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High strength and high conductivity Cu alloys: A review

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High strength and high conductivity (HSHC) Cu alloys are widely used in many fields, such as high-speed electric railway contact wires and integrated circuit lead frames. Pure Cu is well known to have excellent electrical conductivity but rather low strength. The main concern of HSHC Cu alloys is how to strengthen the alloy efficiently. However, when the Cu alloys are strengthened by a certain method, their electrical conductivity will inevitably decrease to a certain extent. This review introduces the strengthening methods of HSHC Cu alloys. Then the research progress of some typical HSHC Cu alloys such as Cu-Cr-Zr, Cu-Ni-Si, Cu-Ag, Cu-Mg is reviewed according to different alloy systems. Finally, the development trend of HSHC Cu alloys is forecasted. It is pointed out that precipitation and micro-alloying are effective ways to improve the performance of HSHC Cu alloys. At the same time, the production of HSHC Cu alloys also needs to comply with the large-scale, low-cost development trend of industrialization in the future.

high strength, high conductivity, Cu alloys

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1 Introduction

Cu possesses the highest rating for both the thermal and electrical conductivity of common metals. High conductivity coupled with intrinsic strength, formability and corrosion resistance make Cu alloys unique as conductors of electricity —making them ideal for connectors and other electrical or electronic products [1–3]. For a long time, there is a strength-conductivity trade-off for the research of HSHC Cu materials, which even runs through the entire conductive material research [4,5]. The strengthening methods in HSHC Cu alloys mainly include solid solution strengthening, precipitation strengthening, fine grain strengthening and deformation strengthening. But these strengthening methods will lead to a large number of microscopic defects appear in the crystal, which will decrease the conductivity of the alloys. The way to sacrifice the conductivity of Cu as little as possible under the premise of a substantial increase in Cu strength, that is, to achieve HSHC of Cu, is an important issue.

The so-called HSHC Cu alloys, generally refer to the tensile strength 1.5–4 times of pure Cu (300–800 MPa), conductivity 50%–95% of the pure Cu. The ideal index is tensile strength ≥600 MPa, electrical conductivity ≥80% IACS (International Annealed Cu Standard, 100% IACS=1.72 μΩ/cm). Typical examples include Cu-Ag alloys, Cu-Mg alloys, Cu-Ni-Si alloys, and Cu-Cr-Zr alloys.

This review introduced the strengthening mechanisms of HSHC Cu alloys and reviewed the research progress of Cu alloys in typical alloy systems. Lastly, we propose an outlook on the future development trend of the HSHC Cu alloys.

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2 Strengthening methods

The relationship between the strength and the conductivity of the Cu alloys is no matter what kind of means by which the Cu alloy is strengthened, its conductivity must be declined to some degree. Therefore, how to choose the appropriate strengthening methods according to the requirements of different application environments and striving to maximize the strength within the minimum range of electrical conductivity reduction becomes the key for the research and development of the HSHC Cu alloys. The alloying method is the most commonly used method in the HSHC Cu alloys, that is adding a certain amount of alloying elements in the Cu matrix to form a solid solution or supersaturated solid solution, and then use mechanical processing or heat treatment methods to make changes in the microstructure to let the Cu alloys obtain both high strength and high conductivity. The alloying method mainly includes four strengthening effects, which are solid solution strengthening, fine grain strengthening, precipitation strengthening, and deformation strengthening.

2.1 Solid solution strengthening

Solid solution strengthening refers to adding a certain amount of solute atoms into the matrix metal to form a solid solution, thereby causing lattice distortion. The stress field is generated by the lattice distortion and the surrounding elastic stress field interact [6]. This interaction hinders the movement of dislocations so that the yield stress of the alloy increases sharply, and the material is strengthened. However, the addition of solid solution atoms will significantly reduce the conductivity of the alloy, because the point defects scatter the electrons more than the dislocations. The principle of using a solid solution strengthening method to prepare HSHC Cu alloys is to choose the solid solution elements which can make good strengthening effect without decreasing much conductivity. In most cases, the solid solution strengthening and aging strengthening are used together.

Heterogeneous atoms added to the pure matrix to form a solid solution, the basic law can be summarized as follows.

(1) In the stress-strain diagram, the stress-strain curves of the alloy increase upward, and the strain-hardening ability of the alloy is generally higher than that of the pure metal.

(2) In general low concentration solid solution, yield stress changes with the solute concentration can be expressed as follows [7]:

$$\sigma = \sigma_0 + KC^m, \tag{1}$$

where σ is the yield stress of the alloy; σ_0 is the yield stress of the pure metal; C is the atomic concentration of the solute; K and m are constants related to the properties of the matrix and alloying elements, the value of m is between 0.5–1.

(3) In the same matrix, the solubility of different solute elements reflects the difference in their strengthening effect very clearly. The general rule is that at the same concentration, the increase in strength is proportional to the reciprocal of the solubility of solute elements. Obviously, the solubility is only an appearance. The solute and the solvent elements of different atomic size, chemical properties, electrical and other factors will affect the strength of the solid solution more directly.

(4) The general tendency of the yield stress of solid solution to change with temperature is the same as the pure metal, but its temperature sensitivity is larger than that of pure metal, and the higher the concentration, the greater the sensitivity.

In short, the factors that affect solid solution strengthening include elastic factor, electron concentration factor, chemical factor, and structural factor. In addition, the incorporation of a large number of heterogeneous atoms may change the bonding force of the matrix. However, for HSHC Cu alloys, the effect of solid solution strengthening alone is not significant, so there are few Cu alloys developed. Common solid solution elements are Sn, Ag, Zn, and Cd [8]. In addition, the solid solution elements will make the conductivity of the material decreased linearly, so in the high conductivity Cu alloys, the element content of solid solution state is low, generally below 1%.

2.2 Fine grain strengthening

By Hall-Petch formula [9,10]:

$$\sigma = \sigma_0 + kd^{-1/2}, \tag{2}$$

where d is the average grain diameter; k is a constant. In polycrystalline, the finer the grains and the higher the yield strength. The dislocations are blocked by the grain boundaries and pinned on the grain boundary during the deformation of the polycrystalline, thereby forcing the sliding within the grain boundaries to be difficult. Finally, the alloy is strengthened. As the grain refinement only increases the crystal interface, which has little effect on the conductivity. In order to obtain an ultra-fine grain structure, the following methods can be used.

(1) Optimizing the crystallization process in the solidification conditions. On the one hand, trying to increase the cooling rate; on the other hand, adjusting the composition of the alloy to produce a high rate of grain nucleation and obtain the fine grain structure [11].

