

Influence of the iron content on the solidification behaviour of cast aluminium bronze used in marine applications

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Abstract

The effect of iron addition to Cu-Al-Ni alloys (in the zone of the chemical composition of commercial aluminium bronze) has been studied. The quaternary alloys were melted from a base Cu-Al-Ni alloy with iron additions up to ~6 at.%. Simultaneous Differential Thermal Analysis and Termogravimetry (DSC/TGA) and isothermal homogenisation with rapid cooling have been employed to determine the equilibrium phases at different temperatures and the existing invariant reactions. The alloys were observed by Optical Microscopy (OP) and by Scanning Electron Microscopy (SEM). The chemical analysis of the phases has been determined by Energy-Dispersive Spectroscopy (EDS).

The results obtained allow the determination of the effect of the iron content in the sequence of phase formation. The chemical compositions of the phases obtained are compared with the same phases in the commercial alloys, with other alloying elements being present.

The effect of iron content on the “*liquidus*” temperature and phase compositions of the invariant reactions detected, in the range of compositions studied, are presented.

1. Introduction

The Al bronze alloys are used for propeller applications because of their mechanical properties and good corrosion resistance (1,2,3). As the usual volume of this kind of pieces is very large, the cooling rate can be very different from the centre to the periphery (1). The effect of the cooling rate on the solidification path is an important aspect to determine how the phases are distributed inside the propeller, according to the local cooling rate, and possible composition gradients.

The aim of this work is to determine the effect of the iron content in the cooling path and the distribution of that element in the equilibrium phases detected.

The equilibrium microstructures obtained are compared with others from an industrial type propellers.

2. Experimental procedure

A base alloy of Cu - Ni - Al was prepared by melting, using pure elements (≥ 99.9 % purity) in a High frequency induction furnace under inert atmosphere (constant flow of high purity Ar). This alloy was remelted to introduce different contents of Fe, in the range of 0 to ~6 at. %.

The “*Liquidus*” temperature and solid state temperature transformations of the alloys, with different contents of Fe, were determined by differential thermal analysis (DSC/TGA). The experiments were conducted in a *TA - SDT 2960* equipment (simultaneous thermogravimetry and differential thermal analysis) in inert atmosphere, obtained by a constant flow of high purity helium (100 ml/min. - 99.999%). The heating rate was 10 °C/min.. An alumina crucible (50 µl) has been employed for samples with 3 mm of diameter and 1 mm height. By the TGA results it was also registered the weight variation during the thermal cycle.

The so produced alloys were homogenised at different temperatures, below and above the transformation temperatures, which have been detected by DTA. The samples were heated at 1130 °C and slowly cooled (at 2 °C/min) down to the homogenisation temperature. After the stage at that temperature, the samples were rapidly quenched in a solution of salted water and ice at ~0 °C. The thermal cycle is presented in figure 1.

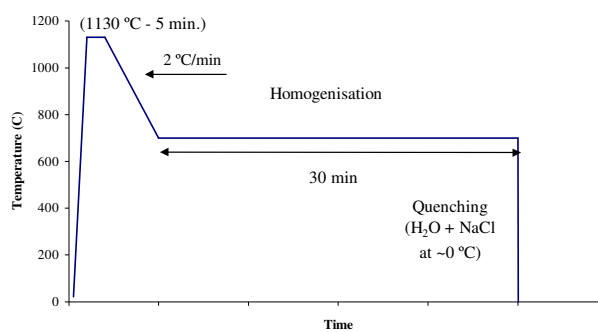


Fig. 1: Thermal cycle used in the homogenization experiments followed by quenching.

After the DTA and the homogenisation experiments the alloys were observed by Optical Microscopy (OP), Scanning Electron Microscopy (SEM) and the chemical analysis of the phases have been determined by Energy-Dispersive Spectroscopy (EDS).

3. Discussion of results

The chemical composition of the melted alloys, with different Fe additions, is presented in table 1. On alloy N° 5 low contents of residual elements, like P, S and Mg, were detected.

Table 1: Chemical composition (at. %) of the alloys used in this work, obtained by SEM/EDS analysis.

Alloy N°	% Cu	% Al	% Ni	% Fe	Others
1	73,3	20,8	5,9	-	-
2	70,7	22,0	5,8	1,5	-
3	71,3	20,1	4,9	3,7	-
4	64,9	23,7	5,3	6,1	-
5	67,9	20,9	4,6	4,8	Mn: 1.4 %; Si: 0.3 %

The samples with Fe additions, slowly cooled from the liquid state, have different microstructures when compared with the Cu-Al-Ni base alloys. The changes in the microstructures are presented in figure 2, for alloys with different Fe content.

