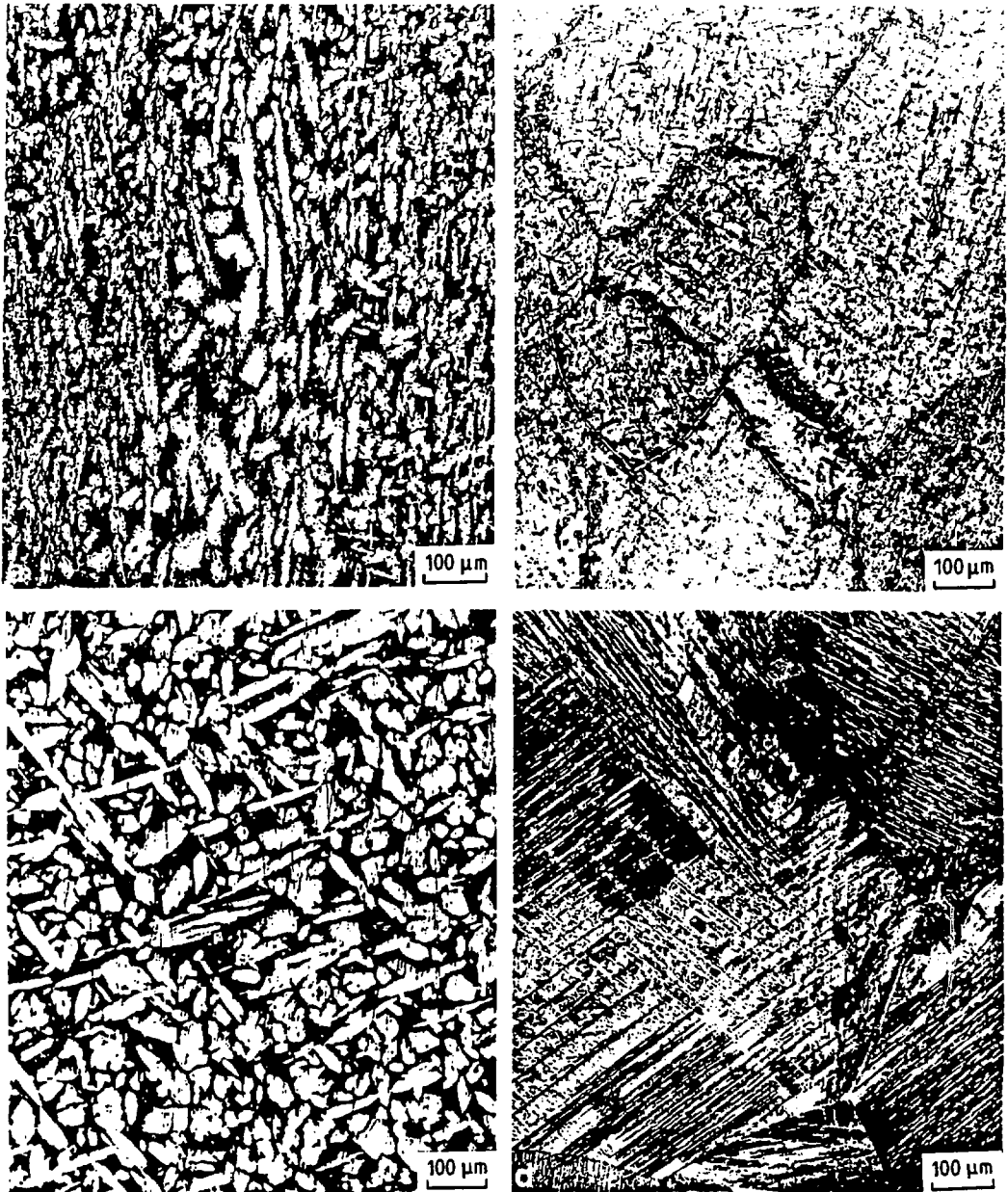


Fig. 4. Microstructure of material A (Cu-Al-Fe-Ni) in as-cast condition (a) and after water quenching (b), material B (Cu-Al-Fe-Mn) in as-cast condition (c) and after water quenching (d)

