

# The Effect of Alloying Elements on the Properties of Copper-Aluminium-Nickel-Iron Quaternary Cast Alloys\*

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The effect of adding additional elements such as manganese, silicon, zinc, tin, lead, beryllium, phosphorus, magnesium, cobalt, titanium, boron and chromium to the copper-aluminium-nickel-iron quaternary alloys on the microstructure and the mechanical properties have been investigated. From the results it was found that the effects of adding the above mentioned elements are classified into the following three groups from their behaviors:

(a) The elements that dissolve in the  $\alpha$  solid solution and, when exceeding the solubility limit, cause the alloy to precipitate the  $(\alpha + \delta)$  eutectoid and increase the brittleness. Tin, beryllium, silicon, manganese and zinc are in this group, of which tin, beryllium and silicon produce a detrimental effect.

(b) The elements that produce hard spots or deteriorate the castability. Lead, chromium, boron, phosphorus and magnesium are in this group.

(c) No effect was observed when cobalt was added, which was considered to have an effect as a precipitation hardening constituent, perhaps owing to the small amount added.

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## 1. Introduction

The investigation of the microstructures and the mechanical properties of copper-aluminium-nickel-iron quaternary alloys have been described in the author's previous reports. The copper-aluminium-nickel-iron quaternary alloys have proved the possibility of being used for propellers as they become precipitation hardening alloys when the proper amounts of nickel and iron are added and the mode of the  $\kappa$  phase precipitation is considered to be an influencing factor on the microstructures and the mechanical properties of the alloys.

Although the copper-aluminium-nickel-iron quaternary alloys have quite excellent properties by themselves, it will be necessary to observe the variation of the mode of the  $\kappa$  phase precipitation by adding other elements. At the same time, it will be important to know of the precipitation hardening of the alloying element itself as well as the change of the mechanical properties by dissolving in the  $\alpha$  matrix.

This may be a significant work, not only from the standpoint of improving the properties of copper-aluminium-nickel-iron quaternary alloys but also for determining the impurities and their allowable content.

## 2. Specimens and Experimental Procedure

The effect on the microstructures and the mechanical properties have been investigated by adding manganese, silicon, zinc, tin, lead, beryllium, phosphorus, magnesium, cobalt, titanium, boron and chromium to the base alloy containing 9.75% of

aluminium, 4.7% of nickel and 5.3% of iron. The microscopic analysis and the mechanical tests were made using the same procedure as in the author's previous reports.

## 3. Experimental Results and Discussion

### (1) The effect of manganese

Most of the aluminium bronzes generally have added about 1% of manganese. The reason is not so clearly known but it is said to be added as a deoxidizer at the time of melting before charging aluminium, or for the purpose of improving castability. It is also expected that the addition of small amounts of manganese may increase the strength of the  $\alpha$  matrix by dissolving in the  $\alpha$  solid solution.

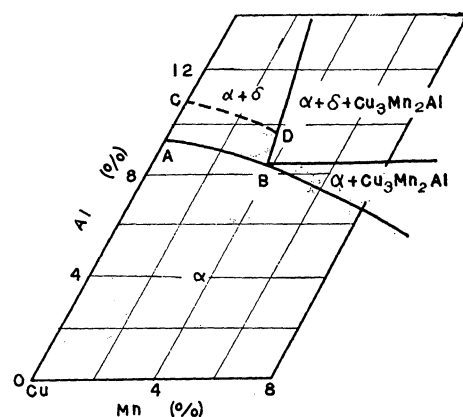


Fig. 1 The equilibrium diagram of a Cu-Al-Mn ternary alloy. CD represents the probable solubility limit line in 4.7/5.3 alloy.

The phase diagram of a copper-aluminium-manganese ternary alloy<sup>(1)</sup> is shown in Fig. 1. In this

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(1) D. R. F. West, D. L. Thomas: J. Inst. Metals, 85 (1956-57), 97.

diagram, the gradient of the solubility limit curve  $\overline{AB}$  within the range of practical composition is a matter of question. In the alloy containing 5% each of nickel and iron, the curve  $\overline{AB}$  shifts upwards in extending the domain of the  $\alpha$  phase. However, it seems to decline to the lower right side and reduce the  $\alpha$  domain as the manganese content is increased. This shows that the addition of manganese has a limit in the quantity against the content of aluminium of the base alloy even from the metallographical point of view. As for the microstructure, no change is observed by adding manganese up to 1%, while, with more content, it reduces the  $\alpha$  grain size and with 3.92%, remains considerably large amount of  $\beta$  phase (this decomposes into  $(\alpha + \delta)$  eutectoid) as shown in Fig. 2. Not much change is observed in the form of the  $\kappa$  phase precipitates.