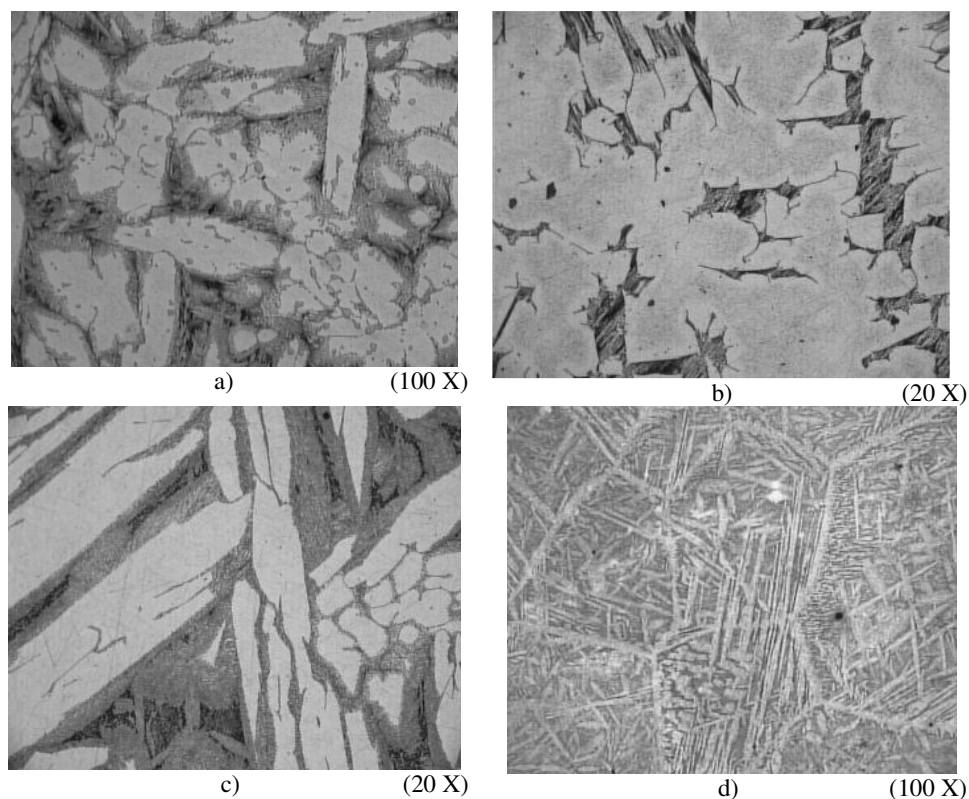


Fig. 2: Microstructure of alloys, by OP, with different contents of Fe after slow cooling: a) alloy N° 5, b) alloy N° 1, c) alloy N° 3 and d) for alloy N° 4.

The presence of iron in the alloys modifies clearly the final microstructure and the melting temperature. Microstructures presented in figure 2 shows the effect of the iron content in the lowering of the alloy grain size.

The temperature of “*liquidus*” of the alloys becomes higher with the iron content, as shown in figure 3. The temperatures of “*liquidus*” presented, determined in the cooling path of the DSC experiments (figure 3), might be affected by the undercooling effect. The peaks obtained in all the alloys correspond to the formation of a solid phase followed by the eutectic transformation of the Cu-Al phase diagram (4). The differences in the obtained temperatures may be explained by the presence of Ni and Fe, in the ternary and quaternary alloys.

Table 2: Temperature of “*Liquidus*”, obtained in the DSC experiments, for alloys with different Fe contents.

Alloy N°	“ <i>Liquidus</i> ” temperatures (°C)
1	1044
2	1061
3	1063
4	1086

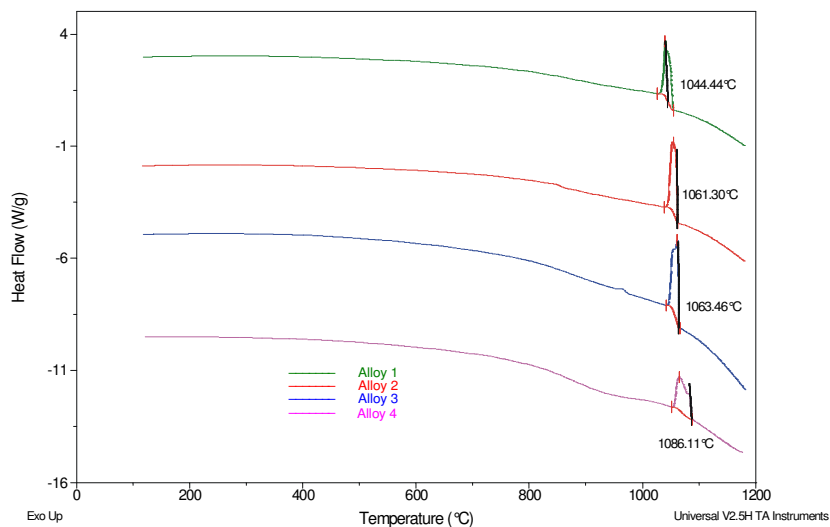


Fig. 3: DSC curves, of the cooling path, obtained for the alloys with different iron content.

