Effects of Ni Addition on the Mechanical and Electrical Properties of Cu-15 mass\%Cr In-Situ Composites

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Effects of Ni and Al addition on the mechanical and electrical properties in the Cu-15 mass\%Cr in-situ composite are examined. The process consists of melting, hot forging, heavy cold rolling and aging. Ni is partitioned into the Cr phase to make an intermetallic precipitates. The Cr phase in the Cu-15 mass\%Cr-10 mass\%Ni shows 3.6 times harder compared with the Cu matrix resulting in the poor cold drawability and low strength. The addition of 1 mass\% Ni and 0.15 mass\%Al is recommended to get good cold drawability and high strength, but it is necessary to make a compound such as Ni\textsubscript{3}Al to increase the electrical conductivity.

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1. Introduction

The development of Cu base alloys with high strength and high electrical conductivity (EC) is a matter of great concern in the application of electronic materials. A newly developed alloy, Cu-15 mass\%Cr in-situ composite, has tensile strength of 900 MPa and EC of 75\%IACS\textsuperscript{1,2}. The addition of 0.1 to 0.2 mass\% Ti, Zr or Sn to this in-situ composite gives the strength level of 1150 MPa and EC of 70\%IACS by optimizing the thermomechanical heat treatments consisting of process variables such as hot working, solution treatment, cold drawing followed by aging. The strengthening is resulted from (a) refining of Cr lamellar spacing, (b) high density of dislocations in the Cu matrix and (c) precipitation of fine Cr particles in the Cu matrix. The EC decreases in proportion to the amount of soluble elements in the Cu matrix, thus aging treatment is quite useful to reduce solute atoms in the Cu matrix. The second phase Cr is very active to scavenge the impurity elements such as O and Fe from the Cu matrix and it is also helpful to increase the EC.

In this paper, the effect of Ni and Al addition on mechanical and electrical properties of a binary Cu-Cr composite was studied. Although Ni is a very attractive element in many aspects, there has been no report on the examination of its behavior in these alloys. Ni is soluble in both the Cu matrix and the second phase Cr to a large extent and contributes to the strengthening at room temperature and also at elevated temperature. Ni addition is known to decrease EC less amount compared with addition of other transition metals such as Fe and Mn. However, it is a wise selection to make an intermetallic compound, Ni\textsubscript{3}Al with simultaneous addition of Al, leading to the reduction of the amount of solid solution Ni.

2. Experimental Procedure

Four-nine level of pure Cu, Cr, Ni and Al blocks have been prepared and high frequency induction melting in vacuum was done at 1800 K and the cast ingots were 7 kg in weight. The chemical compositions of these alloys are shown in Table 1. Two Cu-Cr-Ni alloys and two Cu-Cr-Ni-Al alloys were prepared. The manufacturing process was schematically shown in Fig. 1. The ingots were hot forged at 1173 K to break the cast structure and produce slabs of 23 mm in thickness (thickness reduction: 70\%), and then solution treated at 1273 K for 1 h, followed by water quenching to room temperature. Cold drawing was performed using a cage roller die (Yoshida Kinen Co.). In order to get almost the same size of final wire specimens (0.69 to 1 mm in diameter), the starting materials were sliced into the cross sectional area from 1.7 to 402 mm\textsuperscript{2}. Thus, the cold drawing strain, \( \eta \), has changed from 0.76 to 7.0. Here, \( \eta = \ln(A_0/A) \) with \( A_0 \) and \( A \) being the initial and final cross sectional areas of the specimen. After cold drawing, wire specimens were subjected to the aging treatment in the range from 723 to 1023 K for 1 h. Specimens after these treatments are named as STCA specimens. On the other hand, STC specimens will mean that they were just solution treated and cold rolled without aging.

