INITIAL AGING PHENOMENA IN COPPER–CHROMIUM ALLOYS

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**Translation from Nippon Kinzoku Gakkaishi, Vol. 37, No. 1, 1973, pp. 13-18:**

**Abstract:** The effects of quenching and aging temperatures on the initial aging curves of Cu-Cr alloy were examined mainly by means of electrical resistivity measurements. Three Cu-Cr alloy specimens having 0.24, 0.74, and 1.0% Cr were solution-treated at 950-1050°C, quenched into ice-water, and subsequently aged at 300-500°C. The results were as follows: (1) At the very early stage of aging (within about 30 sec), an abrupt decrease of resistivity with lowering aging temperatures (T_A) and rising solution temperatures (T_S) was observed at T_A up to about 400°C. In contrast, a transient increase of resistivity with rising T_A and lowering T_S was observed at T_A from about 450 to 500°C. These phenomena seem to be caused by a rapid formation of solute clusters and the reversion of clusters formed during quenching, which are enhanced by quenched-in vacancies, respectively. (2) The amount of precipitation increased at the latter stage of aging with rising T_S and T_A as generally expected, where T_S was not so high as to form secondary defects. (3) As a result, the initial aging phenomena in Cr-Cr alloy were revealed to be complicated against expectations. This was considered to be due to the migration energy of vacancies so larger in Cu-base.
16. Abstract (cont'd)

alloys than that in Al-base alloys, that the clustering or reversion phenomena at the initial stage of aging could be detected.
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Hisashi Suzuki and Motohiro Kanno

I. INTRODUCTION

Recently the post-aging nature of Cu-Cr alloys [1-3], their aging process [4-6], reversion phenomenon [7-8], structure of aging [9], T-T-T curve, etc. [10,11] have become subjects of investigation, and the behavior of this alloy has become fairly clear. Knowledge concerning its initial aging, however, remains incomplete. There are many studies of this type dealing with alloys of aluminum, etc. For example, there has been much discussion of the role of the point defect [12,13], but this has not necessarily been the case with copper alloys. A report on the aging process of Cu-Be alloy at 70-200°C represents the extent of what has been done [14,15]. Accordingly, a study focusing on the relation between heat treatment conditions and the initial aging phenomena for this alloy, based on detailed measurement of relative resistivity, will be presented here.

II. TEST MATERIALS AND EXPERIMENTAL METHODOLOGY

Specimens consisted of three kinds of alloy, Cu-0.24 wt% Cr, Cu-0.74 wt%, and Cu-1.0 wt% Cr, which were made by the method

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* Numbers in the margin indicate pagination in the foreign text.
previously described [8,9] and then cold-extended into a plate 0.5-mm thick. Measurement of relative resistivity consisted of putting the 0.5 x 10 x 170 mm specimen in a stream of argon gas (950°-1050°C) for an hour, then quenching it with ice water, aging it by taking it through the 300-500°C range, then measuring it at 20°C, and repeatedly aging, quenching and measuring it. Aging time was three hours†, but since after about an hour there were no significantly large changes in the position of the aging curve, only the comparison for the first 100 minutes is shown for the sake of convenience. The initial aging curve for the first 5 minutes is given especially detailed attention.

In this study, aging at temperatures below 300°C was not carried out, since at low temperatures like 250°C changes in resistivity are so slight as to be almost unmeasurable.

III. RESULTS

Figure 1 shows the aging curve for Cu-0.24% Cr alloy at solution temperature (T_s) of 950°C. Figure 2 shows the initial part of Figure 1. It shows that the changes in the initial aging curve were more complex than anticipated: (1) When the aging temperature (T_A) was below 400°C, in the very first stage, there was a marked drop in resistivity (ρ) of a maximum of 0.1μΩ cm. The extent of this reduction increased with the lowness of the aging temperature. After the sudden drop of ρ, the change in relative resistivity slowed. (2) When T_A = 450-500°C, the opposite of (1), that is, an increase in ρ, was seen, and the increase was greatest around 500°C with a decrease beginning

† The aging curve is the resistivity-change/time curve. Here the value found just after quenching is used as the standard for resistivity.
Fig. 1. Changes in electric resistivity during isothermal aging of Cu-0.24%Cr alloy. Specimen was solution treated at 950°C, water quenched and subsequently aged at indicated temperatures.

within a relatively short period of time. When aging is carried out, beyond the initial changes, the higher the aging temperature, the more rapid the decline in ρ, as shown in Figure 1.

