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Corrosion resistance enhancement of marine alloys by rapid solidification

S. H. LO, W. M. GIBBON
Ontario Research Foundation, Sheridan Park Research Community, Mississauga, Ontario L5K 1B3, Canada
R. S. HOLLINGSHEAD
Defence Research Establishment, Atlantic, P.O. Box 1012, 9 Grove Street, Dartmouth, Nova Scotia B2Y 3Z7, Canada

Copper–nickel alloys used in marine applications, are known for their anti-fouling properties. However, they are generally of low strength and are moderately susceptible to corrosion when used in a marine environment. Attempts at adding iron to Copper–nickel alloys by conventional ingot metallurgy, to improve their mechanical and corrosion resistant properties, have met with limited success. In this work, rapid solidification technology was employed to produce rapidly solidified (RS) Cu–10Ni and Cu–10Ni–8Fe. It was found that both the RS Cu–10Ni and Cu–10Ni–8Fe exhibited superior mechanical and corrosion resistant properties, compared with their sand-cast counterparts. Furthermore, the addition of iron to Cu–10Ni alloy, produced by RS, increased the corrosion resistance of the alloy, whereas the addition of iron to Cu–10Ni alloy produced by conventional means, had an adverse effect.

1. Introduction

Copper–base alloys are known for their suitability for marine service. They are formed easily, offer reasonable corrosion resistance in quiescent or laminar flowing seawater and possess an inherent anti-fouling property. Unfortunately, copper-base alloys are, in general, of low strength, and measures taken to increase their strength depend on cold working, with the result that they are not suitable for applications involving brazing or welding.

Copper–nickel alloys appear to have the potential to offer a superior combination of strength and toughness. However, attempts to develop high-strength copper–nickel alloys using conventional ingot metallurgy practice, have met with limited success. For instance, the addition of iron to copper–nickel has been shown to be beneficial in increasing the strength of the alloy as well as in improving its erosion and corrosion resistance in seawater [1–3]. However, the addition of more than 1.5 wt % iron, is not practical, because of severe segregation and coarseness of the microstructure. Furthermore, homogenization of the cast material is usually time consuming and may lead to further coarsening [4].

Rapid solidification technology is being investigated as a means of developing new copper–nickel alloys, because it offers advantages not achievable by conventional ingot metallurgy practice. Rapid solidification is known to extend the solid solubility limits of an alloy element and distribute the excess in the form of fine dispersoids, rather than segregated or incongruent particles. These fine dispersoids, if stable and located at grain boundaries, act to prevent grain growth during subsequent hot working, thus retaining the ultra-fine microstructure achieved in the rapid solidification process.

2. Experimental procedure

Cu–10Ni and iron-modified Cu–10Ni were selected in this investigation, in order to study the effect of iron on the mechanical and corrosion resistant properties of Cu–10Ni. In the modified alloy, the iron content was approximately 8.5 wt %, which is very much in excess of the percentage soluble in Cu–10Ni alloy produced by conventional ingot metallurgy.

Table I shows the chemical composition of the Cu–10Ni and Cu–10Ni–8Fe alloys. Both sand-cast and rapidly solidified samples of these alloys were prepared.

The rapidly solidified materials were produced by a planar flow casting (PFC) technique. This was accomplished by ejecting a jet of induction-melted alloy on to a 25 cm diameter copper wheel rotating at 2000 to 4000 r.p.m., to produce ribbon of approximately 25 mm wide and 10 to 160 μm thick. The cooling rate of the copper–nickel alloys produced by this technique was estimated to be in the range of 10^5 to 10^6 K sec^{-1}.

A variety of techniques was used to characterize the microstructural features of the sand-cast and RS alloys, including optical, scanning electron and transmission electron microscopy. The chemical

TABLE I Chemical composition of copper nickel alloys

Type	Copper	Nickel	Iron	Manganese
Cu–10Ni	Balance	10.5	1.42	0.41
Cu–10Ni–8Fe	Balance	11.1	8.5	0.003