(2) Deformation is performed while subsequent recovery and recrystallization processes will be strictly controlled to achieve fine grain structure.

(3) Using dissolution reaction, spindle decomposition, powder sintering, internal oxidation and other methods to produce dispersed second phases in the alloy to limit the

grain growth of the matrix.

(4) Adding some trace alloying elements.

2.3 Precipitation strengthening

The basic principle of precipitation strengthenging is adding elements in the Cu alloys, then solution treating the alloys at high temperature and after quenching, supersaturated solid solutions are formed [12]. Then through the subsequent aging treatment, the supersaturated solid solution decomposes and forms precipitates dispersed in the matrix [13]. The formation of precipitation can effectively prevent the movement of grain boundaries and dislocations so that the strength of the alloy increases greatly. The lattice distortion caused by precipitates is small, so the scattering caused by them is much smaller than that caused by solute atoms. Therefore, the Cu alloys can get high electrical conductivity after precipitation.

2.4 Deformation strengthening

Deformation strengthening mainly uses the work hardening so that the strength and hardness of the treated alloys are increasing. It is also one of the means commonly used for the Cu alloy strengthening [14]. The dislocation density increases in the plastic deformation process, and the cross-cutting leads to the impeding of the further movement of dislocations. The deformation resistance of the material increases, thereby increasing the strength of the materials. Conventional plastic deformation processes, such as cold-rolled, cold-drawing, and other processing methods are easy to achieve large-scale industrial production.

3 Research progresses in HSHC Cu alloys

3.1 Cu-Cr-Zr system

Cu-Cr-Zr system alloy is a typical kind of precipitation strengthening alloys. A great deal of research has been done on it to improve its strength and electrical conductivity, which has been made great progress.

In the Cu-Cr-Zr alloy, the addition of Zr not only refines the Cr phases in the alloy but also makes the Cr phases more spherical. Zr formed Zr-rich precipitate phases at the grain boundaries, which greatly enhanced the strength of grain boundaries, improved Cu-Cr alloy's creep, fatigue properties and medium temperature brittleness [15]. Batawi et al. [16] systematically compared the different effects of four elements of Zr, Mg, Si, and Ti added to the Cu-Cr binary alloy. Among them, Zr element was considered as the most effective additive element, which could maximize the strength of the alloy and retain the strength effectively after annealing at higher temperatures.

From the binary phase diagram of Cu-Cr and Cu-Zr alloys, Cr is almost insoluble in the Cu matrix at room temperature, Cu and Zr can form a variety of CuZr compounds. So the Cu-Cr-Zr alloy may precipitate the Cr phase and the compound phase of Cr and Zr after the aging treatment. Kuznetsov et al. [17] calculated the vertical cross-section diagram of the Cu-0.4wt.%Zr-xCr (x=0.5, 1.5 and 5 wt.%). The results showed that the Cu, Cr, Cu_3Zr, $Cu_{51}Zr_{14}$, Cu_8Zr_3 and $Cu_{10}Zr_7$ phases were involved in this system. Hatakeyama et al. [18] studied the structure of the Cr-rich precipitate in the Cu-Cr-Zr alloy and found that the structure of the Cr-rich precipitate was a core-shell structure after pre-aging at 460°C for 3 h and secondary aging at 600°C for 4 h. The results of Zhang et al. [19] showed that the Cu_5Zr phase existed in the Cu-Cr-Zr alloy. This result was consistent with the experimental results of Holzwarth et al. [20], Huang et al. [21] and Kermajani et al. [22]. Huang et al. [21] also believed that the alloy has $Cu_{51}Zr_{14}$ phase with a hexagonal close-packed (hcp) structure.

In recent years, many processes were used to improve the strength and electrical conductivity of the Cu-Cr-Zr alloy. Xia et al. [23] studied the hot rolled-quenched Cu-0.39Cr-0.24Zr-0.072Mg-0.021Si (wt.%) alloy and found that the hardness, strength, and electrical conductivity of the alloy were up to 198 HV, 567 MPa, and 77.8%IACS, achieved by the two-step cold rolling and aging processes. Fu et al. [24] obtained the Cu-0.98Cr-0.057Zr (wt.%) alloy with 669 MPa and 74.5%IACS by 95% rolling deformation at room temperature combined with aging at 450°C for 1 h. Sun et al. [25] prepared bulk nanostructured Cu-1.0Cr-0.1Zr (wt.%) alloy composed of nanocrystals by dynamic plastic deformation at liquid nitrogen temperature. This one-step deformation treatment of the nanostructured Cu-Cr-Zr alloy owned a tensile strength of 700 MPa and electrical conductivity of 78.5%IACS. Li et al. [26] prepared the Cu-0.3Zr (wt.%) alloy and rolled it at liquid nitrogen temperature, then did an aging treatment. The alloy achieved a tensile strength of 602.04 MPa and an electrical conductivity of 81.4%IACS. Mishnev et al. [27] investigated the ultrafine-grained microstructures, mechanical properties and electrical conductivity of a Cu-0.87Cr-0.06Zr (wt.%) alloy subjected to multiple equal channel angular pressing (ECAP) at temperatures of 473–673 K. The yield strength increased from 215 to 480 and 535 MPa after eight ECAP passes at 673 and 473 K, respectively. The formation of ultrafine grains containing high dislocation density led to a small reduction in electrical conductivity from 80 to 70%IACS. Morozova et al. [28] obtained that the yield strength of Cu-0.1Cr-0.06Zr (wt.%) alloy after ECAP deformation increased from 100 to 390 MPa and the conductivity was 80%IACS. Purcek et al. [29] obtained the Cu-Cr-Zr alloy with 213 HV and 71%IACS using a combination of ECAP and aging at 425°C for 240 min processes. Liang et al. [30] prepared Cu-0.45Cr-

