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Microstructure and Properties of a Hot Rolled-Quenched Cu-Cr-Zr-Mg-Si Alloy

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The microstructure and properties of a hot rolled-quenched Cu-Cr-Zr-Mg-Si alloy were investigated by transmission electron microscopy observations, micro-hardness and tensile strength testing, and electrical conductivity measurement. The results show that the hot rolling-quenching (HR-Q) process and subsequent thermomechanical treatments are successfully developed to manufacture Cu-Cr-Zr-Mg-Si alloy strips. Solution treatment can be finished during the HR-Q process, and good combinations of strength, conductivity, and softening resistance are obtained for the thermomechanically treated strips. Ordered fcc structure precipitates which exhibit a cube-on-cube orientation relationship with the matrix are responsible for the improvements of properties. The properties of hot rolled-quenched Cu-Cr-Zr-Mg-Si alloy strips can be further improved by two-step rolling and aging process. The improvements of properties are attributed to the interactions of precipitation strengthening and strain hardening.

Keywords Cu-Cr-Zr-Mg-Si alloy, hardening, high conductivity, high strength, hot rolling-quenching, precipitation

1. Introduction

Copper-based alloys, which are among the most important commercial metallic materials because of their excellent electrical, thermal conductivity, and ease of fabrication, have been widely used in applications, such as railway contact wires (Ref 1), lead frame materials (Ref 2), and connectors (Ref 3), where both the mechanical strength and electrical conductivity are required. As pointed out by Liu et al. (Ref 4), the materials used for lead frame on a large and super large-scale integrated circuit should have high strength (>600 MPa), high hardness (>180 HV), and high electrical conductivity (>80 %IACS).

Copper-Chromium-Zirconium (Cu-Cr-Zr) alloy strengthened by precipitation is one of the most potential alloys to meet the demands of lead frame materials. Many attempts of improving the strength and electrical conductivity of Cu-Cr-Zr alloy have been carried out (Ref 5-9). For example, Su et al. (Ref 8) reported that Cu-Cr-Zr alloy with a hardness of 165 HV and an electrical conductivity of 79.2 %IACS could be gained after solution treatment and subsequent thermomechanical treatment. However, the manufacturing process of all the previous studies contained solution treatment before cold work and aging, so the manufacturing process was discontinuous and the manufacturing cost was high. In this study, a manufacturing process which consists of online hot rolling-quenching (HR-Q), cold work, and aging has been applied to manufacture the Cu-Cr-Zr strips. Solution can be finished by homogenization treatment and rapidly hot rolling in the present process (Ref 10).

Two-step rolling and aging process is widely applied in aluminum and copper alloys. Chemingui et al. (Ref 11) found two-step aging treatment increased the micro-hardness and tensile strength owing to a finer dispersion of GP zones in Al-Zn-Mg alloy. As for Cu-Ni-Si alloy (Ref 12), two-step rolling and aging process increased the tensile strength to 640 MPa by refining the size of Ni_2Si precipitates to 4 nm. However, few studies about two-step rolling and aging process have been reported for Cu-Cr-Zr alloy.

The purpose of this study is to develop an effective and practical process to manufacture Cu-Cr-Zr-Mg-Si alloy strips with high strength and high electrical conductivity. The microstructure and properties of a hot rolled-quenched Cu-Cr-Zr-Mg-Si alloy were investigated, and the suitable conditions were determined.

2. Experimental Procedures

Material with a composition of Cu-0.39 wt.%Cr-0.24 wt.%Zr-0.072 wt.%Mg-0.021 wt.%Si alloy was prepared using electrolytic copper, pure chromium, magnesium, silicon, and copper-13 wt.% zirconium master alloy in a vacuum induction furnace, and then cast in an iron mold with a size of $180 \times 120 \times 30$ mm.