Figure 3 and Figure 4 show the aging curve for the same alloy, Cu-0.24% Cr when $T_s = 1000°C$ and $1050°C$. Compared with $T_s = 950°C$ in Figure 1, the general tendency of the curve as a whole is about the same, though the longer term changes in $\rho$ are greater. For aging temperatures of $400°C$ and $450°C$, the long-term decrease in $\rho$ was somewhat greater for $T_s$ at $1000°C$.
than for 1050°C. Furthermore, at 300°C and 350°C, the time within which the aging curve reversed was shorter as \( T_s \) became higher.

Fig. 3 Changes in electric resistivity during isothermal aging of Cu-0.24%Cr alloy, solution-treated at 1000°C, quenched and aged at indicated temperatures.

Fig. 4 Changes in electric resistivity during isothermal aging of Cu-0.24%Cr alloy, solution-treated at 1050°C, quenched and aged at indicated temperatures.

Figure 5 is a summary of the effects of \( T_s \) on initial phase aging behavior at \( T_a = 300°C \) and 500°C. According to its representation, the very first stage shows greater declines in resistivity as \( T_s \) becomes higher, though there is no great discrepancy at 1000°C and 1050°C. Next, observing the increase in \( \rho \), it is seen that the respective increases for \( T_s = 1000°C \)
and 950°C are the same, and the increase is of short duration, reversing into a decline within a rather short period of time. No increase is observable at 1050°C. Furthermore, even at a relatively high aging temperature such as 500°C, when the rate of decline in resistivity is observed, the higher \( T_s \) becomes, the greater the rate of decline, and this, at first glance, appears

![Graph showing effects of quenching temperatures on the initial part of aging curves of Cu-0.24%Cr alloy, aged at 300 and 500°C, respectively.](image)

...to be the effect of the vacancies left over from the quenching.

*From observation of Figures 1, 3 and 4 with \( T_A \) of 500°C and time up to about 30 min., such an effect is apparent. However, taking 0.88 eV as the migration energy of the vacancies, at 500°C the diffusion coefficient comes out as approximately \( 10^{-9} \text{cm}^2/\text{sec} \). Now, with \( \sim 10^8 \text{cm}^2 \) as the transposition density, attempting to eliminate excess vacancies through transposition results in an unusually short longevity of several multiples of 10 seconds. Accordingly, the result is that this is not thought to be the direct effect of excess vacancies, but the role these vacancies play in the formation of Cr clusters at the very beginning (30 seconds or less) of the aging process. This point will be subject to revision and later discussion.
The above deals with the results $T_s$ produces in first phase test material, while the alloys Cu-0.74% Cr and Cu-1.0% Cr are the second phase test material. Since the melting point of Cr combined with Cu at a level of 0.26-0.60 wt% is 950-1050°C [3], in this case if $T_s$ was raised, the supersaturation of the melted material at the aging temperature would increase. Figure 6 shows the effects of $T_s$ on the aging curve at $T_A$ at 300°C and 500°C for Cu-1.0% Cr alloy, while Figure 7 shows details of the initial part of this process. A comparison of Figure 7 with Figure 5 (Cu-0.24% Cr alloy) shows that when $T_s = 950°C$ and $T_A = 300°C$, shows a slightly smaller decline during the initial aging stage (under 30 seconds), while at $T_A = 500°C$ the decline in $\rho$ is less within the first five minutes. Since supersaturation is almost the same for both alloys, the lower rate of aging in this case was attributed to the presence of diffused Cr particles, which eliminated surface vacancies which are created mainly during quenching. The phenomenon described above also occurs in Cu-0.74% alloy.

At $T_s = 1000°C$, aging is somewhat faster than for the Cu-0.24% Cr alloy, and at 1050°C, there is a marked acceleration, and the change in $\rho$ is large as well. In these cases, although the elimination of vacancies could be thought of as due to diffused Cr particles which were included in the alloy while it was molten, it is thought, rather, that this result is due to the major role played by the increase in supersaturation as $T_s$ rises. With Cu-0.24 Cr alloy, when $T_s = 950-1000°C$ and $T_A = 400-450°C$, there was a rise in $\rho$ at the initial stages, but for Cu-1.0 Cr alloy, such a rise was observed only at $T_s = 950°C$.

Figure 8 gives a comparison of the aging curves of Cu-0.74% Cr alloy and Cu-1.0% Cr alloy for $T_A = 400°C$. It shows that for each $T_s$ the 1.0% Cr alloy ages slightly more slowly than the 0.74% Cr alloy, and both alloys show a marked acceleration in aging in comparison to the 0.24% Cr when $T_s$ rises, which is as anticipated.
Figure 6. Effects of quenching temperatures on aging curves of Cu-1.0% Cr alloy, aged at 300 and 500°C, respectively.

