The Critical Cooling Rates Determined by the Jominy Tests in the Age-Hardening Cu-Cr, Cu-Be and Cu-Co₂Si Alloys*

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The Cu-0.7% Cr alloy, the Cu-2.5% Be-0.3% Co alloy, and the Cu-4% Co₂Si alloy were used with the object of studying the critical cooling rate (CCR) for the solution treatment of an age hardening copper base alloy. The author introduced an idea of the critical cooling rate, defining it as the cooling rate necessary to obtain a supersaturated solid solution at room temperature. In this paper the critical cooling rate of each alloy was determined by Jominy end quenching methods using a specimen of 25 mm diameter and 100 mm length. The CCR obtained was 17°C/sec at 925°C for the Cu-Cr alloy, 60°C/sec at 500°C for the Cu-Be alloy, and 20°C/sec at 940°C for the Cu-Co₂Si alloy.

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I. Introduction

In an age-hardening copper base alloy subjected to solution treatment at a slow cooling rate, a super-saturated solid solution cannot be obtained at room temperature, and its age hardenability deteriorates considerably. So far as we know no systematic research or general explanation seems to have been established for the effect of cooling rate in the solution treatment for the age-hardening copper base alloys^{(1)~(3)}. The cooling rates in the solution treatments have not been the subject of prior research, because thin wire or plate specimens so far used have a large ratio of surface area to volume, namely a small mass effect. The industrial application of the massive age-hardening copper base alloys has been limited. Generally in the case of copper base alloys the cooling rates are relatively large due to their high thermal conductivities; therefore, a certain extent of the cooling effect is also exhibited even in the thick products. Concerning this subject the author has defined the critical cooling rate as the minimum cooling rate sufficient to obtain a supersaturated solid solution at room temperature.

Studies of age hardenability of Cu-Cr alloys were made by Köster⁽⁴⁾ in 1954. After the aging treatment the Brinell hardness of a Cu-0.6% Cr alloy varied according to the cooling rate from the solution treatment temperature. As the cooling rate decreased in the order of water quench, oil quench, and air cool, the hardness after the aging treatment became small. From these data the existence of a critical cooling rate necessary to obtain the supersaturated solid solution at room temperature was suggested. However, the expression for the cooling rate was not quantitative but qualitative. According to Newkirk⁽¹⁾ a Cu-Cr alloy which was cooled rapidly

from the solution treatment temperature had a lower hardness value than that which was cooled slowly, and the rapidly cooled alloy showed a higher hardness value after aging treatments. He did not make any quantitative investigation on the cooling rate in solution treatment. To our best knowledge a critical cooling rate in the Cu-Cr alloy system has not been determined previously.

Geisler⁽²⁾ investigated the effects of the cooling rate in solution treatment on the age hardenability in wire specimens of a Cu-1.3% Be alloy. After solution treatments the water-quenched specimens exhibited a higher hardness than the air cooled ones. In the water-quenched specimen the aging time necessary to reach a half of the ultimate hardness took a longer time than in the air-cooled specimens. However, the ultimate hardness after the aging treatments was the same in the case of both water quenching and air cooling. It was concluded that a completely supersaturated solid solution was formed even by air cooling, because thin wire were used in these experiments. The plastic strain which was induced by water quenching was determined as the cause for the acceleration of the aging time. The critical cooling rate for obtaining the supersaturated solid solution was not investigated in Cu-Be alloys.

No research appears to have been done for determining the critical cooling rate in the Cu-Co₂Si alloy system.

One of the experimental methods for determining the critical cooling rate of the age-hardening copper base alloys was the Jominy end quenching method. A rare paper which dealt with the Jominy method for a nonferrous alloy was reported by Bryant⁽⁵⁾. He studied the effects of the cooling rate in the solution treatment on the age-hardening characteristics for a high-strength aluminum alloy (Al-6% Zn-3% Mg-1% Cu-0.2% Cr) using Jominy end quench specimens of one inch diameter and eleven inch length.