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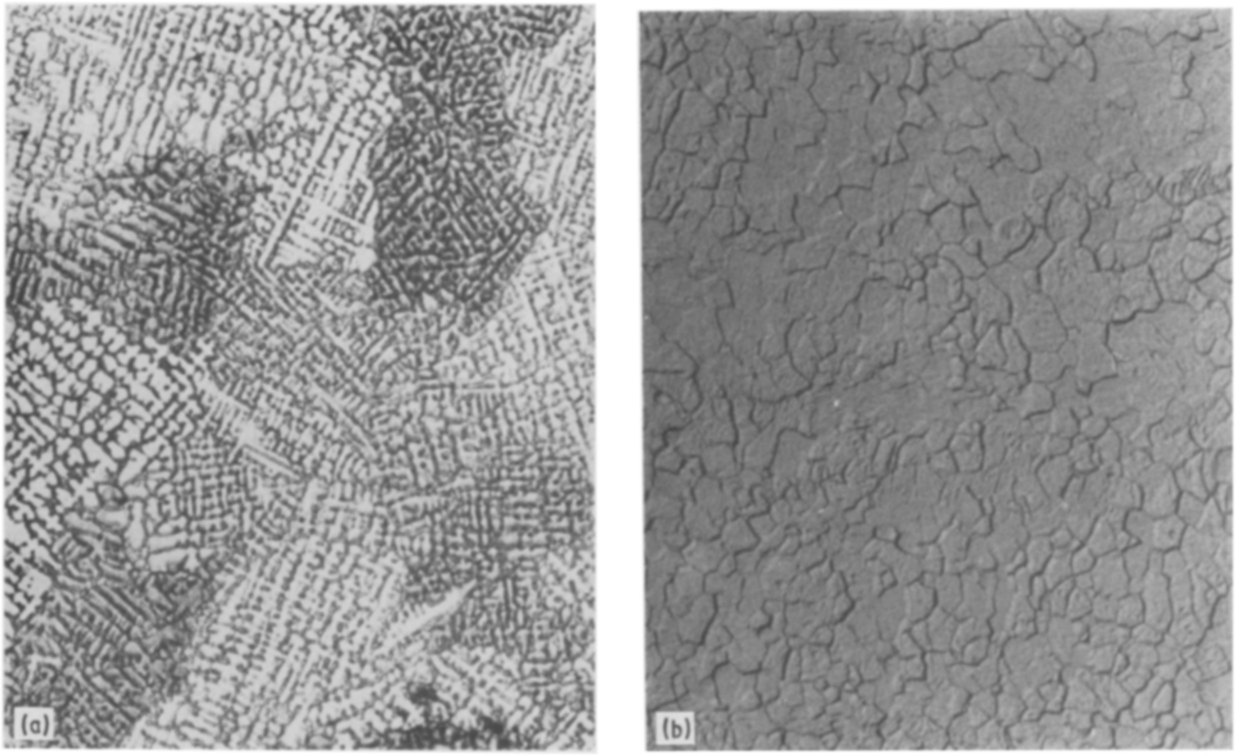

Figure 1 Microstructure of (a) a sand-cast and (b) a rapidly solidified Cu–10Ni alloy. × 1000

composition of the RS Cu–10Ni–8Fe sample was obtained using a Philips 400T scanning transmission microscope (STEM) fitted with an X-ray analyser.

The corrosion potentials of the cast and rapidly solidified alloys were measured with respect to time, using an EG and G Princeton Applied Research Model 350 corrosion measurement system. The electrolyte was natural seawater from Halifax harbour, with a pH ranging between 7.5 and 7.9, filtered through a 3 μm filter. The electrolyte was maintained at a temperature of 25° C and was aerated for 20 to 30 min in the corrosion cell before a sample was immersed in it. Aeration was continued during each test.

3. Results and discussion

The distinct difference between the microstructures of rapidly solidified and sand-cast Cu–10Ni alloy is