0.12Zr (wt.%) alloy by ECAP processes followed by aging treatment at 460°C. Its hardness reached the peak value of 219 HV at 1.5 h and then decreased slowly. The electrical conductivity recovered to 70.7%IACS after 1 h, and then kept going up, reached to 83.1%IACS at 8 h, as shown in Figure 1. Zhang et al. [19] fabricated Cu-1Cr-0.1Zr (wt.%) alloy strips by a two-stage cryorolling and an intermediate aging treatment. The results showed that the desired combination of the 690.13 MPa and 67%IACS were obtained after a primary 30% thickness reduction, aging at 450°C for 2 h and a secondary 60% thickness reduction at the cryogenic temperature (Figure 2). Zhang et al. [31] prepared Cu-0.4Cr-0.15Zr-0.05Ce (wt.%) alloy by cold rolling and aging. They found that the hardness and electrical conductivity of the alloy could reach 170 HV and 66%IACS, respectively, after 80% cold rolling and aging for 16 h at 300°C (Figure 3). Liu et al. [32] prepared the Cu-0.55 Cr-0.05 Zr (wt.%) alloy by solid solution, rolling and aging treatments. The results showed that the peak hardness of 131 HV was achieved after aging at 500°C for 1 h, corresponding to an electrical conductivity of 85.3%IACS (Figure 4). Shangina et al. [33] studied that quenching, high-pressure torsion (HPT) and subsequent aging at a temperature of 450°C, led to both high microhardness (2.70 GPa) and electrical conductivity (63%IACS) of the Cu-0.3Cr-0.5Zr (wt.%) alloy (Figure 5). Wang et al. [34] fabricated a Cu-0.55Cr-0.2Zr alloy by cryogenic friction stir processing followed by annealing. A combination of high strength (840 MPa) and pronounced electrical conductivity (89%IACS) was obtained, as shown in Figure 6. Huang et al. [35] prepared a high-performance Cu-0.3%Cr-0.1%Zr-0.05Mg alloy with a high UTS of 612 MPa and an electrical conductivity of 84.7%IACS by a severe rotary swaging and a two-step peak-aging treatment. Li et al. [12] found that a balance between the UTS (648 MPa) and electrical conductivity (79.80%IACS) was achieved in a Cu-1Cr-0.1Zr (wt.%) alloys by the coexistence of refined deformation bands and nano-scale deformation twins introduced by two-step cryorolling treatment and nanoprecipitates introduced by the aging process.

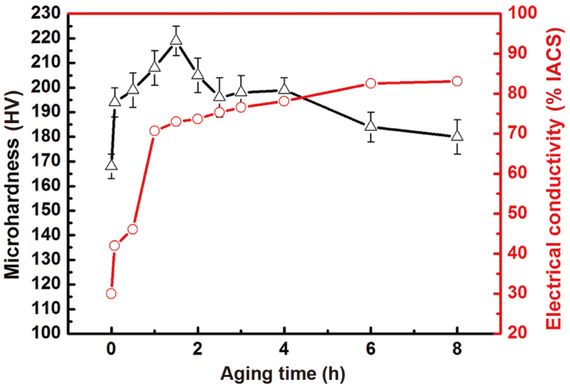

Figure 1 (Color online) Variations of hardness and electrical conductivity with aging time of the Cu-Cr-Zr alloys [30].

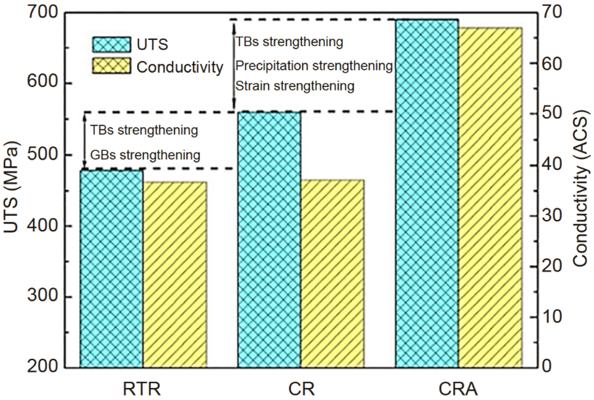

Figure 2 (Color online) The variations of the UTS and electrical conductivity under different conditions and the strengthening mechanisms of Cu-Cr-Zr alloys [19].

To sum up, the Cu-Cr-Zr system alloy has been deeply studied in some aspects. A great number of researches have focused on the influence of Cr and Zr on the Cu matrix. Multiple conventional or novel processes have been applied to Cu-Cr-Zr alloys to explore better mechanical performance. It is worth noting that precipitation strengthening is the main strengthening method in Cu-Cr-Zr alloys, but there is a big dispute about the precipitation process and mechanism in the alloys which need to be further studied.

3.2 Cu-Ni-Si system

Cu-Ni-Si alloy is a kind of high-strength, medium-conductivity alloy, which belongs to typical aging-strengthening

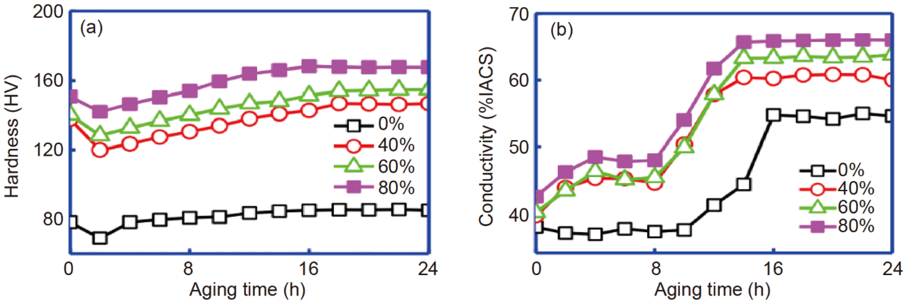

Figure 3 (Color online) Cold deformation effect on (a) hardness and (b) conductivity of the Cu-Cr-Zr-Ce alloy aged at 300°C [31].

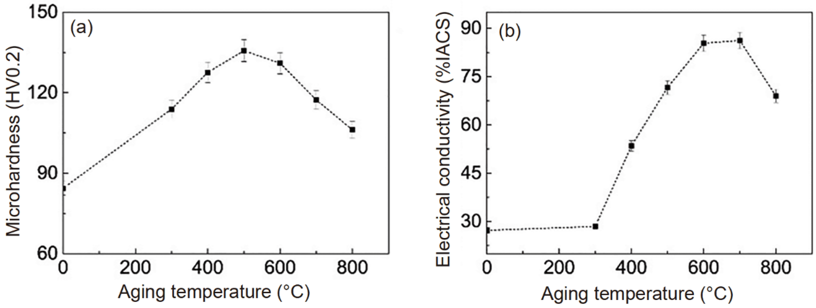

Figure 4 (a) Micro-hardness and (b) electrical conductivity of the Cu-0.55 Cr-0.05Zr (wt.%) isochronally aged for 1 h at various temperatures [32].