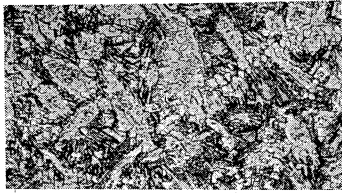


Fig. 2 3.92% Mn addition,  $\alpha$  + partially decomposed  $\beta + \kappa$ .  $\times 300$

As the mechanical properties are shown in Fig. 3, increase of hardness and decrease of elongation occurs as manganese dissolves more in the  $\alpha$  solid solution, and then the elongation is remarkably decreased by

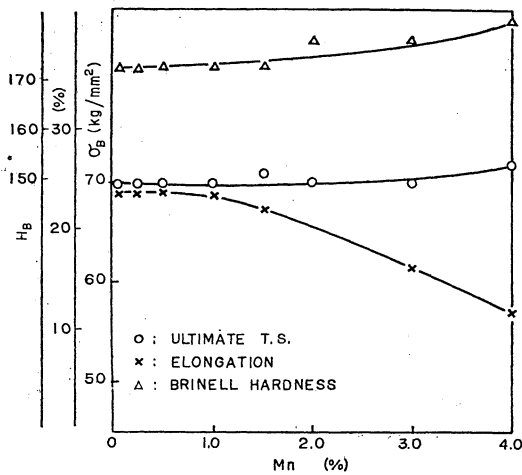


Fig. 3 The effect of Mn addition. (rate of cooling, 5°C/min.)

the precipitation of the eutectoid.

From the above results, it is concluded that the significance of adding manganese to the aluminium bronze can not be considered concerning the structure or the mechanical properties but on the melting or casting.

(2) The effect of silicon

In aluminium bronze, silicon may get mixed from crude aluminium and iron or from the refractory brick of the melting furnace. The diagram of the copper-aluminium-silicon ternary alloy is shown in

Fig. 4.<sup>(2)</sup> As shown in Fig. 4, the gradient of the  $(\alpha/\alpha + \delta)$  solubility limit curve is steeper compared with that of the copper-aluminium-manganese alloy, and it is apprehended that the eutectoid may be precipitated even with the addition of a small amount of silicon. As shown in Fig. 5, the precipitation

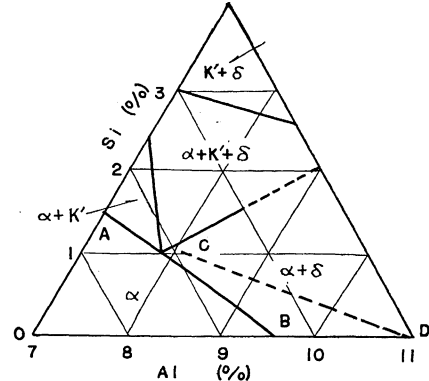


Fig. 4 The equilibrium diagram of a Cu-Al-Si ternary alloy.  $\overline{CD}$  represents the probable solubility limit line in 4.7/5.3 alloy.



Fig. 5 0.37% Si addition,  $\alpha$  + partially decomposed  $\beta + \kappa$   $\times 300$

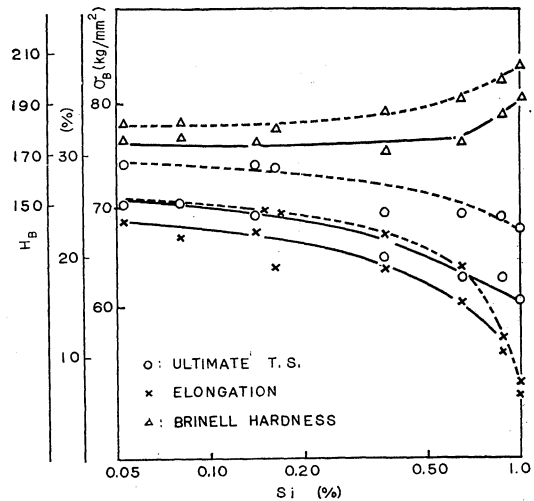


Fig. 6 The effect of Si addition. Key to Fig. 4~Fig. 9  
 — rate of cooling, 5°C/min.  
 - - - rate of cooling, 24°C/min.

of the eutectoid is already observed in the specimens with 0.37% of silicon added, and adding of silicon also changes the precipitation of  $\kappa$  phase to the lamellar form from about 0.15%. As the change of the mechanical properties is shown in Fig. 6, the addition of silicon increases the hardness and decreases both the tensile strength and the elongation, this effect becoming more remarkable as the silicon content exceeds 0.15%. These behaviours are considered to be influenced by the precipitation of the

(2) F. H. Wilson: AIME, T. P. No. 2349 (1948).

eutectoid as well as the lamellar precipitation of the  $\kappa$  phase.

