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REVIEW OF MODERN METHODS FOR IMPROVING COMPLEX PROPERTIES OF Cu-Cr ALLOY

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Annotation

This article describes modern techniques for producing a Cu-Cr alloy for various applications. From modern articles, the latest methods of alloying with elements are described, which allow improving the strength characteristics at the same time, while maintaining or even increasing the electrical conductivity of the alloy. As another method for improving the properties of an alloy, applications of severe plastic deformation are described in detail.

Keywords: Copper, chromium, alloy, strength, electrical conductivity, micro hardness, aging.

Introduction

High strength and high conductivity are two internal properties that are difficult to combine in a metal alloy structure, because: almost all hardening mechanisms lead to a decrease in electrical conductivity. Dispersion hardening with nanoscale particles turned out to be the best way to achieve an optimal combination of strength and conductivity in copper-based alloys. However, the known dispersion-hardening copper alloys are limited by the concentration of dissolution of substances, which limits the volume fraction of hardening released particles of the second and third phases.

It was found that rapid solidification in the cast tape led to an increase in solubility and grinding of chromium-rich phases. The X-ray diffraction pattern data suggest that the Cr content in the solid solution was up to 6 wt.%. Certain parameters of the crystal lattice confirmed the multiple expansion of the Cr solid solution into Cu. Studies of thermal aging of cast tapes have shown that peak aging occurs after about twenty minutes. The peak hardness at exposure ranged from 200 to more than 300 HV. The maximum peak aging hardness of 380HV was obtained for an alloy containing 6 wt. % Cr, but with a conductivity of about 50% IACS. The best combination of strength and electrical conductivity was obtained for an alloy of 4 masses % Cr with a hardness of 350 HV and a conductivity of 80% IACS (Figure 1,2). The observed high strength is explained by the increased volume fraction of semi-coherent nanosized particles with a high chromium content, which were formed from an oversaturated Cu-Cr solid solution, which was achieved due to high cooling rates due to the casting process of the tape.

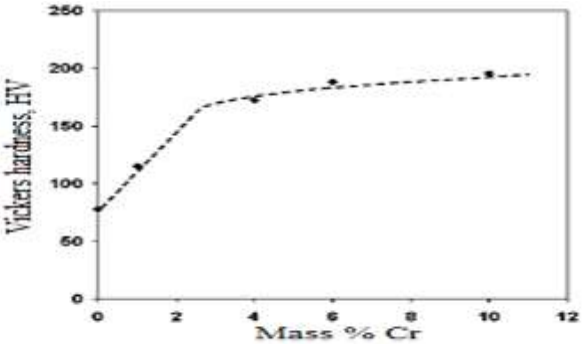

Figure 1. The effect of the mass content % Cr on the hardness of the cast tape.

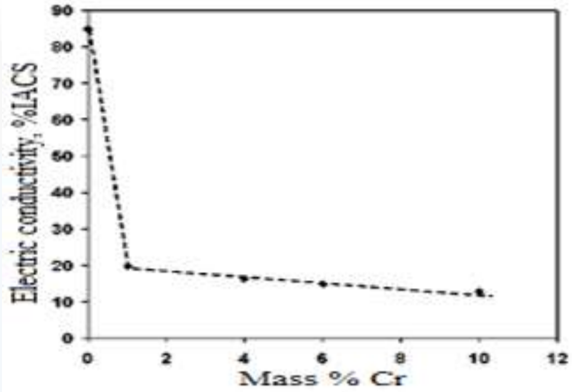

Figure 2. The effect of the mass content % Cr on the electrical conductivity of the cast tape

Methods of Obtaining the Alloy

Cu-1.56% Cr alloy was prepared for the study. Its structure at different stages of aging was observed using transmission electron microscopy. At the initial stage, a modulated structure was discovered, which is an ordered intermetallic phase, called modulated structure I, and another modulated structure, called modulated structure II, was discovered after aging at 500 °C for 45 min. The results show that the sequence of particle separation in the Cu-Cr alloy during aging does not refer to the traditional direct transformation from the HCC structure to the BCC, but to the sequential and gradual transformation of the modulated structure into another modulated structure.