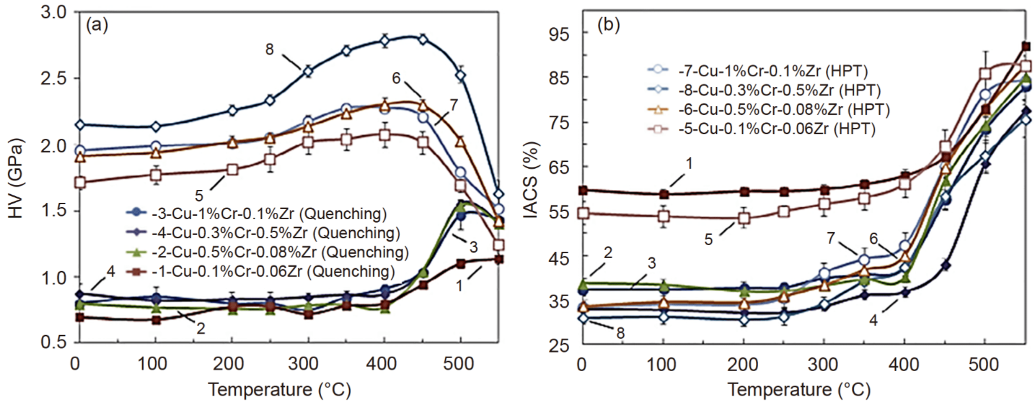

Figure 5 (Color online) Change of microhardness (a) and electrical conductivity (b) of the alloys as a function of 1 h aging temperature [33].

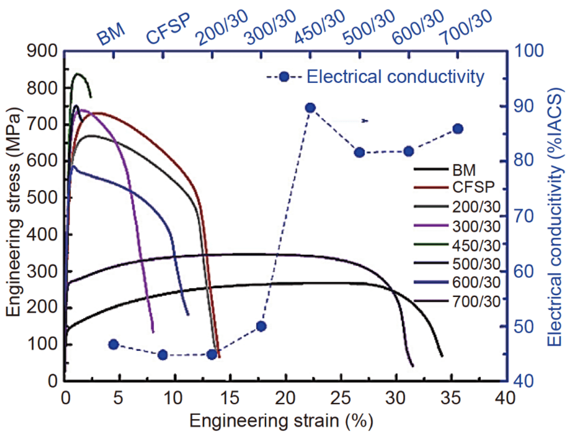

Figure 6 (Color online) Stress-strain curves and electrical conductivity of the cryogenic friction stir processed Cu-Cr-Zr alloy at different annealing temperatures [34].

alloys. The aging strengthening effect was first discovered by Corson [36] in 1927. Recently, many studies have been devoted to mechanical and electrical characterizations as well as microstructure characteristics of Cu-Ni-Si alloy.

According to the quasi-binary section of the ternary Cu-Ni-Si phase diagram, the most probable precipitation phase is δ-Ni_2Si. Large quantities of reports suggest that the strengthening of Cu-Ni-Si alloy results from the precipitation of supersaturated Ni and Si atoms as δ-Ni_2Si in Cu-rich solid solutions, although other types of precipitates, such as β-Ni_3Si, $(Cu,Ni)_3Si$, β-Ni_5Si_2 and other metastable phases, might coexist [37–42]. Zhao et al. [43] found that when Cu-3.2Ni-0.75Si (wt.%) alloy was aged at 723 K after solution heat treatment, the modulated structure with Si-rich and Si-poor regions formed firstly, then the ordering $(Cu, Ni)_3Si$ nucleated from the modulated structure, and δ-Ni_2Si precipitates formed at last with the increase of aging time. Azzeddine et al. [41] used *in situ* synchrotron X-ray diffraction to study the decomposition kinetics of a metastable Cu-2.5Ni-0.6Si (wt.%) alloy after severe plastic deformation by ECAP and HPT. Two types of precipitates, namely δ-Ni_2Si and γ-Ni_5Si_2, were identified. After the aging treatment, the fine dispersed δ-Ni_2Si phase particles can interact with the dislocation and impede the dislocation movement, so that the strength of the Cu alloy is drastic. At the same time, as the solute elements are precipitated from the Cu matrix, the scattering of electrons in the Cu matrix weakens, thereby improving the conductivity.

More alloy systems were prepared by designing Cu-Ni-Si alloys using small addition elements such as Ti, Cr, Fe, Co, Mg, and Al to obtain additional mechanical properties with a less adverse effect on conductivity [44]. The addition of Al and Mg influences the rate of precipitate formation and increases the precipitation kinetics [45]. The addition of a small amount of Mg also increases the strength and the stress relaxation resistance by the effect of Mg-atom drag on the dislocation motion [46]. In addition, Mg atoms improve the stress relaxation resistance by solid solution hardening because of the large difference between the atomic radii of Mg and Cu [47,48]. Moreover, Mg also promotes the formation of silicides. Watanabe et al. [49] studied the effect of adding Ti on the properties of Cu-Ni-Si alloy. They found that when the mass fraction of Ti was added to 0.2 wt.%, the formation of $Ni_{16}Si_7Ti_6$ in the alloy could be induced and the volume fraction of δ-Ni_2Si precipitates decreased, leading to the decrease of the strength. When the alloy content was 0.04 wt.%, the average spacing between the precipitated phases can be effectively reduced to increase the strength. Fe can significantly improve both the strength and conductivity [44]. Han et al. [50] showed that the Cu-2.8Ni-0.7Si (wt.%) alloy could obtain a good combination of electrical conductivity and hardness by adding 0.1 wt.% V. The addition of Zr element has a detrimental effect on the mechanical properties of the Cu-Ni-Si alloy, whereas the best performance is obtained in the presence of Zr and Cr [51].

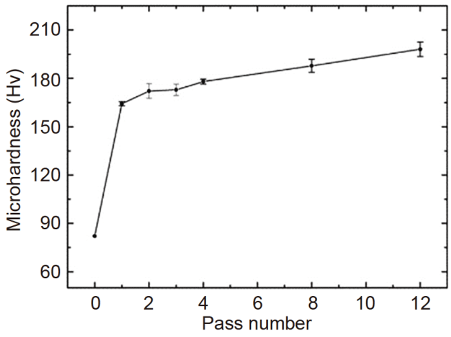

Figure 7 Microhardness evolution after ECAP processing [52].