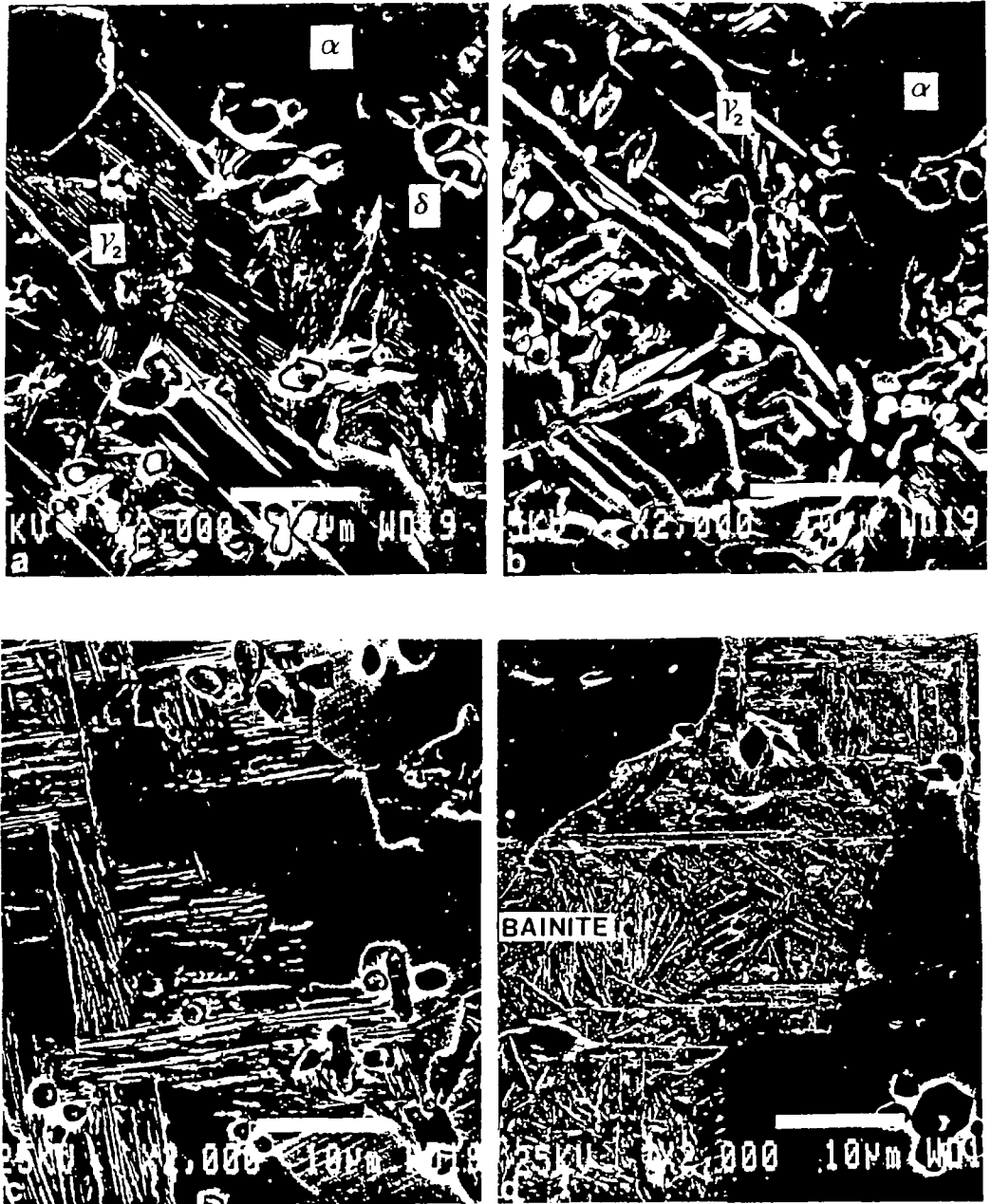


Fig. 5. SEM-micrographs of material B (Cu-Al-Fe-Mn) in as-cast condition (a) and in heat treated conditions: (b) 450 °C/3 h, (c) 600 °C/3 h and (d) 700 °C/3 h .

significantly worse. Tempering of the as-cast material A has no marked effect on the dealloying resistance (solid line in Fig. 6a). Solution annealed and water quenched conditions show a slightly decreased dealloying resistance (dashed line in Fig. 6a). The dealloying resistance is healed by tempering the water quenched materials at temperatures from 600 to 700 °C (see Fig. 9).

