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Arc erosion resistance of CuCrMo films deposited via magnetron sputtering

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Abstract

Copper-chromium (CuCr) alloys are widely used as electrical contact materials, and their arc erosion resistance can be improved by reducing the sizes of the Cu and Cr phases or by adding Mo. In this study, supersaturation solid solutions of CuCr and CuCrMo films were prepared via magnetron sputtering. After annealing at 773 K, the CuCr and CuCrMo films are composed of a small Cu-rich face-centred cubic phase and a Cr-rich body-centred cubic phase. Meanwhile, the addition of Mo reduces the diffusion rate during annealing. The lattice distortion of the CuCrMo thin film exceeds that of the CuCr film, and the elastic modulus and hardness increase. Compared with those of the CuCr film, the erosion area of the CuCrMo film is larger, and the depth of the erosion pit is lower. The arc erosion experiment proved that CuCrMo films exhibit satisfactory arc erosion resistance.

1. Introduction

The electrical contact materials of vacuum circuit breakers require a high electrical and thermal conductivity, high breakdown strength, low chopping current, and also high welding resistance and suitably mechanical properties. Copper-chromium (CuCr) alloys exhibit the aforementioned properties and are widely used in vacuum circuit breakers. With the development of vacuum circuit breakers, more stringent requirements are expected for contact materials.

Preparing CuCr alloys with fine and uniform structures as well as high density is one of the main methods to improve the properties of CuCr alloy contact materials. Rieder [1] showed that refining the particles in the Cr phase can effectively improve the hardness and breakdown strength of the alloy while reducing the chopping current, and that refinement of Cr particles can also increase the breakdown strength of CuCr alloys [2]. When Durakov [3] compared different CuCr alloy preparation processes, it was found that the size of primarily precipitated Cr particles decreases from 50–150 mm to 1.8 mm and that of the secondarily precipitated particles decreased from 1 mm to 0.500 mm; moreover, the chopping current of the CuCr alloy decreased. Yang [4] compared the arc erosion performance of micron and nanocrystalline CuCr5 alloys. On the microcrystalline CuCr5 alloys, the cathode spots were concentrated in the Cr phase, and the chopping current was high. For the nanocrystalline CuCr5 alloy, the cathode spots move smoothly and continuously on the surface without concentrated ablation, the arc is stable, and the chopping current is reduced by approximately 50%. Yu [5] used a high-speed camera to observe the cathode spot distribution of nanocrystalline and coarse-grained CuCr25 alloys. Under the same current and switching conditions, the number and size of cathode spots on the surface of the nanocrystalline CuCr25 alloys were much more and smaller, respectively, while the cathode spots on the nanocrystalline surface were uniformly distributed. The average current value of each cathode spot on the surface of the material was approximately 33% of that of the microcrystalline material, which indicates that the nanocrystalline material had a better arc ablation resistance. According to Munz [6], the CuCr50 alloy cathode...
material with a nanoscale grain distribution has a higher arc movement rate and a lower ablation rate than that with coarse grains. After 200 vacuum breakdown cycles, the surface ablation pit depth of the coarse-grained material was 7–8 times that of the nanocrystalline material, which proves that the nanocrystalline CuCr alloy had a strong arc ablation resistance.

Doping a third component into an alloy is also a feasible approach for improving the performance of contact materials. For example, in CuW alloys, doping La$_2$O$_3$ particles can not only inhibit the growth of the W skeleton and refine the W grains but also improve the arc stability and arc ablation resistance of the CuW alloy owing to its low work function [7]. Doping elemental Te into CuCr alloy leads to the Cr phase being well-distributed in a spherical shape, which can improve the welding resistance and reduce the chopping current because of the formation of more microstructural defects; however, it also leads to a decrease in the hardness of the alloy [8, 9]. Doping Mo into Cu can increase the hardness of the alloy, refine the grain structure without changing the electrical conductivity, and improve the withstand voltage and breaking capacity of the CuCr alloy [10].

Notably, CuCr alloys with fine sizes and a uniform distribution of Cu and Cr phases are difficult to produce via traditional CuCr alloy preparation techniques, such as infiltration, arc melting, and hot press sintering, owing to the limitations of these methods. Shen et al first prepared a CuCr composite powder with an average particle size of 25–35 nm through mechanical alloying, followed by the spark plasma sintering method [11], to prepare a CuCr alloy with approximately 100 nm-diameter Cr particles uniformly dispersed in it. Nanopowders prepared by means of mechanical alloying have high surface energies and are easy to agglomerate; however, it is difficult to ensure the uniformity of the mixing of multi-component powders, which makes it difficult to ensure the uniformity of the alloy composition after sintering.