In the experiments for determining the critical cooling rates on the age hardening copper base alloys the following three type specimens were used, i.e., Cu-Cr, Cu-Be, and Cu-Co₂Si alloys.

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(1) R. F. Mehl : *Precipitation from Solid Solution*, ASM, (1959), p. 121.

(2) A. H. Geisler : *Phase Transformation at Interface*, ASM, (1952), p. 269.

(3) G. Bunge, E. R. Honak und W. Nielsch : *Z. Metallk.*, 44 (1953), 71.

(4) W. Köster und W. Knorr : *Z. Metallk.*, 45 (1954), 350.

(5) A. J. Bryant : *J. Inst. Metals*, 90 (1961~62), 406.

II. Experimental Methods

The following three types of alloys were used as the specimens: (a) An alloy of simple precipitation. This alloy type shows a simple precipitation process, and a solute metal precipitates from the super-saturated solid solution in the shape of a monomer⁽⁶⁾, i.e., the Cu-Cr alloy. (b) An alloy of transient precipitation. This alloy type shows a complicated precipitation process, and it passes through a transient state during the precipitation, i.e., the Cu-Be alloy⁽⁷⁾. (c) An alloy which precipitates an intermetallic compound. Although the details of this precipitation type are not yet clarified, a precipitate shows an intermetallic compound after full aging treatment, i.e., the Cu-Co₂Si alloys⁽⁸⁾.

The preparations of specimens were follows: The ingots of the Cu-Cr and Cu-Co₂Si alloys were made by air-melting, and those of the Cu-Be by vacuum-melting. These ingots were tap forged into bars of 35 mm diameter at 500°~800°C, and the Jominy specimens of 25 mm diameter and 100 mm length were machined from the bars. The chemical compositions of each type of the specimens were Cu-0.68% Cr, Cu-2.46% Be-0.3% Co, and Cu-4% Co₂Si respectively, and the data of chemical analysis are shown in Table 1.

Table 1 Chemical compositions

Alloy	Chemical composition (wt%)					
	Cu	Cr	Be	Co	Si	Fe
Cu-Cr	99.27	0.68	—	—	0.01	0.02
Cu-Be	97.22	—	2.46	0.27	0.01	0.03
Cu-Co ₂ Si	96.01	—	—	3.21*	0.76*	0.02

(* Co₂Si 4 wt%)

Although a Jominy test on a nonferrous alloy was not common, the experiment was performed in conformity with the testing method which was designated for iron and steel by ASTM. The specimen was 25 mm in diameter and 100 mm in length. In the Jominy test the solution treatment were held for one hour each at 950°, 1000° and 1050°C for the Cu-Cr alloy, 750° and 800°C for the Cu-Be alloy, and 1000°C for the Cu-Co₂Si alloy. The atmospheres of the solution treatment were hydrogen (dew point -30°C) for the Cu-Cr alloy, and argon for the Cu-Be and Cu-Co₂Si alloys. The specimen which was held at its solution treating temperature was taken from the furnace and end-quenched within three seconds by a water jet with a free-height pressure of 65 mm and at 24°C. Thus, the specimens were made in which the cooling rates varied continuously from the quenched-end to the opposite side. The surface of the specimen was planed parallel to its axis by removal of 4~6 mm of metal. The Vickers hardness (load 5 kg) was measured at intervals of 2.5 mm from the quenched-end, and the relation between the hardness and the distance from the

quenched-end immediately after solution treatment was determined. After the end-quenched specimen was subjected to the aging-treatment the Vickers hardness was measured repeatedly. The aging conditions were as follows: (a) The Cu-Cr alloy; for 10~180 min at 450°~525°C, (b) The Cu-Be alloy; for 20~1000 min at 300°~350°C, and (c) The Cu-Co₂Si alloy; for 10~240 min at 450°~550°C.

In the Jominy test piece holes of 3 mm diameter and 6 mm depth were drilled at distances of 2.5, 5, 10, 30, 50 and 80 mm from the quenched-end. The cooling rates were measured with a pen-recording type oscilloscope.