The ingot was homogenized at 1193 K for 5 h and rapidly hot rolled from a thickness of 30 to 5 mm, followed by quenching into cold water. The hot rolled plate was planed on both sides to remove surface defects, and then cut into several samples with desired sizes. Samples were cold rolled with 40%,

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60%, or 80% reduction, respectively, and subsequently isochronally or isothermally aged in a salt-bath furnace. Two-step rolling and aging process, consisting of cold rolling and aging at 723 K for 2 h, followed by another cold rolling and aging at 723 K, was also carried out.

Vickers hardness was tested on HV-5 type micro-hardness tester applying 2.5 kg loads and 10 s loading time. Tensile tests were performed using static Instron tester with cross head speed of 1 mm/min. Electrical resistance was measured at room temperature by QJ-19-type double bridge. The resistivity was calculated and transformed into conductivity according to International Annealed Copper Standards. TEM samples were prepared by double jet electropolishing technique using a 30% nitric acid in methanol solution at about 243 K. TEM observations were carried out by a FEI Tecnai G^{2}20 transmission electron microscope operating at 200 kV.

Four processes of two-step rolling and aging, (A)-(D), corresponding to the various deformations and heat treatments, were labeled as follows:

(A) Hot rolling-quenching (HR-Q) + cold rolling (CR) 60% + aging (AG) at 723 K for 2 h + cold rolling (CR) 40% + aging (AG) at 723 K for different times
(B) HR-Q + CR 60% + AG at 723 K for 2 h + CR 60% + AG at 723 K for different times
(C) HR-Q + CR 80% + AG at 723 K for 2 h + CR 40% + AG at 723 K for different times
(D) HR-Q + CR 80% + AG at 723 K for 2 h + CR 60% + AG at 723 K for different times

3. Results and Discussion

3.1 Isochronal Aging

The hot rolled-quenched and cold rolled samples were isochronally aged (aging for 1 h) at temperatures increasing in steps of 50 K, to determine the suitable aging temperature of Cu-Cr-Zr-Mg-Si alloy. The suitable aging temperature is considered to be the temperature at which good combinations of hardness and conductivity of the alloy could be obtained after 1 h aging. Figure 1 shows the hardness (Fig. 1a) and conductivity (Fig. 1b) isochronal aging curves of the alloy after CR 60% and CR 80%. Hardness and conductivity of the alloy increase considerably with increasing aging temperature up to 773 K. Hardness peaks of the 60% and 80% cold rolled alloys both occur after aging at 723 K, and reach 174 and 187 HV, respectively. Above 773 K, the overaging occurs, and hardness values decrease to 95 and 92 HV, respectively, after aging at 923 K. Conductivity reaches a plateau after aging at 723 K for 1 h, and then increases slightly. Therefore, 723 K is chosen as the suitable aging temperature for the alloy, because the hardness gets to the peak and the conductivity reaches a high and stable value after aging at this temperature. The hardness of 80% cold rolled alloy is about 13 HV higher than that of 60% cold rolled alloy after aging at 723 K. However, almost same conductivity of the different deformed alloys is obtained. This result indicates that the resistivity, in this structural state, is dominated by foreign atoms in (supersaturated) solid solution (Ref 13).