Kheredine et al. [52] researched the evolution of hardness and microstructure in a commercial Cu-2.5Ni-0.6Si (wt.%) alloy during HPT process at room temperature and ECAP process at 423 K. The hardness increased gradually up to 195 HV after 12 passes ECAP without attaining saturation conditions, as shown in Figure 7. Li et al. [53] prepared microalloying Cu-Ni-Si alloy with Cr, Fe, Mo or Zr elements. After solid-solution treated at 950°C for 1 h plus water quenching, the alloys were aged at 450°C for different hours. The experimental results showed that those alloys exhibited excellent hardness (HV>1.7 GPa) and good electrical conductivity (≥35%IACS). Specifically, the quinary Cu-3.32Ni-0.93Si-0.37(Cr/Fe)-0.3Zr (wt.%) alloy possessed both high hardness with HV=2.55–2.67 GPa, and good electrical conductivity (35–36%IACS). Lei et al. [45] designed a kind of Cu-Ni-Si-Al alloy. After homogenization treatment at 940°C for 4 h, hot rolling by 80%, solid solution treatment at 970°C for 4 h, cold rolling by 50% and aging at 450°C for 1 h, the hardness reached 343 HV and electrical conductivity reached 28.1%IACS (Figure 8). Lei et al. [54,55] also designed a kind of Cu-6.0Ni-1.0Si-0.5Al-0.15Mg-0.1Cr (wt.%) alloy and after the same processing, the strength achieved 1090 MPa and conductivity reached 26.5%IACS. Wang et al. [51] researched the effects of Cr and Zr additions on microstructure and properties of Cu-Ni-Si alloy and founded best-integrated performance was obtained through co-addition of Cr and Zr elements. The UTS, elongation and electrical conductivity were 706 MPa, 9.5% and 48.2%IACS, respectively. Wang et al. [56] researched Cu-7.4Ni-1.3Si-1.2Cr (wt.%) alloy produced by powder metallurgy and found that the optimal heat-treated Cu alloy (solution heat treatment at 970°C for 8 h followed by aging at 450°C for 6 h) had a tensile strength up to 820 MPa and an average thermal conductivity up to 110 W m K^{-1}, as shown in Figure 9. Gholami et al. [57] used swaging to generate an ultrafine-grained microstructure in Cu-2.5Ni-0.5Si-0.06Mg (wt.%) alloy, along with an optimized precipitation hardening. As a result, an elongation to fracture of 14% and tensile strength of 800–900 MPa were achieved. Watanabe et al. [58] studied the Cu-2.5Ni-0.55Si alloy subjected to the solid solution, HPT processing, and aging, and combination properties of UTS 960 MPa and electrical conductivity 42%IACS was

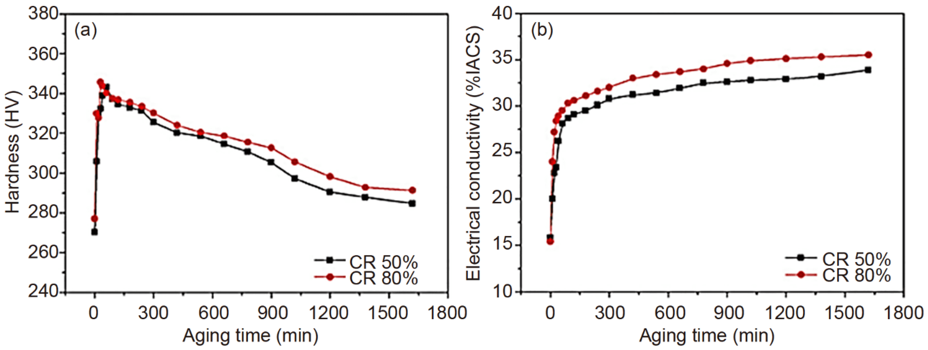

Figure 8 (Color online) (a) Hardness and (b) electrical conductivity of Cu-Ni-Si-Al alloys that underwent solution treatment and cold rolling followed by ageing at 450°C for different durations [45].

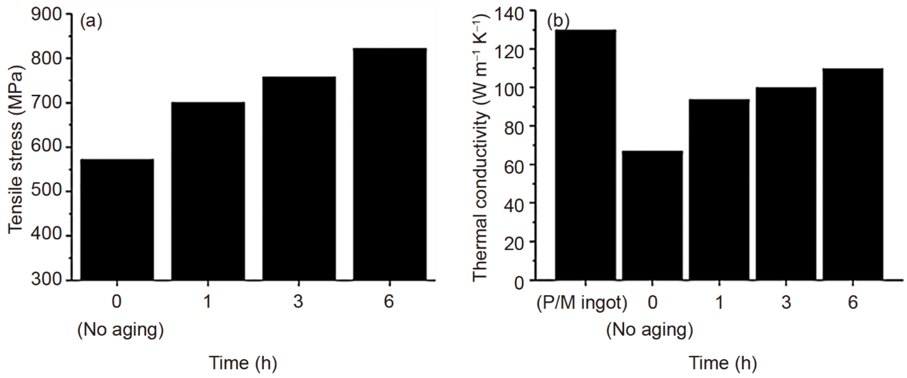

Figure 9 The variation in (a) tensile strength (b) thermal conductivity values of the alloy for various periods of aging [56].

obtained in the alloy aged at 300°C for 60 h. Liao et al. [59] investigated the effects of different cold rolling reduction rates on properties of the commercial C70250 Cu-Ni-Si alloy. Mechanical and electrical properties of the alloy under different cold rolling reduction rates are shown in Table 1, Huang et al. [60] fabricated a Cu-4.5Ni-1.2Co-1.0Si-0.15Mg alloy by a two-step thermo-mechanical treatment, and super-high strength (1111 MPa), high hardness (329 HV) and high electrical conductivity (30.2%IACS) were achieved.

In summary, Cu-Ni-Si system alloy is a typical kind of precipitation strengthening Cu alloy, which mainly uses a reaction between Ni and Si elements to precipitate compound phases. From the above review, we can see that Cu-Ni-Si system alloy has a relatively high hardness but a relatively low electrical conductivity. Thus how to control the addition ratio of Ni to Si to completely precipitate the alloying elements, that is, to purify the Cu matrix and increase the electrical conductivity, is a key consideration in the future research of Cu-Ni-Si alloy.

3.3 Cu-Ag system

Cu-Ag alloy has attracted considerable attention over the last twenty years due to their superior strength and good conductivity [61].

According to Benghalem et al. [62], when the content of Ag was less than 6 wt.%, the Cu-Ag alloy was composed of a single Cu-rich α-phase. When the content of Ag was more than 6 wt.%, Ag-rich solid-phase β appeared in the primary α-phase dendrite. At 6 wt.%–15 wt.%, the Cu-Ag microstructure mainly consisted of α phase of the Cu-rich solid solution and the eutectic phase (α phase + β phase), and the eutectic structures were discretely distributed at the dendrite gap to form an island. However, the microstructure of Cu-24 wt.% Ag is mainly composed of the Cu-rich phase and reticular eutectic structure. With the increase of Ag content to 71.9 wt.%, the entire microstructure becomes a eutectic structure composed of two phases of the α phase and β phase [63]. During cold working operations such as forging, drawing, swaging or rolling, two phases, a Cu-rich and an Ag-rich solid solution, are compressed and elongated, gradually form a fine, dense microcomposite structure. The strength of this micro composite structure increases strongly with the deformation degree [64]. If the cold working combined with the optimized intermediate heat treatment process, the alloy can achieve high strength while maintaining a relatively high conductivity [65,66].