Microstructural examination was done by optical microscopy, SEM (JSM-6100) and TEM (JEM-2000FX) equipped by EDX analyzer. Thin foils were prepared by

| Chemical compositions of alloys (mass\%). |
|------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Cr | Ni | Al | C | S | Ca | Fe | Si | Cu |
| 10Ni | 16.9 | 10.1 | 0.003 | 0.003 | <0.001 | <0.001 | 0.011 | <0.002 | Bal. |
| 10NiAl | 13.8 | 10.4 | 4.36 | 0.002 | <0.001 | 0.072 | 0.003 | <0.002 | Bal. |
| 1Ni | 13.7 | 0.955 | 0.002 | 0.002 | <0.001 | 0.009 | <0.001 | <0.001 | Bal. |
| 1NiAl | 14.3 | 0.955 | 0.15 | 0.002 | <0.001 | 0.04 | <0.001 | 0.002 | Bal. |
twin jet polishing using an electrolyte of phosphoric acid plus methanol. Thin foils were polished electrolytically under the condition of 10 V and 0.1 A at 260 K, followed by ion milling for 10 min at 293 K and 3 kV. The EC of wire specimens was measured by four point terminal method in a thermostatic bath at 293 K. It was then calculated as an average of two measurements with the polarity reversed on the terminals 200 mm apart.

3. Experimental Results

3.1 The distribution of Ni into Cr phase and Cu matrix

In order to see the distribution of Ni in the Cu and Cr phases, the Cr phase was extracted and chemically analyzed after the Cu matrix was etched away with nitric acid (30%HNO₃+methanol). The result was shown in Table 2. It was found that 6.09 mass% of Ni was in Cr phase in the 10Ni alloy and 0.45 to 0.48 mass% of Ni existed in the Cr phase for 1Ni and 1NiAl alloys. These results mean that about 10% of the added Ni is enriched into the Cr phase. It is also noted that 0.32 to 0.58 mass% of Cu is distributed into the Cr phase.

3.2 Cold drawability

Cold-drawn structures of 1Ni and 10Ni are shown in Figs. 2 and 3. The 1Ni alloy drawn more than \( \eta = 6.2 \) exhibits a homogeneous composite microstructure with Cr lamellar in

| Table 2 Chemical compositions of Cr phases in the alloys (mass%). |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Ni       | Al     | Cu     | S      | Ca     | Fe     | Si     | C      | Cr     |
| 10Ni     | 6.09   | <0.001 | 0.58   | 0.003  | 0.003  | 0.041  | <0.01  | 0.034  | Bal.   |
| 1Ni      | 0.48   | <0.001 | 0.34   | 0.001  | 0.008  | <0.001 | <0.01  | 0.008  | Bal.   |
| 1NiAl    | 0.45   | 0.003  | 0.32   | 0.001  | 0.002  | <0.001 | 0.039  | 0.007  | Bal.   |

Fig. 1 Schematic representation of manufacturing process of in-situ composites.

Fig. 2 Optical micrographs of longitudinal cross section of Cu-15Cr-1Ni(1Ni) wires cold drawn to \( \eta = 0, 0.76, 1.6, 3.2, 4.5, 5.3, 6.2, \) and 7.0.

Fig. 3 Optical micrographs of longitudinal cross section of Cu-15Cr-10Ni(10Ni) wires cold drawn to \( \eta = 0, 0.84, 1.6, 4.5, 5.3, 6.2, \) and 7.0.
the Cu matrix, while 10Ni shows a heterogeneous structure even after heavy reduction and the Cr phase showed little cold drawability. This point will be examined and discussed in details later.

### 3.3 Lamellar spacing and hardness against cold drawing strain

Figure 4 shows the relation between the thickness of Cu, \( d \) (= interlamellar spacing of the Cu matrix) and the thickness of Cr phase, \( t \). In the 1Ni and 1NiAl alloys, \( d \) and \( t \) become smaller as \( \eta \) increases. On the other hand, \( d \) and \( t \) of 10Ni show weaker dependence on \( \eta \).

The effect of drawing strain on the macrohardness in 1Ni, 1NiAl and 10Ni is shown in Fig. 5. The hardness increases linearly with drawing strain after \( \eta = 0.6 \) in the 1Ni and 1NiAl alloys, giving a similar result to that of Cu-15%massCr base alloy.\(^6,7\) The 10Ni alloy shows very high increase in hardness in the early stage of drawing and stays at almost the same hardness level after \( \eta = 4.5 \).