III. Experimental Results

The results of the Jominy tests on the Cu-0.6% Cr alloy are shown in Fig. 1 and Fig. 2. The cooling rates of the Jominy test pieces are shown in Fig. 3. The critical cooling rate of the Cu-Cr alloy is shown in Fig. 4. In Fig. 4 the abscissa is the cooling rate of the Jominy specimens at 925°C and the ordinate is the Vickers hardness which corresponded to the cooling rate of the abscissa. The mass effect of Cu-Cr alloy in the solution treatment is shown in Fig. 5. Fig. 5 demonstrates the relation between the cooling rate at the nose temperature

Fig. 1 Jominy tests on the Cu-Cr alloy

(6) W. Gruhl und R. Fischer: Z. Metallk., 46 (1955), 742.

(7) C. S. Barrett: *Structure of Metals*, McGraw Hill, (1954), p. 540.

(8) T. Toda and H. Takeuchi: J. Japan Inst. Metals, 26 (1962), 570.

Fig. 2 Jominy tests on the Cu-Cr alloy

Fig. 3 Cooling rates of the Jominy specimens in the Cu-Cr alloy

(925°C) of the C curves and the distance from the water quenched edge of the Jominy specimen.

The results of the Jominy tests on the Cu-2.4% Be-0.27% Co alloy are shown in Fig. 6. The cooling rates of the Jominy test pieces of the Cu-Be-Co alloy are shown in Fig. 7. The critical cooling rate of the Cu-Be alloy

Fig. 4 The critical cooling rate determination by the Jominy tests in the Cu-Cr alloy (* nose temperature of C curve)

Fig. 5 The mass effect on the solution treatment in the Cu-Cr alloy (*at 925°C, nose temperature of C curve)

is determined by the same procedures as for the Cu-Cr alloy, and the result is shown in Fig. 8. The mass effect of the Cu-Be alloy in the solution treatment is shown in Fig. 9.

The results of the Jominy test on the Cu-4% Co₂Si alloy are shown in Fig. 10. The cooling rates of the Jominy specimens, the critical cooling rate, and the mass effect are shown in Fig. 11, Fig. 12 and Fig. 13 respectively.

IV. Discussion

1. The Cu-Cr alloy

From Fig. 4 on the critical cooling rate of the Cu-Cr alloy, the following conclusions can be drawn. The cooling rates (dx/dt , x : temperature, t : time) of the Jominy test specimen are not definite as seen in Fig. 3. On the other hand, from the result of the isothermal heat treatment⁽⁹⁾ the nose temperature of the Cu-Cr alloy is at 925°C, and it has been determined that the cooling rate at 925°C dominates the formation of the super-saturated solid solution in the Cu-Cr alloy. Therefore, the

(9) T. Toda: Trans. JIM, 11 (1970), 30.

Fig. 6 Jominy tests on the Cu-Be alloy

Fig. 7 Cooling rates of the Jominy specimens in the Cu-Be alloy

Fig. 8 The critical cooling rate determination the Jominy tests in the Cu-Be alloy (* nose temperature of C curve)

Fig. 9 The mass effect on the solution treatment in the Cu-Be alloy (* at 500°C, nose temperature of lower C curve)

cooling rate (dx/dt) at the nose temperature of 925°C is used.

The solid solubility of the chromium in the copper⁽¹⁰⁾ is 0.6% at 1050°C, 0.26% at 950°C, 0.17% at 900°C, and the change of the solubility is very sharp between 900° and 1050°C. The maximum hardness after the aging treatment is proportional to the solubility of the chromium in the copper, because the hardness changes according to the solution treating temperature, i.e.,

1050°C: Hv 168, 1000°C: Hv 148, and 950°C: Hv 131. Although the maximum hardness after the aging treatment changes according to the solution treating temperature, if the cooling rate in the solution treatment at 925°C is more than 17°C/sec, the maximum hardness is constant for each solution treatment temperature. Therefore, we conclude that the critical cooling rate of the Cu-Cr alloy is 17°C/sec at 925°C.