In a modified mill, a Cu–Cr alloy was obtained by mechanical alloying of the powder. The results showed that the cooking temperature is much lower using a modified mill than with traditional equipment. Also, no differences were found in the obtained alloys prepared using a vibrating and planetary mill. Activated carbon powder was found to exhibit excellent reducing ability for metal oxides, while graphite powder was found to be unacceptable for this process. Based on the experimental results, a nanoscale Cu–Cr alloy grain can be obtained by mechanical alloying in a modified mill at 325°C for 3 hours with a mass ratio of 15:1. The phenomenon of crystal agglomeration was also detected in the alloy powder, leading to an increase in the particle size.

Cu-1.37%Cr alloy powders were prepared by gas spraying, and the cooling rates of the alloy powders were calculated using the principle of convective heat transfer. The morphology, distribution of alloy elements, and microstructure of Cu-1.37%Cr alloy powders were characterized using an X-ray diffractometer and a scanning electron microscope. The results showed that with an increase in the cooling rate from 9.75 = 103 K /s to 1.08 = 105 K / s, the grain size decreases from 150 to 45 microns. The morphology of the alloy powders has a spherical or similar spherical shape together with smooth surfaces.

The grains have a uniform size, and the Cr particles are evenly distributed in the Cu matrix. With a decrease in particle size, the diffraction angle shifts by a small angle, which indicates a greater solubility of Cr in the Cu phase.

In a supersaturated solid solution of Cr in Cu with a subnanometer-sized structure was successfully synthesized by mechanical alloying. The prepared alloy Cu-60 wt. % Cr contains crystalline and amorphous phases, and a sample ground for 40 hours contains more than 50 kJ/mol of stored energy. This high energy provides the thermodynamic driving force needed to achieve doping, and it is mainly caused by the abundant free volume in the amorphous structure. In addition, the grinding process generates many diffusion channels that facilitate the diffusion of disordered Cu atoms into the Cr matrix, thereby improving doping. The diffusion of Cr atoms into the Cu lattice is very difficult, even when a large number of defects are present in the Cu lattice.

Application of Alloying and Other Methods to Improve Properties

The study of the properties of the Cu-Cr-Zr-Mo alloy yielded the following results the micro hardness of the "insitu" composite Cu-0.85%Cr-0.5%Zr-0.5%Mo increases rapidly at the initial stage of aging, and then decreases with increasing exposure, and the electrical conductivity increases with increasing aging time and temperature. The best combination of hardness and conductivity is achieved at 500 °C for 4 hours, and the values of micro hardness and electrical conductivity are 171 HV and 81.3% IACS, respectively (figure 3).

The release of the secondary phase can be accelerated by cold deformation before aging. Cu-Cr-Zr-Mo composite in situ demonstrates high strength and high conductivity only after aging treatment and plastic deformation. The separation of alloying element particles from the supersaturated copper matrix leads to an increase in electrical conductivity and micro hardness. Cold deformation can accelerate the release of Cr, Zr, or Mo from the copper matrix, since dislocations act as heterogeneous centers and nucleation centers. The influence of Ad on the microstructure and mechanical properties of cast, cold-rolled and aging-treated Cu-Cr alloys was investigated in this paper. The results showed that the addition of a small amount of Ag significantly improves the mechanical properties of Cu-Cr alloys with little effect on electrical conductivity.

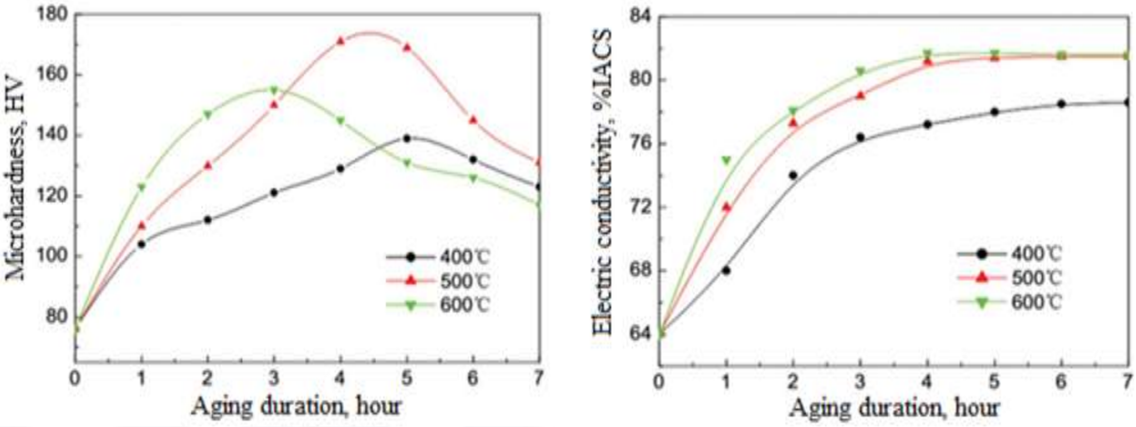

Figure 3. Changes in the micro hardness and electrical conductivity of the alloy at different aging temperatures