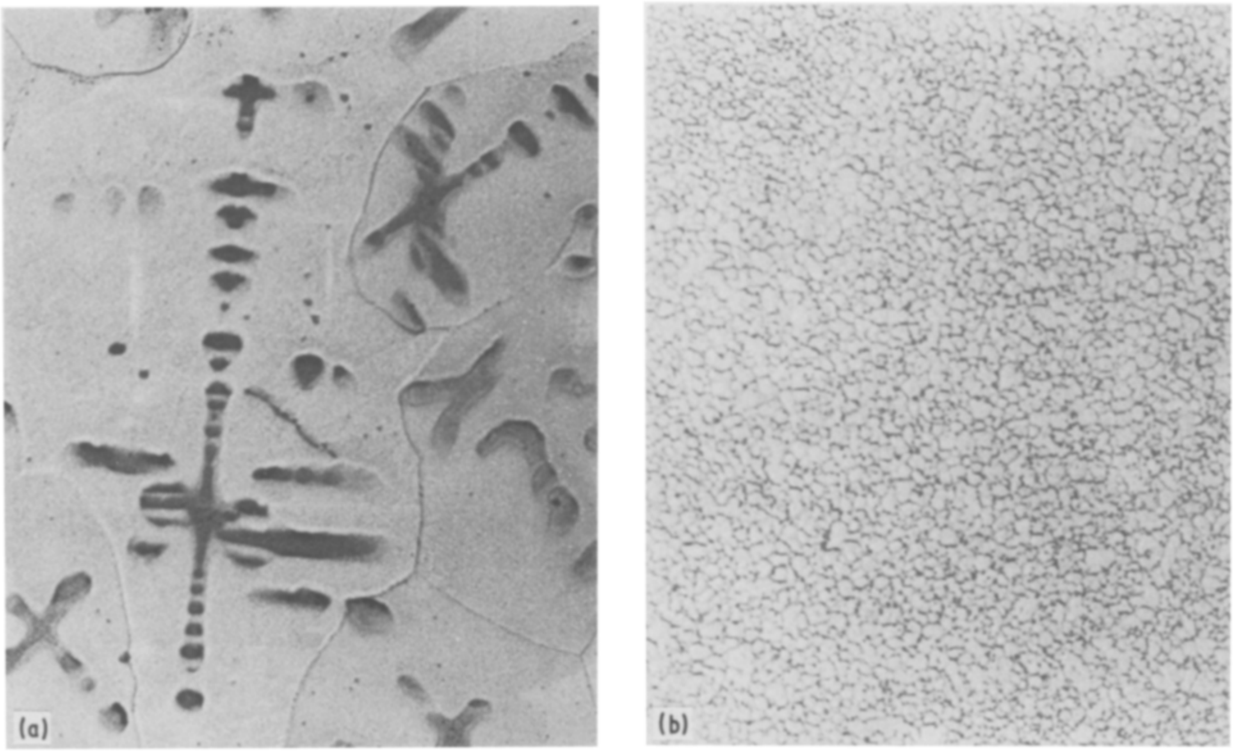

Figure 2 Microstructure of (a) a sand-cast and (b) a rapidly solidified Cu–10Ni–8Fe alloy. × 800

TABLE II Microhardness values of cast and rapidly solidified materials

	Cu–10Ni (VHN)	Cu–10Ni–8Fe (VHN)
Rapidly solidified material	120 ± 2.6	172 ± 6.4
Sand-cast material	106 ± 2.8	112 ± 1.3

shown in Fig. 1. The average grain size of the original sand-cast alloy is 500 μm, whereas that of the remelted and rapidly solidified alloy is 4 μm. In the case of Cu–10Ni–8Fe, the average grain sizes are 100 and 1 μm for the sand-cast and rapidly solidified materials, respectively. Microhardness values of the RS and sand-cast copper–nickel alloys were also measured, and are listed in Table II. Consistently higher hardness values are exhibited by the RS materials in comparison with their sand-cast counterparts, a direct consequence of the grain refinement achieved by rapid solidification.

In addition to the attainment of higher hardness, another important aspect of rapid solidification is the achievement of chemical compositional homogeneity. This effect is revealed distinctly in the microstructures of the RS and sand-cast Cu–10Ni–8Fe alloy shown in Fig. 2. Both samples were etched to reveal the chemical compositional differences in the samples. In the case of the sand-cast material, the darker regions represent regions rich in iron; and the lighter regions are rich in copper.

The sand-cast material shows localized regions which are either rich in iron or copper, as shown by the colour differences in the figure. However, such compositional differences are not evident in the RS material. The chemical compositional homogeneity of an alloy has a considerable effect on its corrosion resistance. For instance, in the case of the sand-cast Cu–10Ni–8Fe, the development of localized iron-rich regions, makes the material very prone to galvanic attack.

The corrosion resistance of the rapidly solidified and sand-cast copper–nickel alloys was evaluated by monitoring their corrosion potentials in aerated seawater, with respect to time. Fig. 3 shows a corrosion potential against time plot of the sand-cast and RS Cu–10Ni alloy. In this case, the RS material achieved a more noble potential, compared to its cast counterpart, in a much shorter time. Basically, a passivated film formed more readily on the RS material. This phenomenon, was found in Cu–10Ni–8Fe alloy also, as shown in Fig. 4.