(3) The effect of zinc, tin or lead

As for the source of zinc, tin or lead getting mixed in aluminium bronze, using scrap or melting in

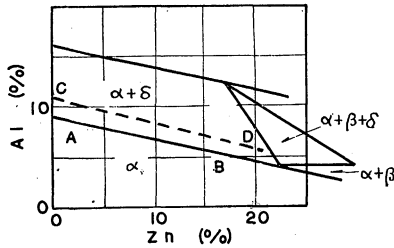


Fig. 7 The equilibrium diagram of a Cu-Al-Zn ternary alloy. CD represents the probable solubility limit line in 4.7/5.3 alloy.

a furnace together with other copper alloys can be considered. The phase diagram of the copper-aluminium-zinc ternary alloy is shown in Fig. 7.<sup>(3)</sup> The gradient of the  $(\alpha/\alpha+\delta)$  solubility limit curve by the addition of zinc is very smooth and the precautions for precipitation of the eutectoid, as understood in the case of silicon or manganese, is not necessary if small amounts of zinc are added. On the other hand, adding of tin seems to reduce remarkably the  $\alpha$  domain and precipitate the eutectoid even with a small content. It can not be said definitely owing to the lack of fundamental data concerning the copper-aluminium-tin alloy, however the precipitation of the eutectoid is observed in 9.7/4.7/5.3 alloy with 0.3% content of tin, as shown in Fig. 8.

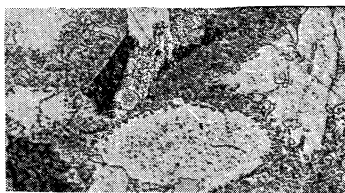


Fig. 8 0.3% Sn addition  $\alpha$ +partially decomposed  $\beta+\kappa$   $\times 300$

Adding of lead, although indefinite, too, may have a larger influence by acting as an oxide inclusion or producing heavy complex oxide with other  $Al_2O_3$  or  $SiO_2$  rather than giving influence on the microstructures.<sup>(4)</sup> The type of  $\kappa$  phase precipitates receives no change by the addition of zinc or lead, but that of tin gets the precipitation density of  $\kappa$  to differ on each of  $\alpha$  crystal grains. Variation of the mechanical properties by adding of zinc, tin and lead is shown in Fig. 9, 10 and 11 respectively. Both the tensile strength and elongation decrease when zinc is added with this tendency getting more remarkable when exceeding 0.1% of the content. Tin also decreases elongation remarkably in casting under the rate of less than 5°C/min, although the effect at rapid

cooling is not clear. As for lead, the properties obtained show scattered values and then it is hard to be known its effect.

(4) The effect of beryllium

Although it is least probable that beryllium gets

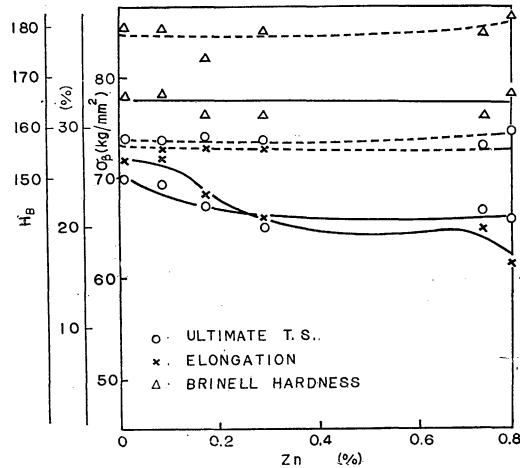


Fig. 9 The effect of Zn addition.

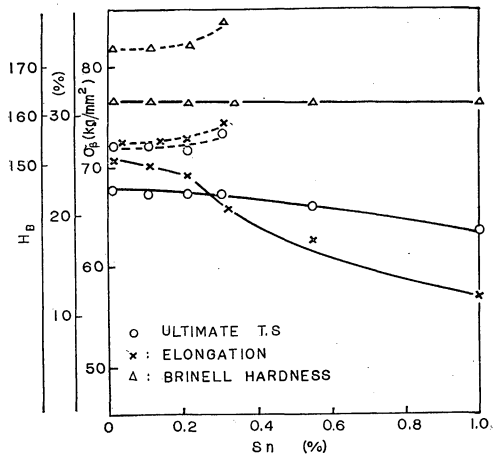


Fig. 10 The effect of Sn addition.