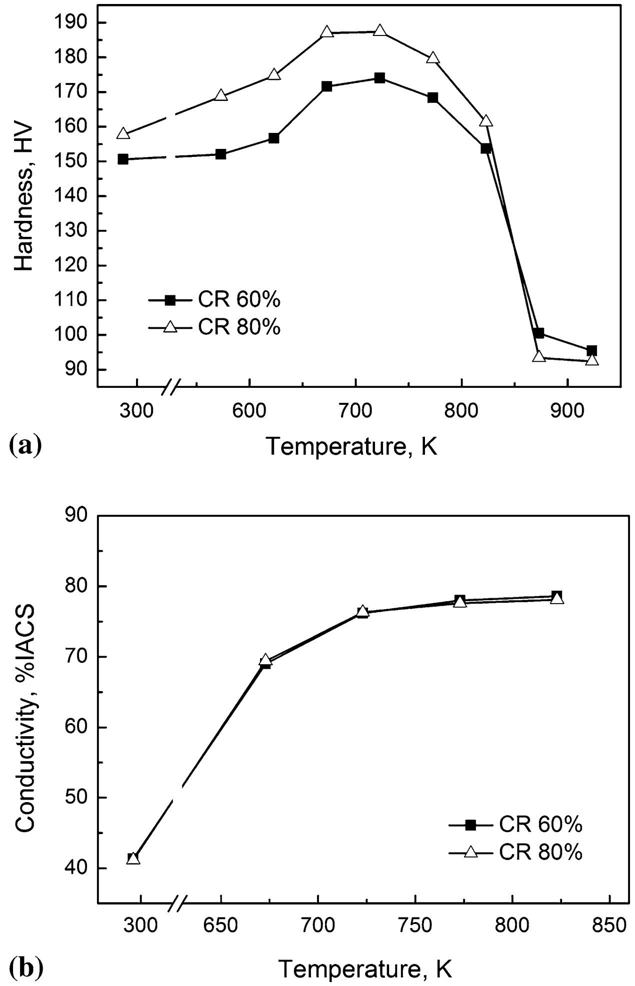

Fig. 1 Hardness (a) and conductivity (b) of the 1 h isochronally aged Cu-Cr-Zr-Mg-Si alloy

3.2 Isothermal Aging

Figure 2 shows the hardness and conductivity curves of the Cu-Cr-Zr-Mg-Si alloy isothermally aged at 723 K. Hardness rises to the peak as aged for 15 min and then decreases. The peak value increases with cold rolling reductions and reaches 170, 175, and 189 HV, for CR 40%, CR 60%, and CR 80%, respectively. The hardness decreases a little after long-time aging: for example, the hardness decrement of the CR 80% alloy is about 11 HV after 20 h aging with a dropping rate of 5.8%. This indicates that the Cu-Cr-Zr-Mg-Si alloy with different deformations has excellent softening resistance during aging at 723 K.

The change of electrical conductivity of the alloy aged at 723 K is shown in Fig. 2(b). As in the case of the hardness, the alloy with different deformations shows large responses during aging, and conductivity reaches favorable values for applications. The electrical conductivity increases rapidly with aging time in the initial stage of aging as solute elements precipitate out of the supersaturated solution. As aging time further increases, conductivity reaches a stable value and then increases slightly as the solute concentration in the copper approaches equilibrium. Almost same conductivity is obtained for the differently deformed samples during aging. The result is in good agreement with that of isochronal aging.

The differences of the peak aged alloy in hardness and conductivity are almost the same as that of the cold rolled alloy. The result illustrates that deformation enhances the strength a lot, but has a little influence on conductivity, because resistivity variations are mainly due to changes in the concentration of foreign