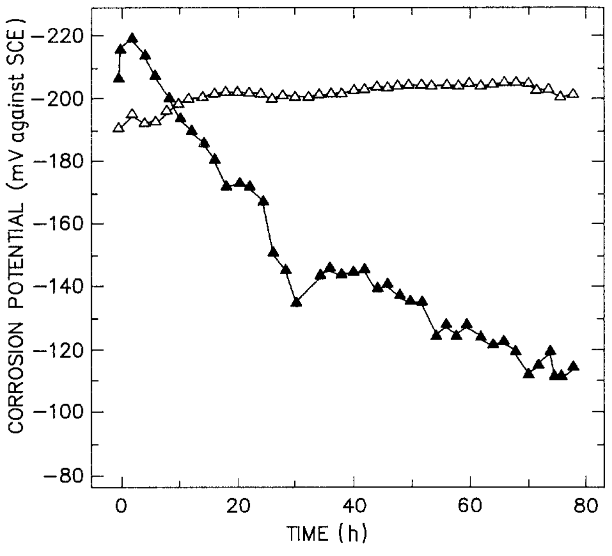

Figure 3 Corrosion potential against time plot of (△) a sand-cast and (▲) a rapidly solidified Cu–10Ni alloy in aerated seawater.

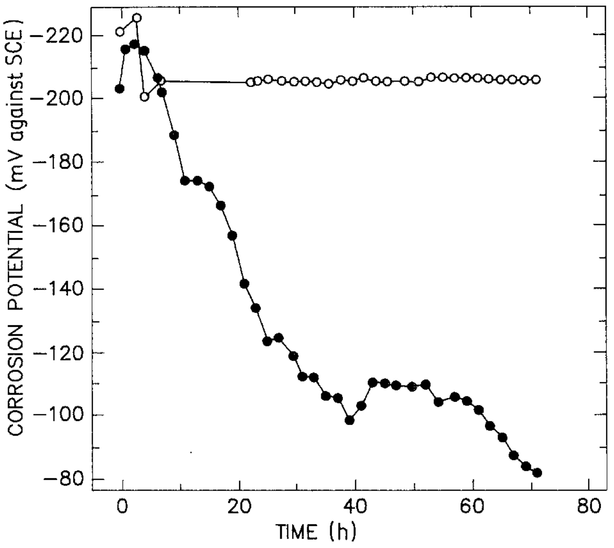

Figure 4 Corrosion potential against time plot of (○) a sand-cast and (●) a rapidly solidified Cu–10Ni–8Fe alloy in aerated seawater.

In order to evaluate the effect of iron addition, the measured corrosion potentials of the Cu–10Ni and Cu–10Ni–8Fe alloys are compared in Fig. 5. In the case of the sand-cast alloy, the addition of iron did not achieve any improvement in corrosion resistance. On the contrary, the cast Cu–10Ni–8Fe appears to be less corrosion resistant than the cast Cu–10Ni alloy, as indicated by the top two curves. This result is consistent with the published information, that the addition of iron, in excess of 1.5 wt %, to Cu–10Ni produced by conventional ingot metallurgy, leads to severe segregation, which is detrimental to the general corrosion resistance of the material. This phenomenon, has been

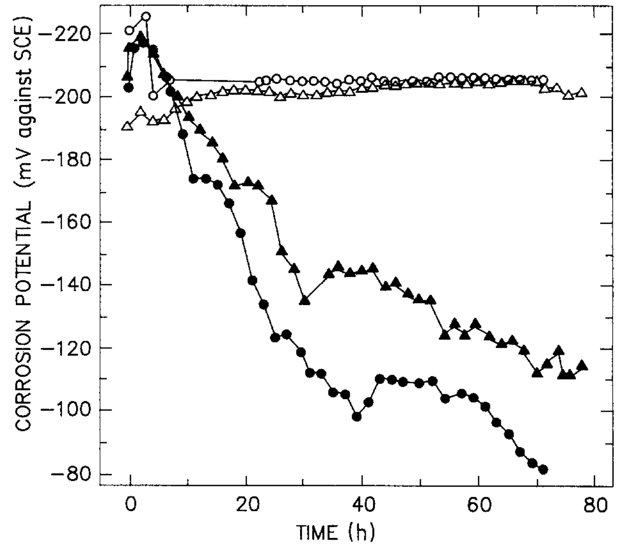

Figure 5 Corrosion potential against time plot of (△, ○) sand-cast and (▲, ●) rapidly solidified copper–nickel alloys in aerated seawater. (△, ▲) Cu–10Ni, (○, ●) Cu–10Ni–8Fe.