By means of induction melting with an intermediate frequency under non-vacuum conditions, at 1000 °C for 60 minutes of solid solution treatment, 95% of cold rolling deformation and 400 °C aging treatment for 90 minutes, the Cu-0.89% Cr-0.44%Ag alloy showed excellent mechanical characteristics and conductive properties – a tensile strength of 541.5 MPa and a specific electrical conductivity of 83.2% according to IACS. Rapid solidification and mechanical alloying can provide a high degree of metastability and microstructure improvement. In the study these two methods are applied to Cu-Cr alloys. Compared in terms of microstructure and mechanical properties obtained after molding from a melt and subsequent pressing by extrusion of powders obtained by rapid solidification and mechanical alloying. Supersaturation does not exceed 2 at % Cr, since primary chromium particles are formed directly from the melt. During high-temperature processing or extrusion, the bimodal distribution of small secretions and large primary particles becomes unstable, and small secretions dissolve into larger particles. Mechanical alloying ensures uniform distribution of almost all chromium used. Accordingly, the few remaining large particles play an insignificant role in influencing the stability of the microstructure, and the structure and properties are preserved to higher temperatures than for rapidly solidified materials. Thus, in this case, mechanical alloying provides significant advantages over rapid solidification. Cu-Cr Ti alloys with different Ti content were obtained by induction melting in vacuum, cold deformation and aging. The microstructure, mechanical and electrical properties of Cu-Cr Ti alloys have been studied at different Ti contents. The results show that an increase in the Ti content can improve the mechanical properties of Cu Cr Ti alloys, while its conductivity is significantly reduced. After cold rolling by 80% and aging at 500 °C for 60 minutes, the hardness, electrical conductivity and tensile strength of the Cu-0.3% Cr-0.05%Ti alloy are 162.6 HV, 82.2% IACS and 510 MPa, respectively. The hardening mechanism of the studied alloys is mainly related to the Orovan mechanism and dislocation hardening. As a conclusion, it was found that the addition of Ti can slow down the growth and enlargement of the allocation of Cr in the aging process. Magnesium was added to the Cu-Cr alloy to overcome the traditional limitations of expensive and large-scale production of Cu-Cr alloys and to reveal the mechanism of Mg's effect on the microstructure and properties of the Cu-Cr alloy. The effect of magnesium on the microstructure and properties of the Cu-Cr alloy was investigated by hardness testing, electrical conductivity measurements, and microstructure studies on a transmission electron microscope. The separation sequence of the Cu-Cr-Mg alloy was similar for the Cu-Cr alloy. Magnesium in the Cu-Cr alloy additionally accelerated the process of excretion nucleation, restrained growth due to segregation on the surface of secretions during aging. This increased the stability of the microstructure and improved the mechanical properties of the alloy. Cu-Cr-Mg alloy showed high complex properties and characteristics of softening resistance than Cu-Cr alloy at elevated temperature. After aging at 480 °C, Cu-Cr-Mg alloy had a tensile strength of 540 MPa and an electrical conductivity of 79.2% on the IACS scale for peak aging states, as well as a tensile strength of 515 MPa and an electrical conductivity of 80.8% IACS after 4 hours of aging. Figure 4 shows the change in the hardness of HV during aging.