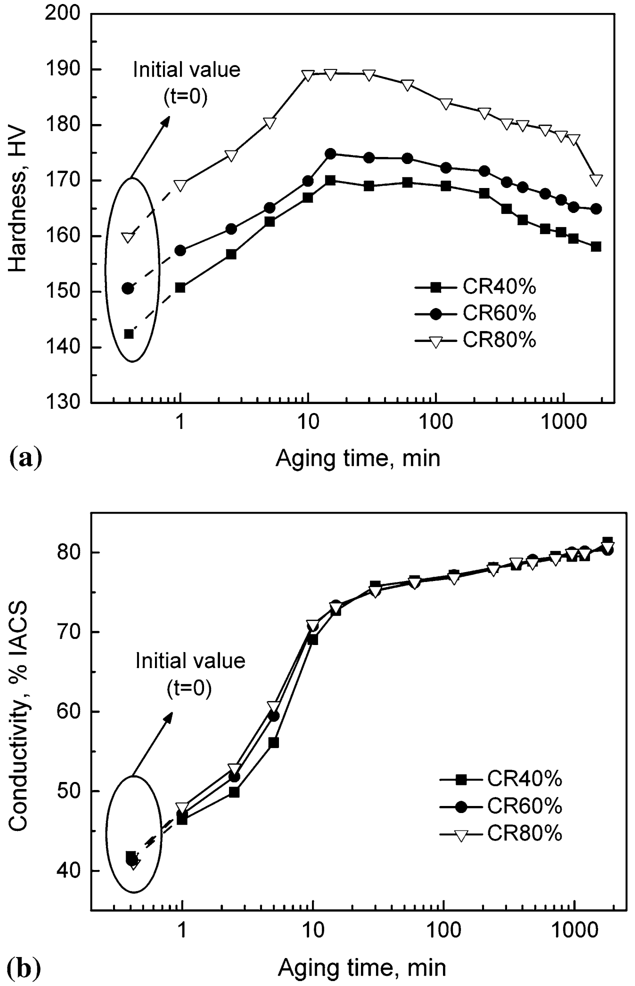

Fig. 2 Hardness (a) and conductivity (b) of the 723 K isothermally aged Cu-Cr-Zr-Mg-Si alloy

atoms in solid solution. The suitable reduction of cold rolling among the deformations appears to be 80%, although heavy deformation can easily lead to overaging, as shown in Fig. 2(a).

On the basis of the foregoing, it appears that Cu-Cr-Zr-Mg-Si alloy has a pronounced age response under the present HR-Q process, and good combinations of hardness and electrical conductivity can be obtained.

3.3 Two-Step Rolling and Aging

Two-step rolling and aging process was tested on the present alloy, to obtain further improvement of its properties. The aging curves of hardness and electrical conductivity for samples, A, B, C, and D (described in section 2), are shown in Fig. 3. It is clear, from Fig. 3(a) that the hardness decreases for each sample with increasing aging time, which completely differs from the isochronal and isothermal aging processes. Furthermore, once the supersaturated alloy is decomposed, the effect of the different degrees of cold-work on the resistivity is no longer marked. As shown in Fig. 3(b), the higher the cold-work, the higher the concentration of lattice defects and the lower the conductivity. Table 1 lists the mechanical and electrical properties of Cu-Cr-Zr-Mg-Si alloy under various conditions. It can be seen that the hardness, strength, and conductivity under process C for 1.5 min are up to 198 HV, 567 MPa, and 77.8 %IACS, respectively, whereas they are 182 HV, 536 MPa, and 77.9%IACS for the 80% cold rolled and 723 K for 4-h aged alloy. These results indicate that strength can be further improved by two-step rolling and aging process almost without reducing the electrical conductivity.