Table 1 Mechanical and electrical properties of the commercial C70250 Cu-Ni-Si alloy under different cold rolling reduction rates [59]

Cold rolling reduction rates	UTS (MPa)	Electrical conductivity (%IACS)
0.25	302±5	21.5±0.1
0.5	379±6	21.0±0.1
0.75	447±10	21.8±0.2
0.975	601±12	22.3±0.1

Tian et al. [67] prepared a typical alternating distribution of Cu and Ag phases in eutectic Cu-71.9Ag (wt.%) alloys (Figure 10). Further study indicated that when the layer thickness of the Cu/Ag phase was about 50 nm, the yield strength could reach about 400 MPa. Cu-28Ag (wt.%) alloy was twisted 20 times by the HPT method, and a nano-scale Cu-Ag composite material with a tensile strength of 1420 MPa was obtained [68]. Tian et al. [69] also found that a tensile strength of 720 MPa was obtained in the Cu-8Ag (wt.%) alloy after 8 passes ECAP. A banded structure was observed on the transverse section, and the tensile strength of the Cu-8Ag (wt.%) alloy reached up to about 1.1 GPa after HPT (Figure 11). Freudenberger et al. [70] prepared Cu-7Ag (wt.%), Cu-24Ag (wt.%) and Cu-Ag-Zr (wt.%) alloys. The Cu-Ag and Cu-Ag-Zr alloys were homogenized and subsequently water-quenched. Further heat treatment of 400°C was used for 4 h to execute the precipitation reaction. Finally, deformation was carried out by rotary swaging, hot forging and drawing. Results showed that UTS of the materials was more than 1.1 GPa at room temperature (Table 2). Chang et al. [71] found the UTS and yield strength of hot-

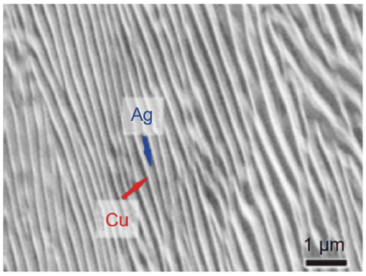

Figure 10 (Color online) Secondary electron map of Cu-Ag alloy [67].

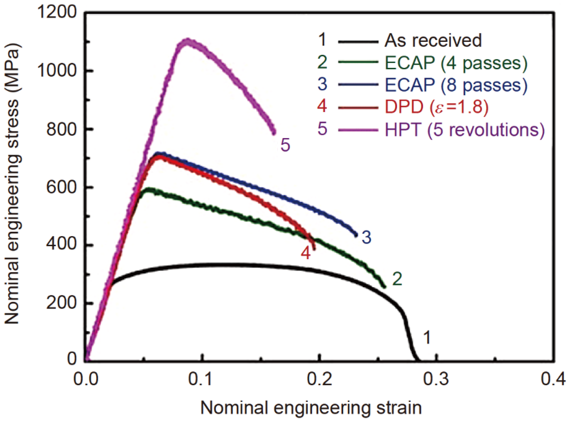

Figure 11 (Color online) Tensile engineering stress-strain curves for the Cu-8Ag alloy in the as-received condition and after processing by ECAP, DPD and HPT [69].

extruded Cu-0.1Ag (wt.%) alloy were 168 and 75 MPa, respectively. Its elongation was about 38%. After cold drawing, the yield strength was improved to be 280 MPa and the elongation was decreased to be 11%. Bernasconi et al. [72] prepared Cu-Ag alloys by the electrodeposited method. Different Ag percentages (range from 3 to 15 at.%) were obtained by controlling the deposition conditions. These as-deposited alloys exhibited high hardness. Particularly in the Cu-15.4Ag (at.%) alloy, as shown in Figure 12, hardness as high as 628 HV was attained. Bao et al. [73] systematically investigated the UTS of Cu, Cu-2Ag (wt.%) and Cu-6Ag (wt.%) versus drawing strain. It was found that when the drawing strain was 6, the strength of Cu-6Ag (wt.%) reached about 1240 MPa, more than twice of the UTS of pure Cu, as shown in Figure 13. Micro-alloying is an effective way to strengthen the Cu-Ag alloy without an obvious decrease in the conductivity. Zhang et al. [74] prepared Cu-6Ag-1Cr (wt.%) alloy with a strength of 1200 MPa and conductivity above 60%IACS. According to Liu et al. [75], 0.3 wt.% rare earth elements were added to Cu-12Ag (wt.%), and high-stress concentration and dislocation density appeared in the Ag fiber regions, resulting in a substantial strengthening of the alloy.

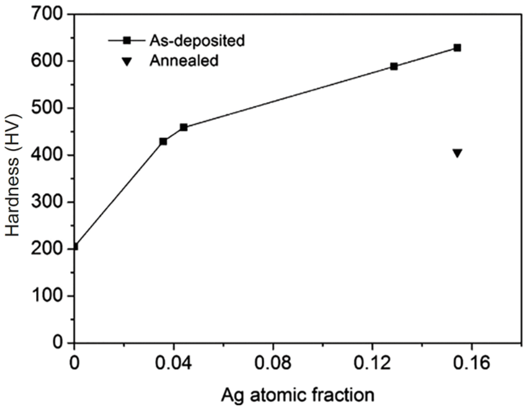

Figure 12 Vickers hardness of as-deposited and annealed Cu-Ag samples [72].

The above review shows that Cu-Ag alloy own a quite high strength. But the Cu-Ag alloy is often strengthened by a large degree of deformation so that the softening resistance needs to be further characterized.