In figure 4, the microstructures of the sample N° 3, homogenised at two temperatures and followed by rapid cooling, are presented, allowing understanding the sequence of solidification of the quaternary alloys. In figure 4a) is presented the equilibrium between the primary α phase and the liquid phase. In figure 4b) is presented the equilibrium microstructure, at 500 °C, with the primary α phase, the eutectic constituent and the zone of the iron rich precipitates (fig. 4b).

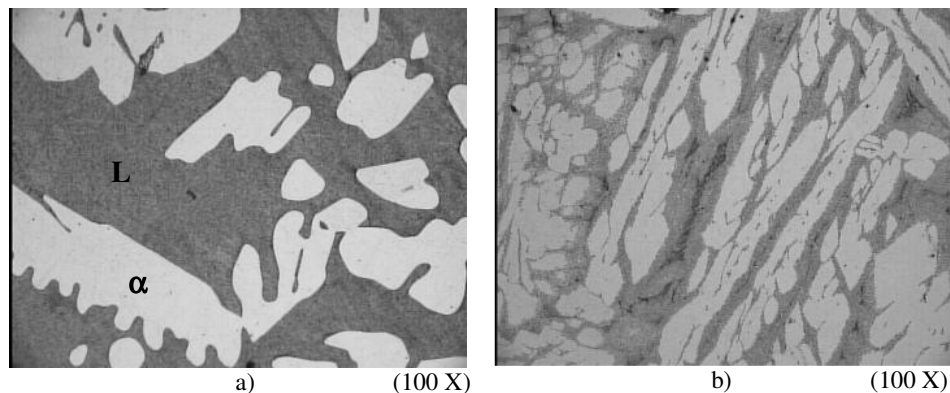


Fig. 4: Microstructures obtained, by OP, in alloy N° 3 after homogenization at a) ~1060 and b) 500 °C.

The iron rich precipitates forms at the end of cooling, as can be concluded by figure 5. In figure 5 b) it is presented a detail of fig. 5 a) showing the shape and the local of formation of the iron rich precipitates.

From these results it can be concluded that the presence of iron, up to ~4 at %, doesn't behave as a nucleation agent in the Cu-Al-Ni alloys. The shape (2) and chemical composition of the iron rich precipitates, in commercial alloys, is also dependent of the presence of iron associated with others elements. With the increase in the iron content, the shape of the precipitates modifies from oval to "cleaver leaves" (6). The modification, of the precipitates, for the dendritic or stars shape was

detected already in the alloy N° 3 (fig. 5b), with iron contents lower then the minimum of ~6.3 % Fe proposed by Rutkowski (6).