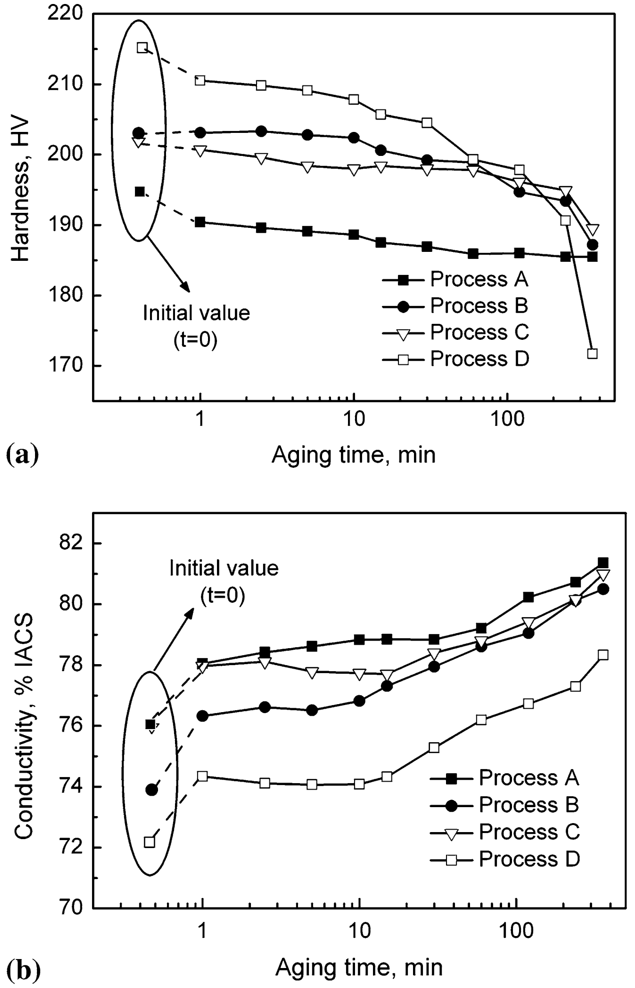

Fig. 3 Hardness (a) and conductivity (b) of the two-step rolled and aged Cu-Cr-Zr-Mg-Si alloy

The effects of precipitation on strength and electrical conductivity are dependent on the initial microstructural parameters, such as dislocation density and grain size (Ref 14). Since the initial microstructure is determined by the previous thermomechanical treatment history, the strength and electrical conductivity can be controlled by the modification of the thermomechanical treatment process (Ref 12). As for the two-step rolling and aging process, the initial cold rolling and aging stage results in control of grain size and finer and uniform precipitation, and the second cold rolling on the well-precipitated alloy leads to heavy work hardening by dislocation accumulation within the precipitate-containing matrix. Precipitation and recovery occur simultaneously during the second aging. Nevertheless, neither precipitation strengthening nor recovery softening is predominant during 1-h aging. Hence, the hardness maintains a stable value, and the conductivity increases slightly; thus, good combinations of strength and conductivity are achieved.

3.4 Microstructure

Figure 4 shows the TEM images of Cu-Cr-Zr-Mg-Si alloy cold rolled 80% and aged at 723 K for 1 h. A high density of dislocations is introduced, and cellular substructure is formed by heavy cold rolling. Aging for 1 h at 723 K causes extensive rearrangement and annihilation of dislocations, so that the subgrains boundaries are clearly visible (Fig. 4a). This reveals that polygonization has developed to a great extent due to partial recovery. A very high density of precipitates and a reduced density of dislocation inside the subgrains are also found (Fig. 4a, b). This indicates that the cold work microstructures, such as cellular substructure and dislocations, remain after aging, and precipitation occurs simultaneously.

Table 1 Mechanical and electrical properties of Cu-Cr-Zr-Mg-Si alloy

Condition	Hardness, HV	Ultimate tensile strength, MPa	Conductivity, %IACS
HR-Q + 40% CR + AG at 723 K for 4 h	168	503	78.1
HR-Q + 60% CR + AG at 723 K for 4 h	173	529	78
HR-Q + 80% CR + AG at 723 K for 4 h	182	536	77.9
Process A (for 1.5 min)	189	554	78.6
Process B (for 1.5 min)	202	573	76.5
Process C (for 1.5 min)	198	567	77.8
Process D (for 1.5 min)	208	584	74.1

The TEM bright-field (BF) micrograph and the corresponding selected area electron diffraction (SAED) pattern are shown in Fig. 4(c) and (d). Great deals of precipitates with lobe-shaped strain-field contrast are dispersed in the matrix. This indicates that the precipitates are coherent with the matrix. Quite apparent extra reflection spots other than those from matrix are detected and marked with arrow N in the SAED pattern. Superlattice diffraction which is marked with arrow M is also found midway between the extra diffraction spot and the transmitted spot in the SAED pattern. The indexing of the SAED patterns indicates that the precipitates, which decompose from the hot rolled-quenched and cold rolled alloy approaching peak aging, have an ordered fcc structure and a unit cell larger than that of the matrix, and exhibit a cube-on-cube orientation relationship with the matrix. The result shows very good consistency with the result of Ref 8, in which the ordered fcc precipitates are considered to be precursors to formation of chromium-rich ordered bcc precipitates (Ref 8). However, there has been no unanimous agreement on the crystal structure of the precipitate in Cu-Cr-Zr alloy. Other investigators (Ref 6, 8, 15) conclude that the precipitates have a bcc structure and exhibit a Nishyama-Wasserman orientation relationship with the matrix. This may be because the previous investigation conditions are in the intermediate or later stages of precipitation, while the present condition is in the initial stage of precipitation. Precipitates decomposed from the supersaturated solution near peak aging are responsible for the improvements of hardness and electrical conductivity.