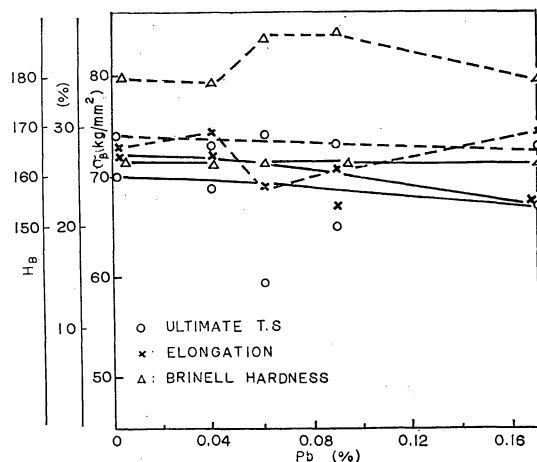


Fig. 11 The effect of Pb addition.

mixed in aluminium bronze, the effect of the small solubility of beryllium to  $\alpha$  solid solution for the complex aluminium bronze is studied. As shown in the microstructure in Fig. 12, precipitation of the eutectoid occurs in addition of 0.21% of beryllium.

(3) O. Bauer, M. Hansen: Z. Metallk., 24 (1932), 73.  
 (4) A. R. French: J. Inst. Metals, 85 (1956-57), 293.

As for the mechanical properties, addition up to about 0.2% increases both the hardness and the tensile strength, while the addition of larger amounts than the point where precipitation of the eutectoid occurs decreases the tensile strength as shown in Fig. 13.

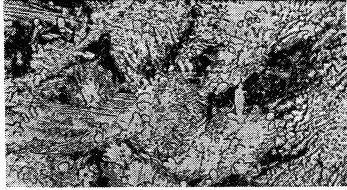


Fig. 12 0.34% Be addition  $\alpha$  + partially decomposed  $\beta + \kappa$   $\times 300$

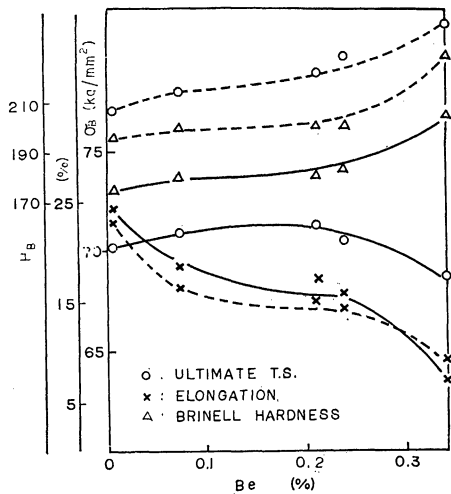


Fig. 13 The effect of Be addition.

(5) The effect of other alloying elements

In addition to the above-mentioned elements, the effect of adding phosphorus, magnesium, which are sometimes charged as a deoxidizer at the time of melting, boron, titanium, which are considered to reduce the grain size, and cobalt, chromium as a precipitation hardening constituent were studied.

The effect of phosphorus and magnesium is not certain as the results are uneven, however no effect is observed on either the structures and the mechanical properties up to 0.02% of phosphorus, while addition of about 0.1% spheroidizes and makes the  $\kappa$  phase coarser as shown in Fig. 14 and seems to deteriorate the mechanical properties like

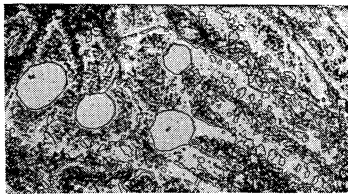


Fig. 14 0.2% P addition  $\alpha + \kappa$ .  $\times 300$

magnesium does.

Boron and chromium tend to produce hard spots,<sup>(5)</sup> and deteriorate the castability. As for titanium

and cobalt, their effect was investigated with the contents up to 0.03% and 0.4% respectively. However, no remarkable change was observed neither on the structures nor on the mechanical properties.

(6) The effect of carbon or hydrogen

Carbon gets mixed mainly at the time of melting in a crucible type furnace or from steel or cast iron as an alloying element, and it tends to produce hard spots when melting copper alloys containing appreciable amounts of iron. The typical forms are shown in Fig. 15.