Tempering of the as-cast material B at 450 °C increases the dealloying susceptibility but tempering at higher temperatures decreases the depth of dealloying (solid line in Fig. 6b). This effect at 450 °C can be explained by γ_2 precipitation, which is known to enhance the susceptibility to dealloying attack. The best resistance to dealloying is obtained by tempering the as-cast material at 700 °C for 3 hours. Water quenching after solution annealing (Fig. 8a) has a beneficial effect on the dealloying resistance (dashed line in Fig. 6b). Further tempering has a varying effect depending on the tempering temperature (see Figs. 6b and 8b).

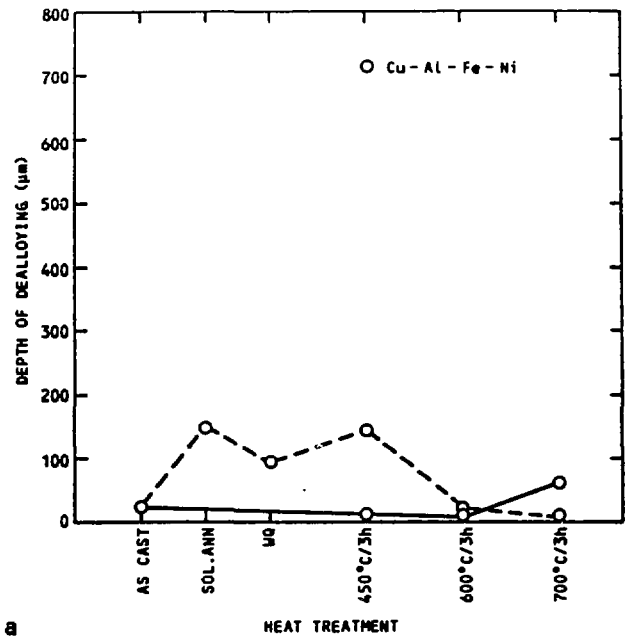
The X-ray microanalysis study of dealloying zones shows that the dealloying attack is localized to the eutectoid phase while the pro-eutectoid α phase with lower Al, Fe and Ni contents is not attacked. The microanalysis of the dealloyed zone shows only Cu and just ahead of the dealloyed zone the general composition of the alloy is obtained without any local composition differences.

ELECTROCHEMICAL MEASUREMENTS

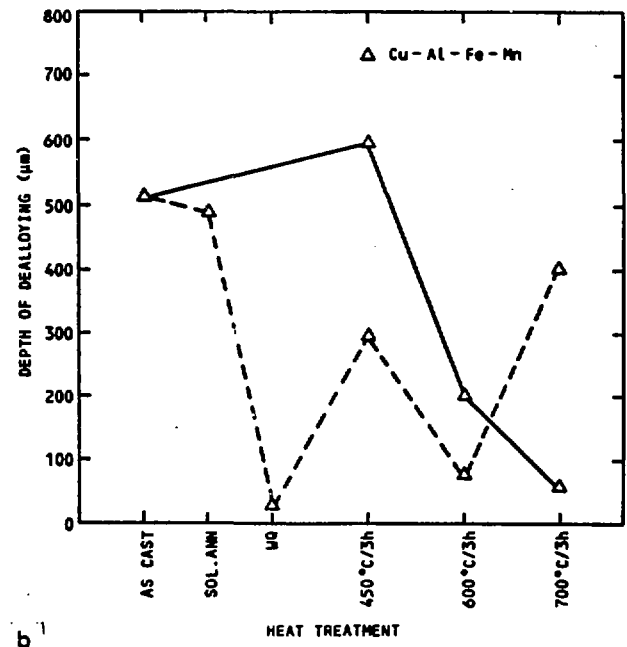
The effect of heat treatment on the electrochemical behaviour of the test materials was studied in neutral (pH ~ 8) and in acid (pH ~ 3) sea water. Anodic polarization curves and corrosion potentials in the heat treated as well as in the as-cast conditions were measured. The heat treatments did not generally have any pronounced effect on the free corrosion potential of the test materials. However, the free corrosion potentials of test materials in all conditions show a clear difference between acid and neutral solutions (Figs. 10 - 12). For material B this can be seen in Fig. 10a and for material A in Fig. 11a. The difference between corrosion potentials in acid and neutral solutions is larger for material B than for material A in the beginning of the exposure. In the long time experiments the differences decrease slightly after one day, Fig. 12. This behaviour is due to the selective dissolution of aluminium and iron rich phases, e.g. δ -Fe, γ_2 - and κ -phases. In acid solutions aluminium is electrochemically more active than copper and thus aluminium rich phases are preferentially attacked in these alloys and the copper rich α -matrix is left on the specimen surface. This was observed from the surface analyses after dealloying tests. This can also be seen from the anodic polarization curves obtained after dealloying tests (Figs. 10b and 11b) which are similar to the polarization curves of pure copper, and there are no differences in the polarization curves or corrosion potentials in neutral or in acid solutions.