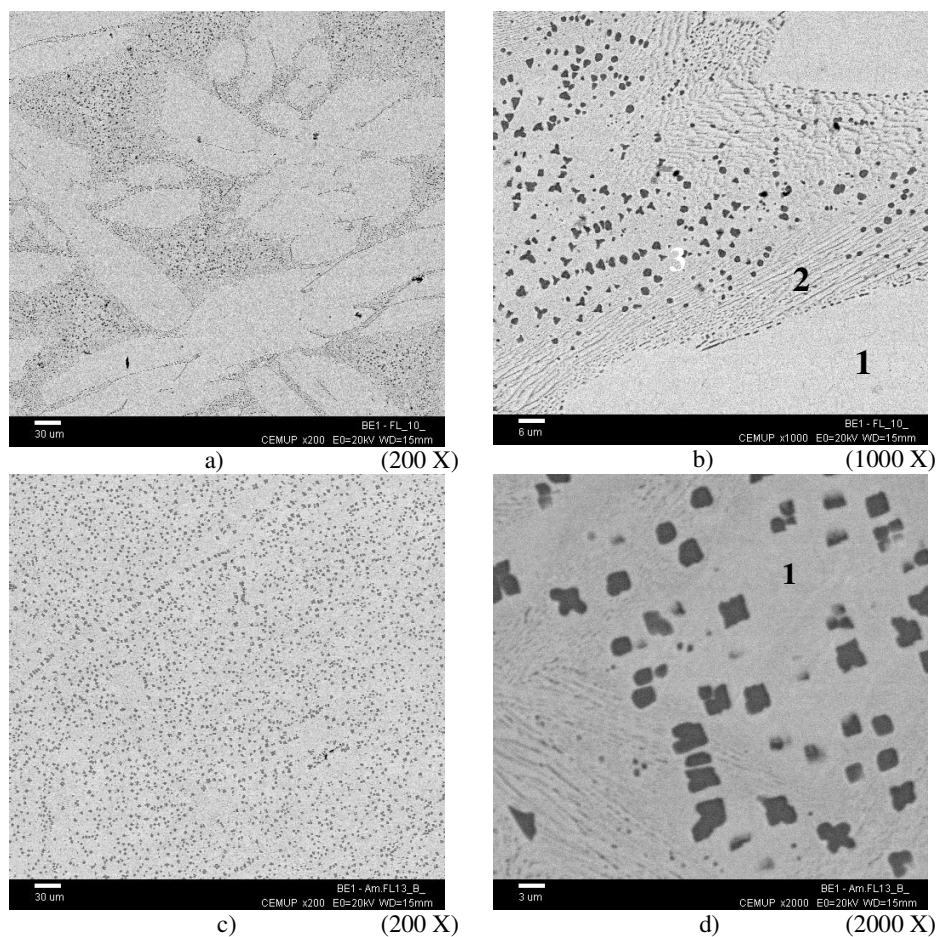


Fig. 5: Microstructures obtained, by SEM, in alloys N° 3 (a and b) and N° 4 (c and d) after slow cooling (10 °C/min): detail of zones with the iron rich precipitates (b and d).

Microstructures, presented in figure 5, shows the changes in the solidification behaviour, in the range of 4 - 6 at.% of iron. In the alloy with less iron content, the precipitates form at the end of cooling (zone 3 in fig. 5b). For higher iron contents, figures 5 c) and d), some of the precipitates are inside of the α phase (zone 1 in fig. 5d), indicating that they form firstly. Hence it seems that iron behaviour as nucleation agent is dependent on its content in the alloy.

The chemical composition of the phases or constituents, obtained in the alloys after slow cooling (10 °C/min), are presented in the table 3. The chemical composition of the precipitates in alloy N° 4 is very different, with higher iron content, than for the others alloys. This is in accordance with the differences already detected in the sequence of formation of that phase. The chemical composition of the precipitates, obtained in the industrial alloy, can be separated in two classes, according with the iron content. The morphology of the precipitates, detected in alloy N° 5 (table 3), is dendritic for type I and “cleaver leaves” for type II (6). The differences in the chemical composition of the precipitates, when commercial alloys are compared with those prepared at laboratory, may be explained by the presence of small quantities of some other elements like manganese and silicon,

for example. For the other phases or constituents, no significative differences in their chemical compositions were found, between commercial alloys and samples prepared in laboratory with pure metals.

Table 3: Chemical composition (at. %) of the phases or constituents present in the alloys, after slow cooling, obtained by SEM/EDS analysis.

Phase/constituents	Alloy N°	% Cu	% Al	% Ni	% Fe	Others
α	1	76,6 \pm 0.3	18,7 \pm 0.4	4,7 \pm 0.3	-	-
	2, 3	75.7 \pm 1.0	18.6 \pm 0.4	4.2 \pm 0.2	0 – 3.5	-
	4	71.0 \pm 1.2	24.2 \pm 1.6	3.2 \pm 0.3	1.6 \pm 0.3	-
Eutectic	1	67,9 \pm 0.2	24,3 \pm 0.1	7.8 \pm 0.1	-	-
	2, 3	67.0 \pm 2.8	24.5 \pm 3.1	6.5 \pm 1.2	0.8 – 3.5	-
	4	70.3 \pm 2.1	22.4 \pm 0.9	4.2 \pm 0.5	3.1 \pm 0.8	-
Fe rich precipitates	2, 3	22,6 \pm 3.1	36,4 \pm 1.4	19,2 \pm 1.1	21,8 \pm 2.2	-
	4	13.3 \pm 0.6	33.0 \pm 1.1	12.9 \pm 0.8	40.8 \pm 1.9	-
	5 – type I	8.7 \pm 1.0	5.8 \pm 0.4	2.8 \pm 0.4	71.6 \pm 3.6	Mn:4.5; Si:0.7
	5 – type II	23.8 \pm 7.7	15.7 \pm 1.0	11.6 \pm 0.9	45.1 \pm 8.7	Mn:2.4; Si:0.7

4. Conclusions

The addition of iron, up to ~6 %, to the Cu-Al-Ni base alloys modifies the “liquidus” temperatures of the alloys. The final microstructure, of slow cooled alloys, has a finer grain size, when iron content is increasing. The iron present in the alloy is essentially present in a phase formed at the end of cooling, for contents up to ~4%. For higher contents, iron has a nucleation effect in the quaternary alloys. Hence it seems that iron behaviour, as a nucleation agent is dependent on its content in the alloy. The addition of other elements, like manganese and silicon, also modifies the chemical composition and the morphology of the iron rich precipitates.

5. References

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Acknowledgements

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