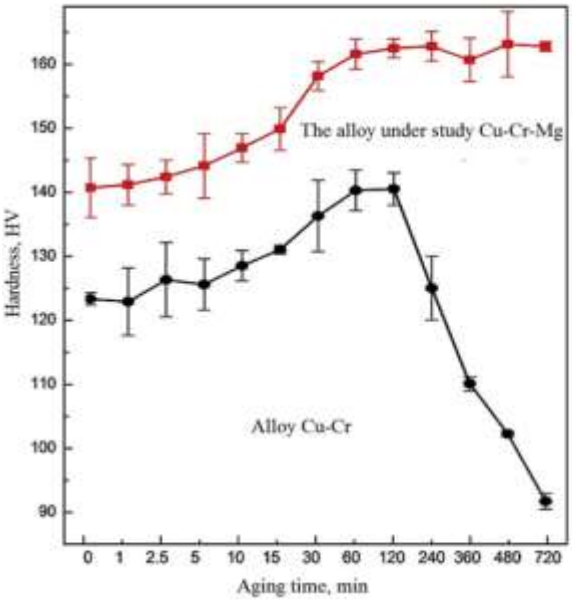

Figure 4. Change in HV hardness during aging

Alloys Cu-0.57% Cr-0.01% Ca and Cu-0.58% Cr-0.01% Zr (wt.%) were manufactured and processed by thermomechanical treatment. Their mechanical and electrical properties and microstructure were studied in detail and compared with the properties of Cu-0.57% Cr alloy. The results showed that the softening resistance of the Cu-Cr alloy was significantly improved by the addition of Ca and Zr elements. Compared to the Cu-Cr alloy, the deformed microstructure of Cu-Cr-Ca and Cu-Cr-Zr alloys is more difficult to recrystallize at elevated temperatures, and the Cr released in the alloys was smaller in size and had a FCC structure during aging. The high strength of Cu-Cr-Ca and Cu-Cr-Zr alloys is mainly due to dislocation hardening provided by high-density dislocations and hardening by small Cr particles. The study showed that the segregation of Cu and Zr atoms at the interface between Cr particles and the copper matrix is favorable from the point of view of energy. This segregation effectively prevented the growth of Cr particles and significantly enhanced the effect of fixation on the movement of dislocations and subgrain boundaries, which ultimately led to an increase in the resistance to softening of the Cu-Cr alloy.

The effect of the use of intensive plastic deformation (IPD) and thermomechanical treatment (TMO)on the properties of the alloy

The effect of TMO on the mechanical and electrical properties of the Cu-Cr-Zr alloy was experimentally investigated in this work. The mechanical properties of the alloy improved as a result of cold treatment and aging, but the electrical conductivity mainly changed depending on the aging temperature. In addition, the mechanical and electrical properties of the alloy changed due to the interaction of material hardening mechanisms depending on the TMO. The increase in strength was associated with deformation hardening caused by cold treatment. Aging can be effective for improving both the mechanical and electrical properties of the alloy due to isolation, but may be accompanied by the restoration of the deformed alloy. Therefore, it would be effective to increase the strength of the alloy due to aging and cold processing. On the other hand, it can advantageously ensure the ductility and electrical conductivity of the alloy by applying cold treatment and aging. According to this study, the above process used after aging for Cu-Cr-Zr alloy can yield 529.4 MPa with 78.6% IACS.

Grain grinding by intensive plastic deformation (IPD) is an effective means of improving the mechanical characteristics of chrome, zirconium and hafnium bronzes. The formation of ultrafine-grained (UMZ) microstructures in copper-chromium alloys has led to an improvement in durability, wear resistance and fatigue strength, which are important operational characteristics when used for contact welding electrodes and switching devices. One of the most effective methods of SPD when grinding grain is high-pressure torsion (HPD). Previous work has shown that the use of CVD can reduce the grain size to 10 nm due to significant hardening of alloys with a high Cr content. At the same time, IPD usually leads to a decrease in electrical conductivity due to the high density of grain boundaries. Changing the microstructure by additional heat treatment after IPD can lead to an improvement in electrical conductivity while maintaining high strength. Most likely, the Cr content in Cu significantly affects the effectiveness of these procedures in achieving optimal properties. In this work the possibility of processing KVD and subsequent heat treatment to obtain a combination of high strength and good electrical conductivity in chrome bronzes with different Cr contents – 0.7%, 9.85% and 27% was demonstrated. The following results were obtained in the work:

1. The treatment of copper-chromium alloys with CVD leads to significant hardening due to the formation of the UMP microstructure. With an increase in the Sgm content, the microhardness increases from about 1700 to 2700 MPa due to a decrease in the average grain size from ~ 209 to ~ 40 nm, as well as an increase in Cr content,

dislocation density and the presence of deformation twins. The electrical conductivity decreases with increasing Cr content due to the greater number of grain boundaries.

2. Heat treatment after KVD leads to a gradual decrease in hardness and an increase in electrical conductivity. With a high Cr content (9.85% and 27%), the appropriate choice of heat treatment temperature allows you to maintain high hardness with a significant increase in electrical conductivity. A significant improvement in electrical conductivity can be explained by the release of Cr and relaxation of grain boundaries. This study demonstrates the possibility of CVD processing and subsequent heating to obtain both high hardness and electrical conductivity in Cu-Cr alloys.