Figure 7. Effects of quenching temperatures on the initial part of aging curves of Cu-1.0% Cr alloy, aged at 300 and 500°C, respectively.

Figure 8. Effects of quenching temperatures on aging curves of Cu-0.74% Cr and Cu-1.0% Cr alloys, aged at 400°C.
IV. OBSERVATIONS

Results for the above results include: (1) In low temperature aging at 300-400°C, the marked decline in resistivity at the very beginning was more pronounced when $T_s$ was higher, or when $T_s$ was higher and Cr content larger, or when aging temperature was lower. (2) At comparatively high temperatures of 450-500°C during the very first stages of aging, there was a temporary increase in resistivity, which was greater as $T_A$ was higher. Moreover, as $T_A$ was higher, the shorter the time within which maximum value for resistivity appeared and the more quickly it disappeared. This tendency was strong in the alloys with high Cr content. (3) After the complex changes in the initial stages, when aging time reached 0.5-1.5 hr., the amount of aging (amount of decline in resistivity) was generally larger in proportion to the elevation of $T_A$, forming aging curves which appeared normal. (4) The effects of $T_s$ on the amount of aging were stronger in high-chromium alloys. These were the main findings, and among them (1) and (2) were considered to be of special interest. Accordingly, they will be focused upon in the discussion of observations below.

First, concerning (1), the phenomenon of resistivity decline in the initial stage of aging also occurs with Al-In alloys [16,17], the reason being ascribed to the matching of solute atoms and vacancies. The same observation can be seen in the article [5] concerning Cu-Cr alloys by Nishikawa et al. However, calculations for this case lead to the conclusion that the matching of vacancies and solute atoms is not the main cause of decline in resistivity*. This alloy has no G.P. [expansion

* With vacancy formation energy of 1.17 eV [18], at 950-1050°C the vacancy concentration is approximately $10^{-5}$. Calculations made by assuming that 0.24% Cr (0.3 at % Cr) would fully capture
unknown] phase, and, moreover, since at temperatures under 400°C, resistivity declines along with aging temperature, the abrupt drop in resistivity at the very first stage is likely due to the formation of clusters related to the Cr molecules present. The rate of formation (N) of Cr clusters at the very first stage of aging (the presence of clusters will be discussed below) is expressed in the formula:

\[ N \propto \exp\left(-\frac{E_f}{kT}\right)\exp\left(-\frac{(\delta f + E_m)}{kT}\right) \]

**Footnote * (p. 10), continued:**

all the vacancies present at $10^{-5}$ concentration, since the contribution of single vacancies in copper to relative resistivity is 1.00 $\mu\Omega$ cm/at% [19], and further assuming the rate of contribution of V-Cr pairing to resistivity is 70% of that for V-In(Sn) pairing and single vacancies in aluminum alloys [16, 20], indicated that the reduction in resistivity caused by the formation of vacancies and clusters was $1.00 \times 10^{-3} \times (1-0.7)$. These calculated results could not explain the actual test results of $1.00 \mu\Omega$ cm. The elimination of all single vacancies and the formation of secondary faults both lead to the same conclusion.