3.4 Cu-Mg system

There are two main reasons why researchers focus on the Cu-Mg system alloy, one is that Mg affects weakly on the electrical conductivity of Cu [76], and the other reason is Mg can provide several degree of freedom to generate microstructures (driving forces for precipitation, eutectic transformation) in contract with Cu-Cr and Cu-Ag. Studies of Cu-

Table 2 Mechanical properties of cold drawn Cu-7Ag, Cu-24Ag and Cu-Ag-Zr materials at 77 K and room temperature, respectively. б$_{UTS}$: ultimate tensile strength, б$_{yp}$: yield strength, E: Young's modulus and $\varepsilon_{pl,UTS}$: plastic strain at б$_{UTS}$ [70]

Mechanical properties	Cu-7Ag		Cu-24Ag		Cu-Ag-Zr	
	77 K	300 K	77 K	300 K	77 K	300 K
б$_{UTS}$ (MPa)	1369 (±4)	1141 (±7)	1318 (±42)	1087 (±3)	1367 (±44)	1174 (±7)
б$_{yp}$ (MPa)	1276 (±18)	954 (±43)	1251 (±30)	994 (±10)	1302 (±26)	1064 (±9)
E (GPa)	117 (±2)	111 (±5)	121 (±8)	104 (±7)	126 (±5)	109 (±4)
$\varepsilon_{pl,UTS}$	0.4 (±0.1)	0.7 (±0.1)	0.4 (±0.1)	0.8 (±0.1)	0.4 (±0.1)	0.7 (±0.1)

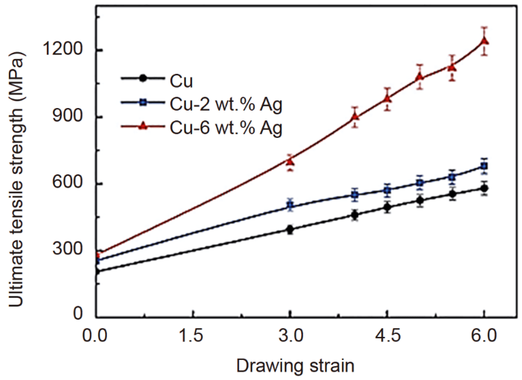

Figure 13 (Color online) UTS versus drawing strain of Cu, Cu-2Ag (wt.%) and Cu-6Ag (wt.%) alloys [73].

Mg system alloy are mainly limited to the aging properties of micro-alloy composition [77–79]. There are many experimental and thermodynamic descriptions of Cu-Mg system alloy in refs. [80–82]. Recent results agree that the Cu-Mg alloy consists of the liquid, Cu solid solution, Mg solid solution, and the intermetallic compounds Cu_2Mg and $CuMg_2$. The solid solubility of Mg in the Cu matrix decreases sharply with the decrease of temperature; thus Cu-Mg alloy has a precipitation strengthening effect. But due to the emergence of the second phase, the machinability of the alloy declines significantly, leading to little practical value. Therefore, the Mg content in Cu-Mg alloy should be less than 1% in the practical application.

Gorsse et al. [83] prepared Cu-Mg alloys with different Mg contents (4.1 at.%, 8.1 at.%, 23.1 at.%). It was found that with the increase of Mg content, the strength of the alloy increased and the conductivity decreased, it was attributed to the high density of Cu_2Mg nanoparticles precipitate (Figure 14). Ma et al. [84] prepared Cu-0.2Mg (wt.%) by ECAP method, found that more ECAP passes led to finer grains. As shown in Table 3 and Figure 15, Cu-0.2Mg (wt.%) alloy exhibited excellent tensile strength (583.4 MPa), high elongation (37.9%) and high conductivity (84.5%IACS) after ECAP 473 K. Zhu et al. [85] obtained the ultrafine-grained Cu-Mg alloy by the combination of 4 passes ECAP plus cold working process. The tensile strength of the Cu-0.2Mg (wt.%) and Cu-0.4Mg (wt.%) alloys were 574.8 and 627.4 MPa, respectively. The electrical conductivity of the Cu-0.2Mg (wt.%) and Cu-0.4Mg (wt.%) alloys were 81.5%IACS and 72.4%IACS, respectively. Their values increased to around 87% and 80%, respectively, after annealing treatment (Figure 16). Li et al. [86] studied the Cu-0.29Mg-0.21Ca (wt.%) alloy and found that its average grain size after cold working reached 400 nm. The Cu-0.29Mg-0.21Ca (wt.%) alloy showed excellent combination properties that the tensile strength was 545 MPa and electrical conductivity was 71.79%IACS.

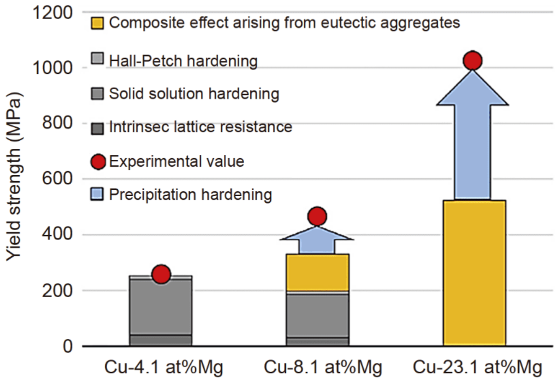

Figure 14 (Color online) Calculated strengthening contributions for the casted Cu-Mg alloys. Cu-4.1Mg is a single-phase fcc-Cu(Mg) solid solution; Cu-8.1Mg is composed of fcc-Cu(Mg) and eutectic aggregates, and Cu-23.1Mg consists of fully eutectic structure [83].

Table 3 Mechanical properties of the samples ECAPed at 473 or 673 K [84]

Sample	Microhardness (HV)	Ultimate tensile stress (MPa)	Total elongation (%)
Conform	102.6	286.4	66.7
473K-4P	162.9	333.2	24.7
473K-16P	201.2	583.4	37.9
673K-4P	150.9	365.5	22.5
673K-16P	168.6	461.1	26.9

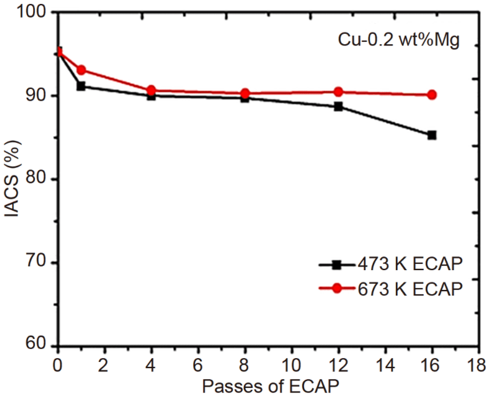

Figure 15 (Color online) Conductivity of Cu-0.2Mg alloy variation with the passes of ECAP at 473 and 673 K [84].

In general, Cu-Mg system alloy is a relatively mature kind of alloy used in numerous industrial fields such as electrified railway contact wires. Due to that its composition and fabrication process is relatively simple, it can be adapted to large-scale industrial production. Solid solution strengthening, aging strengthening, and deformation strengthening are the main strengthening methods applied for Cu-Mg alloy. In the future, it is worthwhile to further improve the properties of the alloy by micro-alloy adding such as Ca, and Zr.