Alloy thin films deposited via magnetron sputtering deposition have the advantage of uniform and precisely adjustable composition. The alloy thin film could have a microstructure or nanostructure, depending on the temperature and time of annealing. Vullers [12] used magnetron sputtering to prepare metastable CuW films with a W content of 0%–100%, such that a CuW alloy with an immiscible nature formed a supersaturated solid solution. In a study conducted by Raghavan et al [13], a Cu67Cr33 alloy film with a single-phase body-centred cubic (BCC) structure was prepared via magnetron sputtering. After annealing at 500 °C, the film underwent composition fluctuations similar to spinodal decomposition, and nanoscale Cr-rich phases were uniformly precipitated in the film. Meanwhile, the microstructure of the alloy film became a Cu-rich phase with a face-centred cubic (FCC) structure and a Cr-rich phase with a BCC structure.

The electrical contact requires the stable contact force during closing and opening, high wear resistance and low power losses [14]. Although there is no direct relationship between the mechanical property and the service life of the cathodes, the mechanical property of electrical contact materials affects the actual contact areas and wear, thus the contact resistance is related to the contact areas and wear surface. The strength of alloys determined by the microstructure. When Cr particles size and the grain size decreasing, the hardness of CuCr alloy increase according to the Hall–Path relationship [15]. When the grain size decreases continuously to critical grain size, the alloys could change to softening behaviour [16], because the plastic deformation mechanism shifts from dislocation slip to grain boundary mediated process. The wear resistance can be improved by increasing material hardness, but result in the contact areas decreasing and contact resistance increasing. The increasing of contact resistance in electrical contact lead to high power losses. The balance between wear resistance and the electrical contact resistance could be optimized by film deposited on the substrate. The strength and wear resistance of film can be improved by refining the grain size, at the same time, the composite hardness of film and substrate is approaching to the hardness of a soft substrate when indentation depths is near to the film thickness [17].

In this study, supersaturated solid-solution CuCr and CuCrMo alloy films with a BCC structure were prepared via magnetron sputtering, and the CuCr atomic ratio was 60:40. Through modulation decomposition during annealing, two uniform phases were formed from the supersaturated solid-solution alloy film. The evolution of the microstructure of the CuCr-based alloy films, as well as the nanomechanical properties and arc ablation resistance, was studied before and after annealing.

2. Experimental method

2.1. Preparation of CuCr film

The substrate used in this study was an N-type single-crystal Si (100) wafer. The substrate was cleaned before coating to improve film–substrate bonding. The thin film samples were prepared using a JGP-450a dual-chamber magnetron sputtering deposition system, which can apply pressures of up to $5 \times 10^{-4}$ Pa. The target purity of Ti, Cu, and Cr was 99.99%, and the film was prepared using the DC magnetron co-sputtering method. First, the Ti film which was deposited on the Si substrate acted as the diffusion barrier to suppress the formation of the Cu3Si phase during annealing. By controlling the sputtering power of the target material, CuCr and
CuCrMo films with an atomic ratio of approximately 60:40 were prepared. The specific process parameters, film thickness, and atomic ratio of the film, which were detected via energy dispersive spectroscopy using a scanning electron microscope, are shown in table 1. Notably, CuCr and CuCrMo were used as sample number for the study on the microstructural and nanomechanical properties, respectively.

### Table 1. Preparation parameters, components, and thickness of the CuCr film.

| Number  | P(Cu)/W | P(Cr)/W | P(Mo)/W | CuCr     | Mo(Cu+Cr+Mo) | Thickness/nm |
|---------|---------|---------|---------|----------|--------------|--------------|
| CuCr    | 90      | 130     | 0       | 61.39    | 0 at%        | 1650         |
| CuCrMo  | 90      | 130     | 150     | 63.36    | 11 at%       | 1320         |

2.2. Characterisation
The phase structure of the deposited film was characterised via x-ray diffraction (XRD, XRD-700). The surface morphology and microstructure of the film were observed via field-emission scanning electron microscopy (SEM; SU600) and high-resolution transmission electron microscopy (TEM; JSM-2100F). The components in the film were analysed with an EDAX energy spectrometer using the SU6000 scanning electron microscope. A Hysitron TI-950 nanoindenter and an RTS-9 four-point probe tester were used to measure the hardness (indentation depth < 100 nm), elastic modulus, and sheet resistance of the film. The average of the values obtained through five tests were considered as the experimental results for the aforementioned parameters.