From the relation between the cooling rate and the distance to the quenched end in the Jominy specimen, the mass effect of the Cu-Cr alloy at the solution treatment is clarified as shown in Fig. 5. Within a distance of 15 mm from the quenched end, the cooling rate is more than 17°C/sec at 925°C, the chromium dissolves completely and a supersaturated solid solution is obtained at room temperature. As shown in Figs. 1 and 2, the hardness after the aging treatment is Hv 170 when the distance is less than 15 mm. The maximum hardness is not obtained when the distance is more than 15 mm, because some amount of the chromium precipitates from the

(10) M. Hansen : *Constitution of Binary Alloys*, (1958), p. 524.

Fig. 10 Jominy tests on the Cu-Co₂Si alloy Fig. 11 Cooling rates of the Jominy specimens in the Cu-Co₂Si alloy Fig. 12 The critical cooling rate determination the Jominy tests in the Cu-Co₂Si alloy (* nose temperature of C curve)

copper during the cooling at cooling rates of less than 17°C/sec.

The aging treatment which shows a maximum hardness is one of the following combinations; 1 hr at 500°C, 2~3 hr at 475°C, and more than 3 hr at 450°C. From the above results we conclude that the aging treatment for 1~2 hr at 475°C~500°C is most suitable for the massive Cu-Cr alloy.

If the solution treatment temperature is either at 1000°C (Fig. 2) or at 950°C (Fig. 2), the age-hardening deteriorates due to the decrease of the solubility of the

Fig. 13 The mass effect on the solution treatment in the Cu-Co₂Si alloy (* at 940°C, nose temperature of C curve)

chromium in the copper. For example, after aging treatment for 1 hr at 500°C the hardness values of Hv 145 and Hv 125 are obtained for the solution treatment temperatures of 1000° and 950°C, respectively.

2. The Cu-Be alloy

In order to determine the critical cooling rate of the Cu-Be alloy, Figs. 6 and 7 are used and the same method as in the Cu-Cr alloy is applied. The critical cooling rate is measured at the nose temperature (500°C) of the lower C curve as shown in Figs. 8 and 9. The hardness of the age-hardened Jominy specimen shows its maximum when the cooling rate is more than 60°C/sec (Fig. 8) or when the distance from the quenched end is less than 5 mm (Fig. 9). From these experimental results it is concluded that the Cu-Be alloy must be quenched to room temperature with a cooling rate of more than 60°C/sec at

500°C to obtain a supersaturated solid solution.

3. Cu-Co₂Si alloy

According to the experimental results of the Cu-Co₂Si alloy in Fig. 10 to Fig. 13, the solid solution must be quenched to room temperature with a cooling rate of more than 20°C/sec at the nose temperature 940°C, or when the distance from the quenched end is less than 10 mm to obtain a supersaturated solid solution. In the case of the as-quenched Cu-Co₂Si alloy the quenched end (or supersaturated solid solution part) of the specimen shows a higher hardness than the partial alloy precipitated part of the other end. This phenomenon of the Cu-Co₂Si alloy is different from the Cu-Cr and Cu-Be alloys, and the reason for the hardening of the fast-cooled end is not clarified yet.

V. Summary

(1) Three kinds of the copper base alloys were used as the specimens; the Cu-0.7% Cr alloy of the simple precipitation type, the Cu-2.5% Be-0.3% Co alloy of the transient precipitation type, and the Cu-4% Co₂Si alloy with an intermetallic compound precipitation.

(2) The Jominy end quenching methods were applied to determine the critical cooling rates. The critical cooling rate was defined as the cooling rate necessary to obtain a supersaturated solid solution at room temperature.

(3) The critical cooling rate derived from the relation between the maximum age-hardenability and the cooling rate in the Jominy specimen.

The critical cooling rate of the Cu-Cr alloy was 17°C/sec at 925°C. This rate was obtained within a distance of 15 mm from the quenched end. In the Cu-Be alloy the critical cooling rate was 60°C/sec at 500°C, and it was satisfied within 5 mm from the quenching end. In the Cu-Co₂Si alloy the critical cooling rate was 20°C/sec at 940°C and the distance was 10 mm.

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