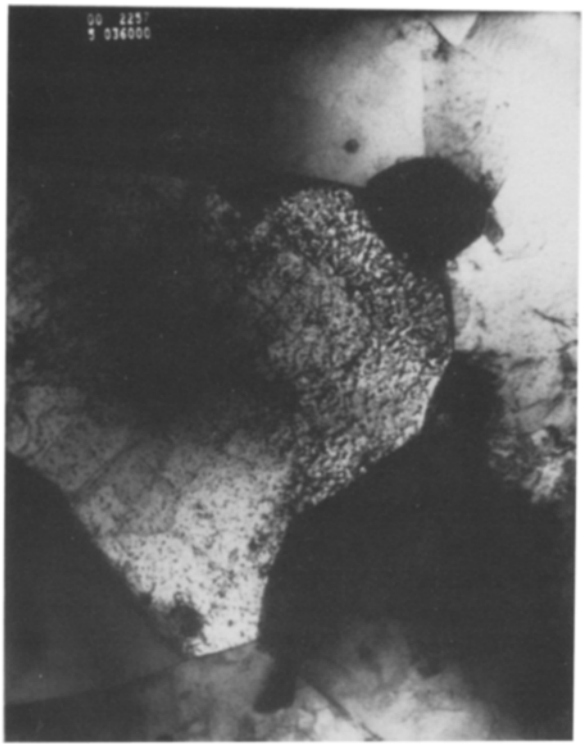

Figure 6 Electron micrographs of a rapidly solidified Cu–10Ni–8Fe alloy. × 36 000

confirmed in previous studies [5], which show that iron additions of less than 1.5 wt % increase the corrosion resistance of Cu–10Ni [5], but that higher concentrations of iron have an adverse effect [2]. Essentially, excess iron in the sand-cast Cu–10Ni causes the formation of iron-rich phases in the grain-boundary network. This, in turn, promotes corrosion of the grain-boundary material due to galvanic coupling, leading to intergranular corrosion attack [6].

Basically, the addition of iron to Cu–Ni alloys, promotes the formation of a film consisting of a corrosion product containing hydrated ferric oxide [7]. It is suggested that this film is effective in reducing the corrosion rate of Cu–Ni alloys [8]. It has been pointed out that, in order for the iron to be effective in increasing the corrosion resistance of Cu–Ni alloys, it should be present either as a fine dispersoid or be dissolved in solid solution [5, 7].

The microstructure of the rapidly solidified Cu–10Ni–8Fe is shown in Fig. 6. Very fine dispersoids are evident both within the cell and at the cell boundaries. This microstructure seems to comply with one of the requirements for increasing the corrosion resistance of Cu–10Ni alloys. Chemical compositional analysis, with STEM, within a cell of the sample, showed consistently high iron contents, of approximately 4 wt %, at all locations examined, i.e. a higher content of iron is dissolved in the rapidly solidified than in the sand-cast Cu–10Ni–8Fe, thus enhancing the corrosion resistance of the alloy.

4. Conclusions

From the results of this investigation, the following conclusions can be drawn. By rapidly solidifying Cu–10Ni and Cu–10Ni–8Fe alloys, a refinement in grain size is achieved. This, in turn, produces improved mechanical properties in the RS materials compared to their sand-cast counterparts. In addition, homogeneity in chemical composition of the alloys is achieved. In this case, coarse segregation of phases with different chemical compositions, is eliminated, thus making the rapidly solidified materials less prone to galvanic attack.

The addition of 8 wt % iron to Cu–10Ni alloy by conventional ingot metallurgy does not produce any increase in the corrosion resistance of the material. However, if Cu–10Ni–8Fe is produced by RS, the corrosion resistance is increased. This is achieved by increasing the solubility limit of iron in Cu–10Ni alloy and uniformly distributing excess iron in fine dispersoids in the material.

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