Table 1. Electrical conductivity and microhardness of alloys.

Alloy	Processing	Initial state		KVD		KVD and vacation *	
		HV (MPa)	% IACS	HV (MPa)	% IACS	HV (MPa)	% IACS
Cu-0.7%Cr	Tempering	804±38	39	1740±74	34	1830±36	35
	Annealing	1000±36	86	1612±38	61	1435±30	72
Cu-9.85%Cr	Tempering	1270±67	37	2140±22	29	1753±44	67
	Annealing	1268±104	63	2107±87	54	1892±137	76
Cu-27%Cr	Cast condition	1402±79	41	2698±90	20	2638±109	42

The influence of the direction of the ND by means of equal-channel angular pressing on grain grinding and structural features of the Cu–Cr alloy has been studied from the point of view of grain shape, size, preferred crystallographic orientation and grain boundary distribution relative to the misorientation angle. The mechanical behavior of samples with various treatments is evaluated both in monotonous and cyclic tests aimed at clarifying the role of various structural factors in the resulting mechanical properties. It has been found that despite significant microstructural differences in grain morphology and texture, the tensile strength and fatigue of processing routes are only slightly affected. However, the choice of the direction of deformation gives small changes in the shape and texture of the grains, as well as some influence on plasticity, which is especially noticeable during cyclic loading.

High strength and high conductivity were achieved in rapidly hardening Cu-Cr alloys with a high Cr content. Rapid solidification indicates an increase in solubility in solids and the grinding of the second Cr phase. The hardened tape was subjected to peak aging to obtain a combination of hardness above 300 HV, which would correspond to a yield strength of 900 to 1000 MPa and a conductivity of 70% IACS. However, these alloys wear out quickly. The combination of chemical potential and hardening in vacancies made it possible to create a favorable atmosphere for germination and growth of the second phase secretions. It is believed that it is possible to stop the growth of the released particles by further alloying with transition elements, which, as is known, merge into stable particles.

In the effect of phosphorus on the Cu-Cr alloy was investigated and the following conclusions were made:

1) in alloys, it was found that the Cr phase with a size of 10-20 nm strengthens the alloy by the Orovana mechanism, and the Cr phase with a size of less than 5 nm strengthens the alloy by coherent hardening;

2) For Cu-Cr-P alloys, the Cr content should be controlled within a certain range to obtain suitable strength and electrical conductivity. When the P content was about 0.01 wt. %, the Cr content should be in the range of 0.36-0.63 wt. %;

3) The tensile strength and electrical conductivity of the Cu-0.36%Cr-0.01%P alloy was 572 MPa and 80% IACS, respectively, after solid solution separation after heating at 980 °C for 2 hours, followed by 95% cold rolling, and subsequent aging at 450 °C for 1 hour. These results are comparable with the properties of Cu–0.6%Cr–0.3%Zr alloy.

Studies have been conducted on the effect of Zr-containing phase isolation on the properties of Cu-Cr-Zr alloy after treatment on solid solution at 1253 K for 2 hours and aging at 763 K for 0-6 hours. The following conclusions were made:

1) the sequence of isolation of Zr-containing secretions in the Cu-Cr-Zr alloy is a supersaturated solid solution rich in Zr atomic clusters and Cu-Zr phases;

2) in the aging process, Zr atoms first segregate in the crystal plane of the copper matrix and form coherent Zr-rich atomic clusters, which consist of monolayers of Zr atoms and have a lamellar shape. Some of the clusters transform into the metastable phase of the Cu-Zr phase with increasing aging time, the crystal plane.

3) The contribution of atomic clusters with a high Zr content and the Cu-Zr phase to the yield strength of the alloy is calculated by coherent hardening and Orovane hardening.

The microstructure and electrical and mechanical properties of Cu-1.3%Cr and Cu-2.5%Cr samples made with optimal laser melting parameters were studied. Subsequently, the effect of heat treatment on the microstructure and properties of the samples was studied.

Conclusion

At the end of the article, I would like to note that the Cu-Cr alloy we are studying has not yet been fully studied. Studies conducted by various researchers prove once again that the study of this alloy has not yet reached its maximum, and no one has yet come to a consensus. The reason for this is the various methods used to obtain the alloy, alloying with various metals and elements, the use of various IPD methods by each individual author and researcher. Also, do not forget that different temperatures for aging allow you to obtain high mechanical properties in combination with electrical conductivity without the use of IPD, which complicates the tasks and makes the work much more interesting.

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