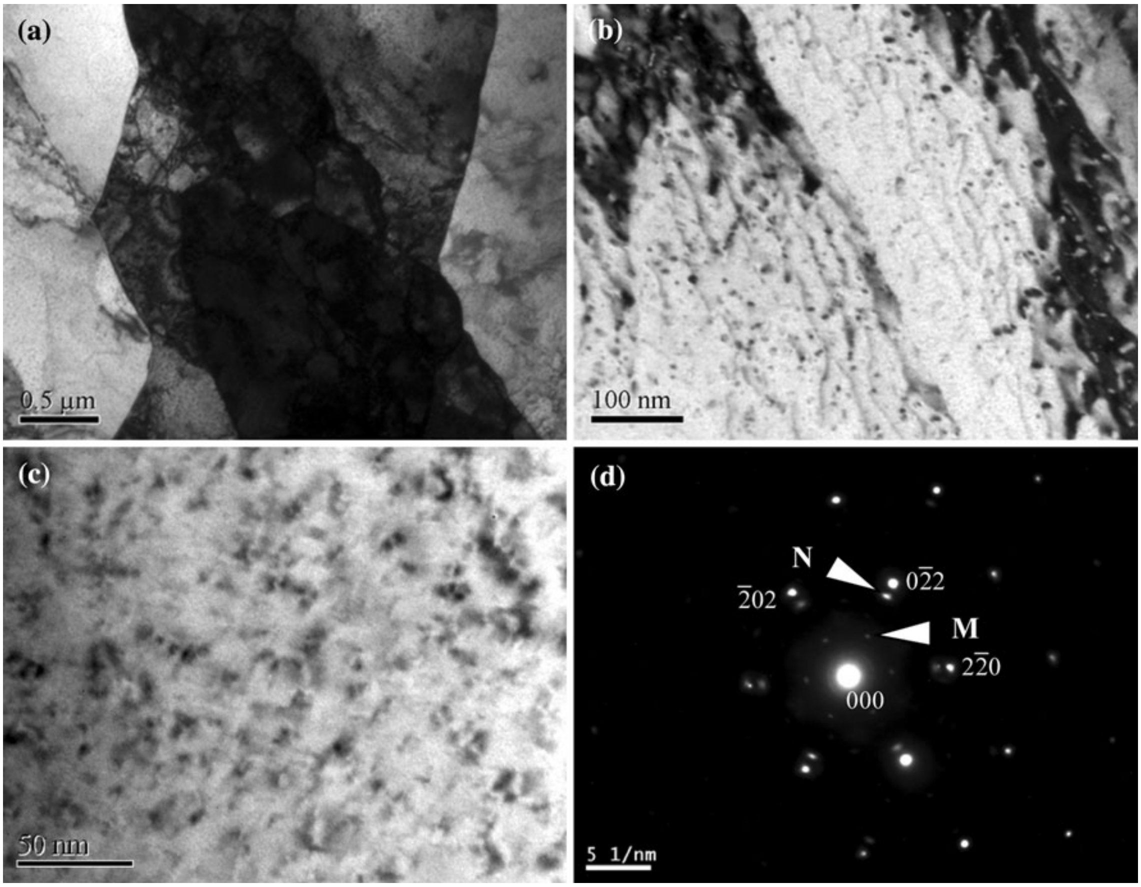

Fig. 4 TEM images of Cu-Cr-Zr-Mg-Si alloy after 80% CR and 723 K aging for 1 h (a) micrograph of substructure; (b) micrograph of the dislocations and precipitates; (c) BF micrograph of precipitates; and (d) SAED pattern of (c), zone axis close to $[111]_{Cu}$