**In the types of alloy that produce increased resistivity in the primary stages, it is generally the case that the increase is produced by the formation of a G.P. phase. With this particular type of alloy, however, no G.P. phase has as yet been detected.** There is an article [4] stating that stable Cr phase is present from the first part of aging on, while in the extremely early stage of aging, Cr polymers exhibit a bcc structure. Such polymers of Cr atoms are expressed here in terms of precipitates or Cr clusters. It is thought that even with production of these Cr clusters, the resistivity of the alloy will decline.
where $\Delta f^*$, $E_f$, and $E_m$ are the barrier energy of nuclear formation, vacancy formation energy, and vacancy migration energy, respectively. Here the first item is to establish that since $\Delta f$ declines in accordance with how low $T_A$ becomes, within the scope of this experiment, the lower $T_A$ becomes, the smaller the value of $(\Delta f^* + E_m)kT_A$, with the result that at the very first stage of low temperature aging, $N$ assumes an unusually large value, and so it is thought that since the clusters are rapidly formed and the concentration of the matrix solute is reduced, the resistivity undergoes an abrupt initial decline. When $T_A$ is constant and $T_S$ is higher, or if $T_S$ is higher and the specimen has a larger amount of Cr in it, the decline in relative resistivity and the rate of decline are both greater, which has already been included in the observations above. Changes after the abrupt decline in resistivity are such that, when $T_S$ is constant, the lower the aging temperature the slower the process (e.g. Figure 1), and this reflects the smaller value for the rate of migration of solute toward the clusters in accordance with lower temperatures. The longevity of excess vacancies at 300–400°C ranges between several hundred and a thousand seconds, as mentioned before, and it is thought that whether the fact that lower the temperatures prolong the effect of excess vacancies depends ultimately upon the low rate of migration on the part of the solute at low temperatures. Next, in cases where $T_S$ changes, for example when the precipitate from aging at 300°C is observed, the case is the same as with the aging at 500°C mentioned earlier, that is, the higher $T_S$ became, the more precipitate appeared over the long term (see Figure 5, Figure 7). This is mainly due to there being more clusters formed at the initial stages when $T_S$ is high, and direct effects of the excess vacancies cannot be observed. This is because once the stage of abrupt decline is past, the slope of the curve is almost independent of $T_S$. The case of 500°C aging will be discussed later.
Since the change in resistivity which was caused by cluster formation was approximately 0.1 \( \mu \Omega \cdot \text{cm} \) higher than that of pure copper, and using a ratio of resistivity to density for calculations, the amount of precipitate accounted for by the clusters was 6.5%. Using transmission electron micrographs on the material aged at low temperature, finding a space between Cr presence of approximately 100 Å [8], and setting that equal to the distance between clusters, it was found that one cluster was the combination of approximately ten Cr atoms.

Next, the phenomenon of increased resistivity described in observation (2) is thought not to depend upon the appearance of the metastable phase, which was alluded to earlier. Considering what is discussed next, this phenomenon is thought to be based upon the reversion of the clusters formed during quenching. This entails the facts that: (i) Resistivity rose in proportion to the aging temperature, which is in conformity with results of experiments [7,8] on reversion in Cu-Cr alloys; (ii) When \( T_s \) is high, the maximum resistivity value was reached within a short period. This is thought to be because as \( T_s \) rises, excess vacancies increase and reversion accelerates. (iii) In high-Cr alloys, when \( T_s \) becomes high the same tendency is shown, and it there is speculation as to whether this is due to increases in supersaturation, consequent decreases in the average size of clusters, and an acceleration in reversion, etc. An initial rise in resistivity can be explained in terms of the formation of clusters during quenching, as set forth above. In this study, the rate of quenching may be regarded as virtually constant, and we wish to study cases where the rate changes at a future time. Incidentally, when reversion of the clusters is complete, in order to attribute some portion of the rise in resistivity to them, the amount of precipitate was calculated in the same manner as before, giving a figure of just below 1% at most, with each cluster consisting of three to five Cr atoms. It goes without saying that in the earlier account of the decline in resistivity
during low-temperature aging, quenched-in clusters (formed during hardening) were present.

The rise in $T_s$ causes an acceleration in the rate of reversion and a reduction in the amount of reversion, which can be explained as follows: The rise in $T_s$ and accompanying acceleration in reversion cause the concentration of excess vacancies to be high, and this encourages both reversion and the formation and growth post-reversion clusters. Accordingly, it is thought that the extent of apparent reversion is reduced due to effects of the formation and growth of clusters, a process which occupies less than 10 seconds in the aging process. Even at 400-450°C when no reversion is apparent, small clusters are undergoing reversion, but this may possibly be offset by the formation of large clusters. Consequently, it is not yet possible to determine the reversion ratio accurately.

However, when $T_s$ is 950°C, as the 500°C curve passes its maximum value at around 30 seconds, perhaps all immediate reversion is in progress. If this is the case, then while reversion was in progress, the excess vacancies were almost extinguished, and, accordingly, the simultaneous formation of clusters around the vacancies which were near thermal equilibrium concentration had taken place. With 500°C aging, the effects of $T_s$ extend over a period of approximately 30 minutes, and the reason it seems that the effects of the excess vacancies were visible, is apparently because clusters formed by this method increase in quantity as $T_s$ increases. On this point, the effect of $T_s$ with respect to the aging curve is similar to the case of aging at 300°C already mentioned. The fact that the aging curve for the 400-450°C range declines steeply after the initial drop, when compared to the curve for the 300-350°C range, is equal in importance to such factors as the number of clusters, the high temperature diffusion rate or the low-temperature effective diffusion rate.
Next, we can get a reasonably good understanding of phenomena (3) and (4) through the discussion of cluster formation and reversion set forth above and the idea of supersaturation. However, the Cu-0.24% Cr alloy precipitates more rapidly at 1000°C than at 950°C, but there is no great discrepancy between the rate at 1000°C and 1050°C. For example, at an aging temperature of 300°C, at the very beginning the rate is more rapid for 1050°C, but after 20 minutes the relative positions of the rates have reversed (compare Figure 3 and Figure 4). Thus there are, especially in the initial part of aging with Ts of 1050°C, a large number of secondary defects, with such results probably due to the fact that concentration of effective vacancies in the matrix is reduced. This was checked with transmission electron micrographs with no detection of structural flaws, but testing for secondary faults was not possible. There exists an article [21] concerning voids in pure copper which indicates that observation of vacancies is difficult.