DISCUSSION

This study indicates that the dealloying susceptibility of as-cast



a



b

Fig. 6. Depth of dealloying in standard test for test materials A (a) and B (b) after different heat treatments. Solid line corresponds to as-cast material and dashed line to water quenched material.

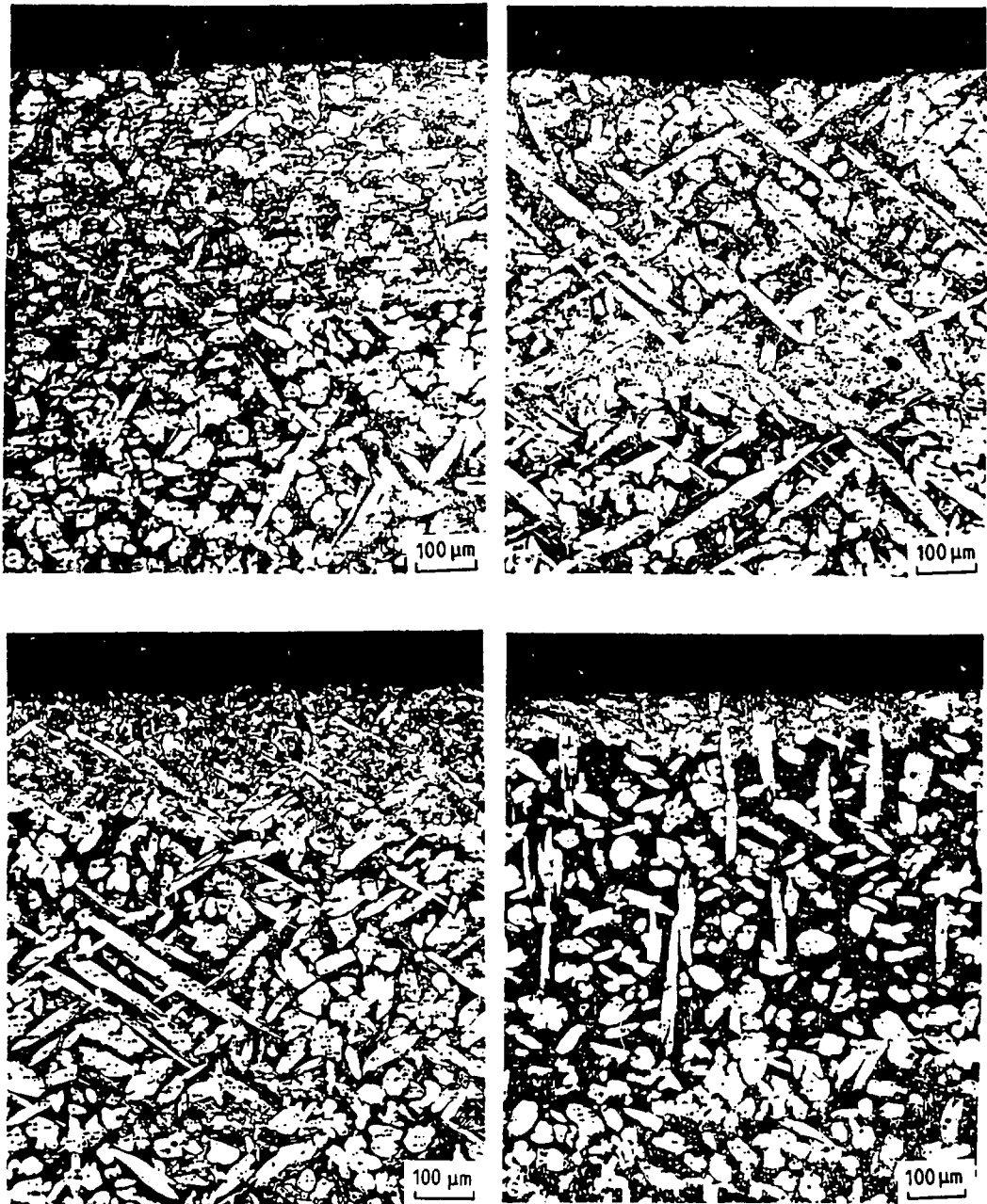


Fig. 7. The dealloying zones of material B in as-cast and heat treated conditions: (a) as-cast, (b) as-cast + 450 °C/3h, (c) as-cast + 600 °C/3 h, and (d) as-cast + 700 °C/3 h.