Small additions of elements are known to have beneficial effects on properties of Cu-Cr alloy. The additions may increase the nucleation rate of precipitates (Ref 16), form element-rich precipitates, and increase the energy of the precipitate/matrix interface (Ref 17). As compared with other studies, the 80% CR and aged Cu-Cr-Zr-Mg-Si alloy shows a higher hardness but a slightly lower conductivity than the 60% CR and aged Cu-Cr-Zr-Mg alloy (160 HV, 78 %IACS, Ref 8) because of the trace addition of Si and the larger degree of cold work. Good combinations of strength and conductivity (570 MPa, 86 %IACS, Ref 18) of Cu-0.5Cr-0.15Zr-0.1Ag are obtained, which are ascribed to the decrease in precipitate spacing and Ag-atom-drag effect on dislocation motion. However, the mechanisms of Zr, Mg, and Si additions to improve the properties are not fully understood, because no fine and other element-rich precipitates have been exactly observed and proved either at the peak-aged or overaged condition, according to the previous investigations (Ref 1, 6, 8, 9).

The dislocations which remain from cold rolling deformation provide nucleation sites for precipitation and are pinned by the precipitates resulting in the interactions of precipitation strengthening and strain hardening, so that good combinations of high strength and high electrical conductivity can be obtained.

3.5 Hot Rolling-Quenching Process

The strength and electrical conductivity depend mainly on the material microstructure, which in turn depends on the deformation and heat treatments.

The results of the present investigation show that the Cu-Cr-Zr-Mg-Si alloy has a large precipitation strengthening response during aging treatment. This confirms that the solute atoms, such as Cr, Zr, Mg, and Si are dissolved into the matrix after hot rolling-quenching, and subsequently decompose from the supersaturated solid solution during aging treatment. The high strength is due to precipitation strengthening and strain hardening, and the excellent electrical conductivity is attributed to the low solubility of solute atoms in Cu matrix, and so the effect of hot rolling-quenching process is almost the same as that of traditional solution quenching treatment. In other words, solution treatment can be finished during the HR-Q process. Jovanovic and Rajkovic (Ref 19) attempted to avoid solution annealing and quenching, and partial success was achieved, but the prepared alloy inclined toward overaging, i.e., aging above 698 K. In this study, online HR-Q process and subsequent thermomechanical treatments are applied to manufacture the Cu-Cr-Zr-Mg-Si strips. As a result, the manufactured strips have good combinations of high strength, high conductivity, and softening resistance. The manufacturing process avoids traditional solution treatment, and thus reduces the manufacturing cost. Therefore, HR-Q process proves to be both effective and practical for manufacturing the commercial precipitation-hardened Cu-Cr-Zr-Mg-Si alloy strips.

4. Conclusions

Based on the results obtained, the following conclusions can be drawn.

HR-Q process and subsequent themomechanical treatments are successfully developed to manufacture Cu-Cr-Zr-Mg-Si alloy strips. The HR-Q process is effective and practical to manufacture commercial precipitation-hardened copper strips.

Good combinations of strength, conductivity, and softening resistance of Cu-Cr-Zr-Mg-Si alloy are obtained under the HR-Q process because of the interactions of precipitation strengthening and strain hardening. The hardness, strength, and electrical conductivity reach 182 HV, 536 MPa, and 77.9 %IACS, respectively, after 80% cold rolling and aging for 4 h at 723 K.

Properties of hot rolled-quenched Cu-Cr-Zr-Mg-Si alloy can be further enhanced by two-step cold rolling and aging process. The hardness, strength, and electrical conductivity of the alloy are up to 198 HV, 567 MPa, and 77.8 %IACS, respectively, under process C for 1.5 min.

Precipitates with an ordered fcc structure and a cube-on-cube orientation relationship with the matrix, which decompose from the supersaturated solution during peak aging, are responsible for the improvements of hardness and electrical conductivity.

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