Microhardness was measured to see the difference of work hardening behavior in the Cr phase and the Cu matrix in these alloys. Figure 6 shows the results for 1Ni and 1NiAl. The Hv values of Cr is almost twice as large as those of the Cu matrix and increase linearly with \( \eta \). The work hardening rate of Cu matrix is almost the same as that of the Cr phase. This is a very important fact to have a good cold drawability of these in-situ composites.\(^8\) On the other hand, Cr in 10Ni shows a wide range of scattered hardness values from 200 to 400 Hv (Fig. 7). These high values are considered to be a main cause of the poor drawability of the Cr phase in 10Ni (Fig. 3), leading to the heterogeneous microstructure even at high drawing strain.

The present and previous experimental results lead us to conclude that if the hardness ratio defined as \( \frac{H_{V\text{Cr}}}{H_{V\text{Cu}}} \) is in the range of \( 1 < \frac{H_{V\text{Cr}}}{H_{V\text{Cu}}} < 2.5 \), a good cold drawability can be expected.\(^8\) When the hardness ratio does not fall within this range, the workability is considered to be poor.

### 3.4 TEM observation and X-ray analysis of hard Cr phase

The high hardness of the Cr phase is considered to be due to the high content of Ni in the Cr phase, as shown in Table 2. In order to find why some of the Cr phase show very high hardness with poor drawability, TEM observation and X-ray
diffraction were conducted using a hot-forged specimen after solution treatment at 1273 K for 1 h and water quenching. Figure 8 shows a TEM micrograph of the Cr phase, in which there are many rod-like precipitates. EDX analysis of these precipitates indicated the signals from Ni and Cr atoms. It is suggested that these precipitates strengthen the Cr phase. The X-ray diffraction spectrum shown in Fig. 9 can be understood if these precipitates are to be Cr$_3$Ni$_2$.

### 3.5 Aging characteristics

Figure 10 shows macrohardness change against aging temperature in the STCA specimens of the four alloys, 10Ni, 1NiAl, 1Ni and 15Cr. It is noted that 10Ni keeps high hardness of 160 Hv even after aging at 873 K. Therefore, Ni addition is effective in assuring the high temperature strength. Another remarkable result is that 1NiAl also shows high hardness for wide range of temperature compared with 1Ni, suggesting the favorable effect of co-addition of Ni and Al.

The dependence of EC on the aging temperature of these alloys is shown in Fig. 11. The 10Ni alloy shows very low EC for all the aging temperatures and EC of the 1Ni and 1NiAl alloys similarly recovers moderately by aging. However, compared with the base 15Cr binary alloy, the EC values remain lower (less than 50% IACS) even after full aging. This point will be discussed later.

### 4. Discussion

#### 4.1 Effects of Ni and Al addition on the cold drawability

The experimental results show that Ni dissolves into the Cr phase for about 6 mass% in 10Ni alloy and increases the hardness of the Cr phase to Hv=600. This hardness value is nearly three times larger than that of the Cr phase in the binary Cu-15 mass% Cr alloy. As mentioned above, TEM and EDX analyses show rod-like Cr$_3$Ni$_2$ precipitates in the Cr phase (Figs. 8, 9). We believe these precipitates cause
precipitation hardening of the Cr phase and are responsible for the poor cold drawability of the alloy. In fact, large hardness ratio \( \frac{H_{V\text{Cr}}}{H_{V\text{Cu}}} \) of more than 2.5 (3.6 for 10Ni) makes the cold drawability very poor and thus makes it difficult to refine the microstructure. In addition to the hardness ratio, work hardening rate between the matrix and second phase is also important. If the work hardening rates are comparable between the matrix and second phase, good cold drawability can be expected. However, the work hardening rates of the two phases for the present 10Ni alloy, for example, are quite different, as shown in Fig. 7. This poor cold drawability leads to the heterogeneous microstructure and thus low strength. Being different from 10Ni, the alloy containing 1 mass\%Ni, 1NiAl, shows a good workability because of hardness ratio is 2.2, and work hardening rate of the Cr phase is similar to that of the Cu matrix (Fig. 6). Therefore, it is natural that this alloy shows homogeneous and fine composite structure.