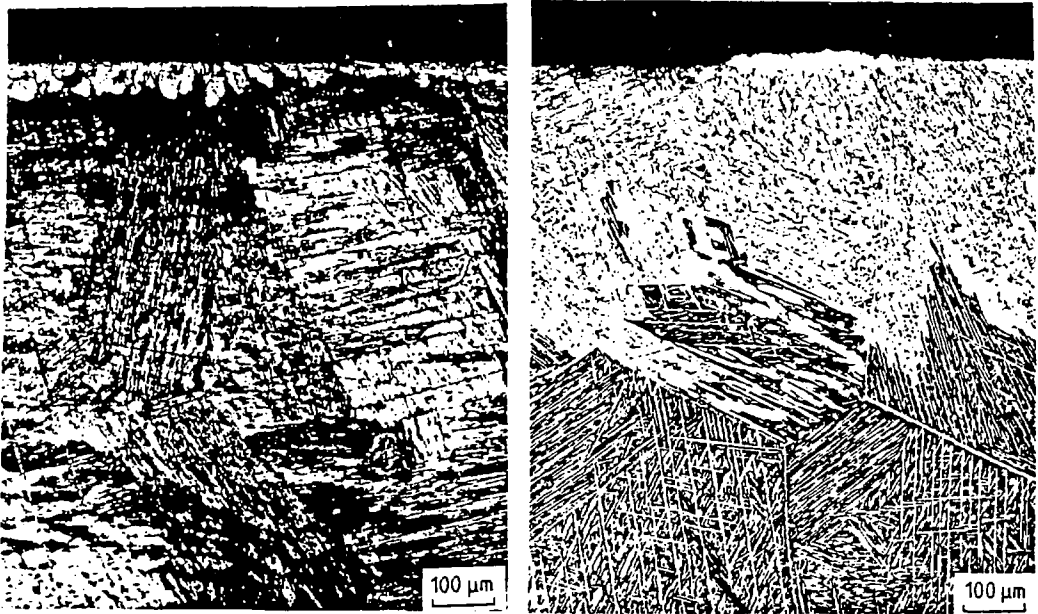


Fig. 8. The dealloying zones of material B in water quenched (a) and water quenched and tempered (700 °C/3 h) (b) conditions.