The oxygen solubility of the melt of aluminium bronze, owing to its large content of aluminium, is

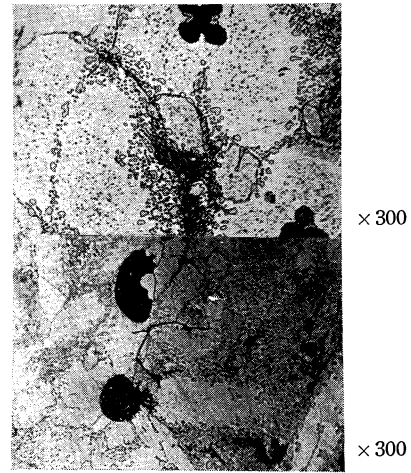
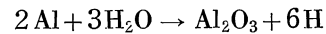


Fig. 15 The micro-type of hard spots in 4.7/5.3 alloys.  $\times 300$

very small, and then it may absorb much hydrogen, perhaps in the following reaction with the vapour in the furnace atmosphere:



The mechanical properties, especially the elongation,

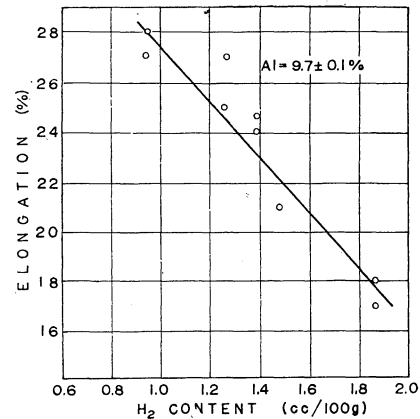


Fig. 16 The influence of hydrogen content on the elongation of 4.7/5.3 alloys. (rate of cooling, 5°C/min.)

become inferior, if hydrogen is present. No serious influence is observed if it is in a type of supersaturated solution, however whereas the porosities take place by resolving into molecularly at the time of solidification, a serious influence has been observed. The relationship between hydrogen content and

(5) Counsel: Metal Ind., 90 (1957), 130.

(6) *ibid*, 91 (1957), 10.

elongation is shown in Fig. 16.

The influence appears at 1.2 cc/100 g of the hydrogen content when solidified at the rate of less than 5°C/min, while no deterioration of the mechanical properties is observed up to about 2.0 cc/100 g of the content when cooled at the rate of 24°C/min.

#### 4. Summary

The effect of adding various elements to the copper-aluminium-nickel-iron quaternary alloys have been investigated. The effects of alloying are classified into the following three groups from their behaviours:

(1) The elements that dissolve in the  $\alpha$  phase and,

effect.

(2) The elements that produce the hard spots or deteriorate the castability. Lead, chromium, boron, phosphorus and magnesium are in this group.

(3) No effect was observed when cobalt was added, which was considered to have an effect as a precipitation hardening constituent, probably because of the small amount added.

Summarized effect on the mechanical properties by adding, up to about 1% of content, the elements of group (a) is shown in Fig. 17. As shown here, addition of these elements to 9.7/4.7/5.3 alloy generally decreases strength even when they dissolve in the  $\alpha$  solid solution. None of them improves the

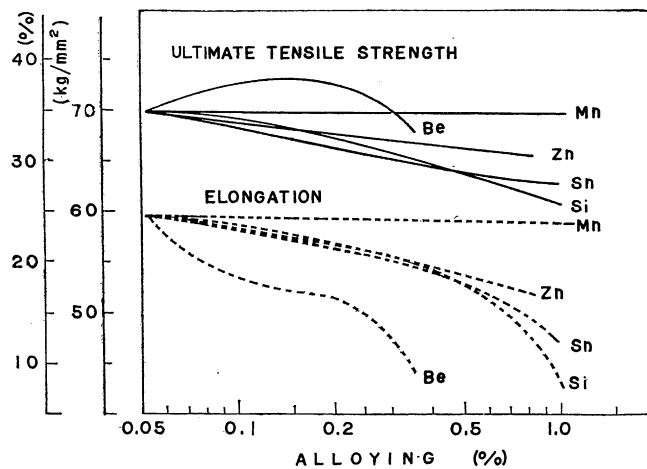


Fig. 17 The comparison between the effects of the alloying element up to 1% on the tensile properties of 9.75/4.7/5.3 alloys.

when exceeding the solubility limit, cause the alloy to precipitate the  $(\alpha + \delta)$  eutectoid. Tin, beryllium, silicon, manganese and zinc are in this group, of which tin, beryllium and silicon produce a detrimental

form of  $\kappa$  phase precipitates. It is concluded, therefore, that these elements are nothing but impurity elements in copper-aluminium-nickel-iron quaternary cast alloys.