### 4.2 Effect of Ni on the electrical conductivity

As shown in Fig. 11, EC of Ni containing alloys, 10Ni, 1Ni and 1NiAl is very low compared with that of the Cu-15Cr base alloy, where soluble Cr in Cu reduces due to the precipitation of Cr-rich phase and thus EC recovers to the level of 80\%IACS by aging. In order to estimate the effect of Ni addition on the EC, the following consideration is used. EC of composite follows to the rule of mixtures as in the eq. (1)

\[
E_{\text{C}}(\text{in \%IACS}) = \frac{\rho_{\text{Cu}}/\rho_{\text{com}} \times 100}{= (f_{\text{mat}} \cdot \rho_{\text{Cu}}/\rho_{\text{mat}})} + \left(f_{\text{pha}} \cdot \rho_{\text{Cu}}/\rho_{\text{pha}}\right) \times 100(\%)
\]

Here, \( \rho_{\text{Cu}} = 1.7241 \mu\Omega\text{-cm} \), and \( \rho_{\text{com}}, \rho_{\text{mat}}, \rho_{\text{pha}} \) are the electrical resistivity of fully annealed pure Cu, the composite, the present Cu matrix and the Cr phase, respectively, and \( f_{\text{mat}} \) and \( f_{\text{pha}} \) are atomic fractions of the matrix and Cr phase. The electrical resistivity of the Cu matrix, \( \rho_{\text{mat}} \), in the Cu-15 mass\%Ni composite is formulated using Matthiessen’s rule and Linde’s rule as follows:

\[
\rho_{\text{mat}} = \rho_{\text{Cu}} + C_{\text{Cr}} \cdot \Delta \rho_{\text{Cr}} + C_{\text{Ni}} \cdot \Delta \rho_{\text{Ni}} + C_{\text{Al}} \cdot \Delta \rho_{\text{Al}}
\]

Here, \( C_{\text{Cr}}, C_{\text{Ni}} \) and \( C_{\text{Al}} \) are the atomic concentrations of soluble Cr, Ni and Al in the Cu matrix and \( \Delta \rho_{\text{Cr}}, \Delta \rho_{\text{Ni}} \) and \( \Delta \rho_{\text{Al}} \) are the contribution of electrical resistivity of Cr, Ni and Al per mass\%. Using these equations, and assuming that Ni and Al do not precipitate by aging, the change of EC due to the reduction of soluble Cr in the Cu matrix by aging is derived as shown in Fig. 12. The decrement of soluble Cr leads to the recovery of EC and the addition of Ni retards this recovery to a great extent. This fact explains well the experimental result shown in Fig. 11. Thus, it is very important to make Ni in the form of intermetallic precipitates such as Ni$_3$Al or NiAl.

### 5. Conclusion

The effect of additions of Ni and Al on the mechanical and electrical properties in the Cu-15 mass\%Cr in-situ composite has been studied. The processing variables include vacuum melting, hot forging, solution treatment, and cold rolling followed by aging. Main results are summarized as in the following.
(1) Ni was enriched into the Cr phase by about 6 mass% in Cu-15 mass%Cr-10 mass%Ni alloy and 0.45 to 0.48 mass% in the Cu-15 mass%Cr-1 mass%Ni, or Cu-15 mass% Cr-1 mass%Ni-0.15 mass%Al alloys.

(2) The hardness of the Cr phase becomes so high (Hv=600) due to the precipitation of Cr$_3$Ni$_2$ in the Cr phase in the Cu-15 mass%Cr-10 mass%Ni alloy. Thus the cold drawability becomes poor because of high value of hardness ratio, $H_v^{Cr}/H_v^{Cu} = 3.6$, and the difference of work hardening rate between the Cu and the Cr phases.

(3) The electrical conductivity is suppressed to a large extent by the addition of Ni.

(4) The addition of both 1 mass% Ni and 0.15 mass% Al is preferable to increase the cold drawability and the strength after aging.

(5) It is suggested that the reduction of soluble Ni by making intermetallic precipitates such as Ni$_3$Al is important to increase the electrical conductivity.

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