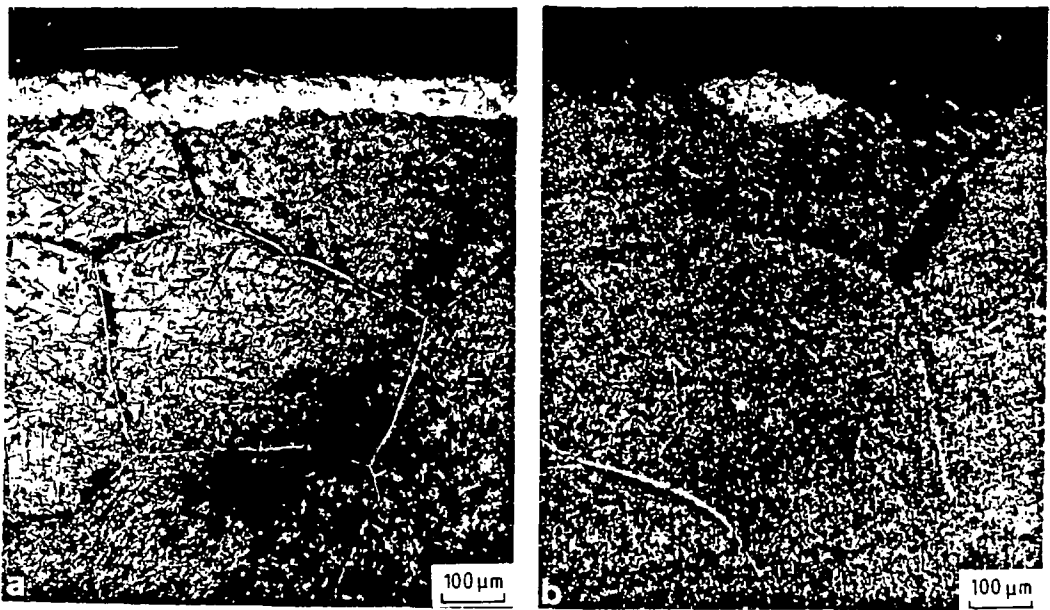


Fig. 9. The dealloying zones of material A in water quenched (a) and water quenched and tempered (700 °C/3 h) (b) conditions.

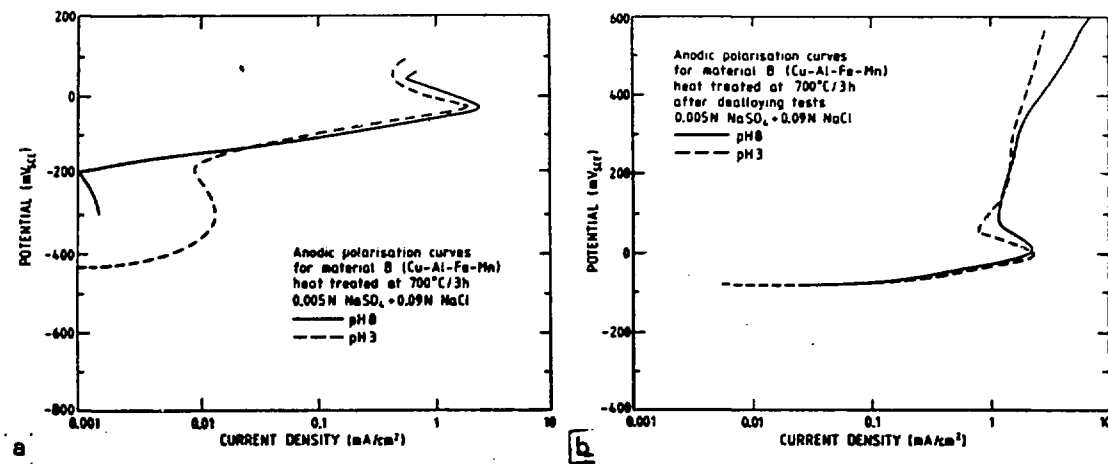


Fig. 10. Anodic polarization curves of heat treated (700 °C/3 h) material B before (a) and after (b) dealloying tests in neutral (pH ~ 8) and in acid (pH ~ 3) sea water.

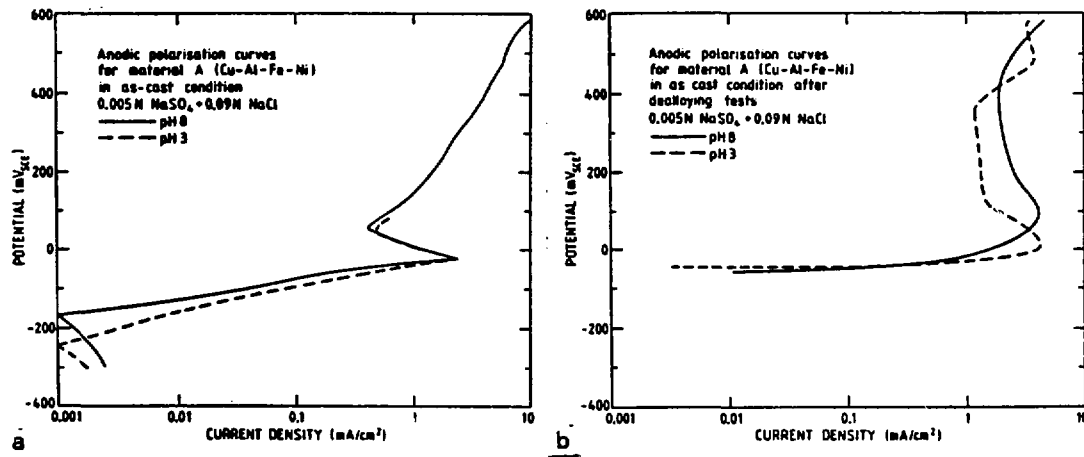
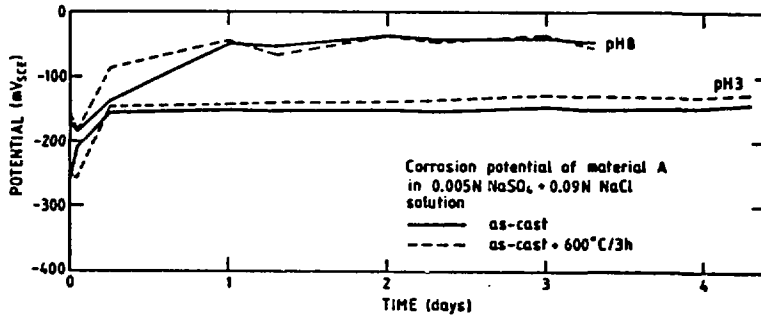
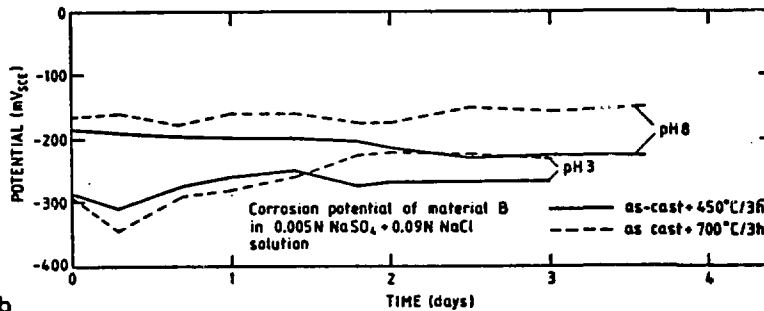