The above has made it fairly clear that in order to shed light on the aging processes, one must take into consideration the formation of clusters during hardening, reversion of clusters during the initial stage, formation of new clusters, behavior of clusters in relation to excess vacancies in the first stages of aging, the subsequent role of the vacancies, etc. This means that the process of aging of this alloy is not as simple as heretofore believed, but is considered extremely complex. The strength, etc., of this alloy after aging and what such an aging process will finally lead to are problems for future research. Moreover, we are hoping for future research on two-stage aging of this alloy focused on cluster formation in the initial stages of aging at 300-400°C.

We would like to comment further on the initial stage /18 behavior of these alloys, the complexity of which distinguishes this process from the normal aging found in aluminum alloys. The
reason for this is that for these alloys, resistivity decline in
the stage of cluster formation seems less important than $E_m$ as a
factor. That is to say that with aluminum alloys, which have a
small $E_m$, it is thought that during the initial stages of aging,
when a large number of quenched-in clusters are formed, these
clusters are mainly involved in growth, though some new ones are
formed, and their interaction leads to increased resistivity,
which produces an ordinary low-temperature aging curve. With a
somewhat higher $T_A$, a decline in resistivity at the initial stage
due to reversion is expected, but to date no article dealing with
this topic is available. This decline would also be due to small
$E_m$. Since the $E_m$ of copper alloys is large, the formation of
clusters by quenching is very limited, but during the first
stages of low-temperature aging, clusters are formed with the aid
of vacancies formed during hardening. However, afterwards the
growth of clusters is delayed because $E_m$ is so large.
Consequently, it appears that the aging curve consists of the
formation and splitting up of nuclei. Such a curve is seen even
in the case of Cu-Co alloys, and generally can be expected with
alloys having large $E_m$. If a large $E_m$ occurs with a high $T_A$, it
is natural that the reversion phenomenon would show up easily on
the aging curve.

Moreover, with alloys such as those with an aluminum base,
the aging curve can be analyzed to discover values for $E_f$, $E_m$,
and the combining energy, but with these alloys, reactions at the
initial stage of aging are so complex, as described above, that
in these reactions $\Delta f*$ is interrelated with $T_A$, so that it is
considered difficult to get the actual value for either, and for
that reason it was decided not to do such analysis. Aging curve
analysis is carried out for this stage with aluminum and similar
alloys considered as not forming new clusters in the initial
stage, but as mentioned before, even in the case of aluminum
alloys, where some of the phenomena which accompany initial-stage
cluster formation might be present, this type of aging curve analysis cannot be made without reservations.

V. CONCLUSIONS

The results set forth below were obtained by studying the resistivity, principally that of the phenomena of the initial stage of aging for Cu-Cr alloys.

(1) At an aging temperature of 300-400°C during the initial stage (30 sec. or less) a marked decline in resistivity was observed. This decline became proportionately larger as low-temperature aging, solution temperature (T_s) was increased and supersaturation was increased. It is thought that this is due to formation of Cr clusters in the initial stage of aging.

(2) At 450-500°C, a temporary increase in resistivity was observed, and this was more defined as the aging temperature was higher and T_s was lower. The probable reason for this was that Cr clusters formed during hardening were undergoing reversion.

(3) Along with the initial stage changes discussed above, the role of excess vacancies formed during hardening was studied. When the initial changes were past, and over an hour of aging had taken place, the amount of aging was observed from the ordinary point of view, i.e., that the higher the aging temperature (T_A), the more aging will have taken place. However, when T_s became excessively high, precipitation no longer showed a commensurate increase.

(4) As stated above, the initial stage behavior for these alloys is not as simple as is generally thought, in fact, it is considered extremely complex. The fact that the aging behavior of aluminum alloys is generally not viewed as having that degree of complexity is mainly because its vacancy migration energy is less than that of copper alloys.
REFERENCES