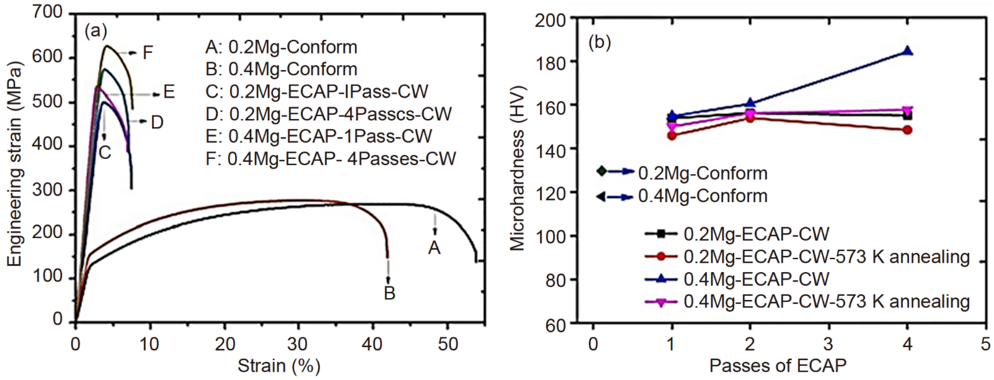

Figure 16 (Color online) Effect of the processing on (a) stress-strain curves and (b) conductivity of the Cu-Mg alloys [85].

3.5 Cu-Nb system

Cu-Nb system alloy has been widely investigated due to its high strength, high conductivity and mechanical workability [87]. The combination of these properties makes this particular material very attractive for applications in the high-field magnet technology and many other fields [88].

Most studies relate the high strength to the microstructures refinement and the crystal structures difference between Cu and Nb in Cu-Nb alloy [89,90]. Moreover, some references [91,92] stated that both the strength and conductivity were strongly dependent on the Nb content, while others [90,93,94] suggested that the spacing between filaments or interfaces dominated the strength. In addition, several studies [95–97] aimed to reveal the impact of texture on strengthening mechanisms. Cu grains in Cu-Nb wires containing Nb nanoribbons were reported to develop a ⟨111⟩ and ⟨100⟩ fiber texture while Nb developed a ⟨110⟩ fiber texture [95] during wire drawing. But both ⟨111⟩ and ⟨100⟩ fiber textures were weakened when the materials were exposed to a large strain, due to the dynamic recovery and recrystallization.

Liang et al. [98] fabricated Cu-16Nb (vol.%) composites by bundling and drawing process. In Figure 17, the structure of Cu-Nb micro composites was a Cu matrix embedded with 5×10^7 continuous Nb nano-fibers with a diameter of 100 nm. Their results showed that the UTS of the composites reached 932 MPa, while the electrical conductivity was as high as 73%IACS, as shown in Table 4. Botcharova et al. [99] prepared Cu-Nb alloy by mechanical alloying and heat treatments. The microhardness of the alloy with a low oxygen content treated at 700°C was about 470 HV, corresponding to the UTS of 1.5 GPa. Lei et al. [100] investigated the mechanical properties and microstructural evolution of the Cu-xNb (x=5, 10, 15, 20 wt.%) powder mixtures during milling. The results showed that the solid solubility of Nb in Cu alloy could be extended to more than 10 wt.% by mechanical alloying at room temperature. The grain size of Cu decreased with milling time increasing, and it could approach 13 nm in Cu-5Nb (wt.%) and 7 nm in Cu-20Nb (wt.%) after milling for 100 h. The maximum microhardness value was about 4.8 GPa when Cu-20Nb (wt.%) alloy was milled for 100 h. Lei et al. [101] also prepared a nanocrystalline Cu-10Nb (wt.%) alloy. The preparation process was hydrogen-annealing the milled Cu, Nb powders at 560°C for 1 h, then vacuum hot-pressing sintering under the pressure of 30 MPa at 900°C for 2 h. Finally, the alloy had a microhardness of 334 HV, a tensile strength of 1102 MPa, and an electrical conductivity of 57%IACS.

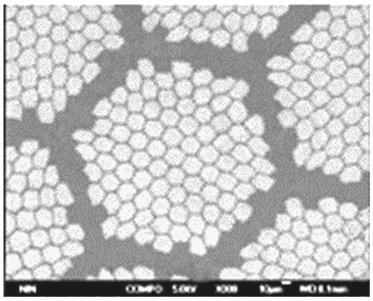

Figure 17 SEM morphology of Cu-Nb microcomposites by bundling and drawing processes [98].

Table 4 Properties of the composites [98]

Cu-16vol.%Nb	Electrical conductivity (%IACS)	UTS (MPa)
300 K	73	932
77 K	391	1090

In short, Cu-Nb alloy has very high strength and is widely used in high-field magnet technology and many other fields. Researchers have done deep researches on Cu-Nb alloy in the early days and fewer researches in recent years.

4 Summary and outlook

HSHC Cu alloys, as a kind of significant structural-functional material, has been widely applied in various fields.

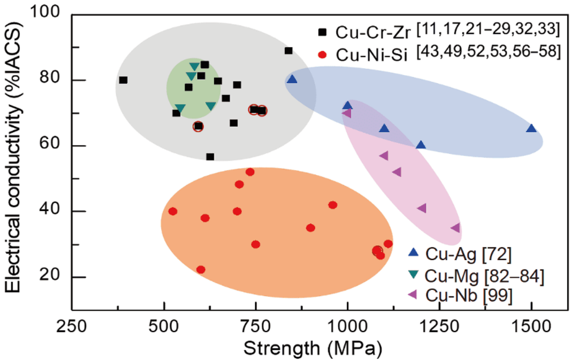

Figure 18 (Color online) The electrical conductivity versus the strength of Cu alloys and Cu matrix composites (some strength values are calculated as 3.5 times of the hardness values, marked with red circle).

The electrical conductivity versus the strength of Cu alloys and Cu matrix composites summarized in this review are shown in Figure 18.

To sum up this review combine with Figure 18, we can draw the following conclusions and prospects.

(1) Precipitation strengthening method is still the main way to produce HSHC Cu alloys. Multiple composite micro-alloying technologies have also drawn more and more attention, which is regarded as an effective means to further improve the overall performance of HSHC Cu alloys.

(2) HSHC Cu alloys require more than just conductivity and strength, but rather a combination of other physical properties. For example, lead frame materials are required to have high strength and high conductivity and better heat resistance, corrosion resistance and oxidation resistance. In addition, residual stress, linear expansion coefficient, machinability, and welding performance also have higher requirements in certain applications.

(3) The ultimate goal of developing high strength and high conductivity Cu alloy is to provide high quality and low-cost conductive Cu alloys for the industrial sectors such as electric power, transportation, and machinery manufacturing. Therefore, the development of HSHC Cu alloys must take into account the trend of industrialization and large-scale.

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