Fig. 11. Anodic polarization curves of as-cast test material A in neutral (pH ~ 8) and in acid (pH ~ 3) sea water before (a) and after (b) dealloying tests.



a



b

Fig. 12. Corrosion potentials of materials A (a) and B (b) in neutral (pH 8) and acid (pH 3) sea water in long term immersion tests.

aluminium bronzes can be decreased by appropriate tempering heat treatments. The best properties in this study were obtained by tempering at 600 °C. The homogenized microstructure obtained by water quenching for material B increased the dealloying resistance. In as-cast condition material A is much less susceptible to dealloying corrosion than material B. Thus, dealloying resistance can not be improved very much in the case of material A.

In material B tempering heat treatment at 450 °C causes the formation of γ_2 -phase, which made the material susceptible to dealloying corrosion. At 600 °C the eutectoid of as-cast material B transforms to $\alpha+\beta$ and at 700 °C mainly to β . After tempering at 600 °C the remaining α in the eutectoid improves the corrosion resistance. In material A tempering heat treatments cause κ -phase precipitation. Because the eutectoid phase has a higher Al-content, tempering of material A at 700 °C may cause β -phase formation, which during cooling can even produce deleterious γ_2 -phase. The increased dealloying of as-cast A material tempered at 700 °C (Fig. 6a) may be explained by this.

The lower corrosion potentials of the test materials observed in acid than in neutral sea water are a consequence of selective corrosion of aluminium-rich phases, which are not stable in these conditions. The observed differences in the resistance to dealloying after different heat treatments without any significant differences in the electrochemical behaviour can be explained by the distribution and amount of aluminium rich phases. After tempering heat treatments the amount of aluminium rich phases is greater than in the as-cast condition which further lowers the free corrosion potential of the heat treated aluminium bronzes. However, the aluminium rich phases are distributed more uniformly in the matrix after heat treatments and do not form a continuous path for the penetration of the selective dissolution of eutectoid phases. When the anodic phase is discontinuous, corrosion is restricted to the surface layers exposed to the solution leaving a surface consisting of the more noble copper phase.

CONCLUSIONS

Based on this study the following conclusions can be drawn:

- 1) The dealloying corrosion resistance of nickel-aluminium bronze is much better than that of aluminium bronze with iron and manganese additions, but it is not immune.
- 2) The dealloying corrosion resistance of aluminium bronzes can be improved by appropriate heat treatments. The best properties were obtained by tempering between 600 - 700 °C, depending on the initial microstructure.
- 3) In crevice conditions, where local acidification can occur, dealloying of aluminium bronzes is a consequence of the preferential attack at aluminium-rich phases. By appropriate tempering a uniform distribution of aluminium rich phases is obtained and the continuous path for selective corrosion is not formed.

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