2.3. Vacuum electrical breakdown
With the same parameters listed in table 1, CuCr and CuCrMo films were deposited on the surface of the Cu contacts, and a vacuum electrical breakdown experiment was performed on an inhouse-built vacuum breakdown platform. The experimental equipment is shown in figure 1(a). The surface roughness of Cu contacts can be quantified by 3D morphologies measured by confocal microscopy as shown in figure 1(b). The maximum depth of the profile below the mean line (Rv) is used to characterising the depth of arc erosion pits. The arithmetic mean deviation of the profile (Ra) which is the arithmetic average between the roughness profile and the root...
mean square slope of the profile (RΔq) are used to describe the roughness varying after ablation. The Rv, Ra and RΔq of Untreated Cu contacts are 24 μm, 4 μm and 5 μm.

Before breakdown, the sample was ultrasonically cleaned in absolute ethanol for 10 min, then rinsed with deionized water, dried in an oven, and put into a vacuum chamber as the cathode. The anode is a conical pure W rod with a diameter of 1 mm and an apex angle of 30°. When the pressure of the chamber vacuum is less than 10⁻³ Pa, a DC voltage of 4 kV was applied between the cathode and the anode to make the cathode as close as possible to the anode until breakdown occurred.

The test method in this article is the fixed voltage method, so the breakdown voltage is all 4 kV, charging the capacitor to the specified voltage value, then closing the charging circuit switch, control the sample stage through the stepper motor, shorten the distance between the anode and the cathode as close as possible to the anode until breakdown occurred, recording the distance d between the anode and cathode (measured by a dial gauge) at this time, using the oscilloscope to record the voltage and current curve during the breakdown. At this time, the breakdown is complete. This method is to fix U and change d. Therefore, the speed of the sample cathode approaching the W needle anode will affect its breakdown voltage. Therefore, the same stepping speed should be used in the experiment. Generally, the speed used in the experiment is 0.2 mm min⁻¹.

The surface morphology after ablation was observed via SEM, while the depth of the ablation pits was measured using a laser confocal microscope.

Through the vacuum breakdown experiment, information such as the breakdown strength, chopping current and arc duration of the contact material can be obtained.

The breakdown strength of the contact material refers to the ability of the material to resist the action of an electric field in a vacuum without being broken down. When electrical breakdown occurs, the metal vapor conductor in the vacuum gap will rapidly decrease the voltage across the arc. At this time, the voltage applied across the cathode and anode is the breakdown voltage, and the distance between the two poles is the breakdown distance, the breakdown voltage can be measured by a multimeter, and the breakdown distance is measured by a dial indicator.

The current interception phenomenon means that when the current is interrupted, as the distance between the two electrodes increases, the arc voltage and current gradually decrease. The metal vapor in the vacuum gap can no longer meet the needs of maintaining the arc. The arc suddenly extinguishes and the current becomes zero. When the electrical breakdown occurs, the current will drop rapidly. When it decreases to a certain value, the current will fluctuate, and then suddenly become zero. The current value at the sudden change point is chopping current, the arc duration is the time from the occurrence of electrical breakdown to the interception phenomenon.

2.4. Vacuum annealing
The sample was annealed in a VTHK-350 vacuum annealing furnace. During annealing, the vacuum degree was 5 × 10⁻⁴ Pa, the temperature was 773 K, and the annealing time was 2 h. The sample was removed after cooling to below 50 °C under vacuum conditions.

2.5. Controlled arc ablation experiment
The CuCrMo film was deposited on the surface of the CuCr contact. The deposition parameters are listed in table 1. The thickness of the deposited film was 5 μm. The controlled arc ablation experiment was conducted in a vacuum arcing chamber. The circuit of the chamber, which consists of a capacitor bank and a reactor, is shown in figure 2. The LC oscillation circuit provides the short-circuit current required for the experiment, and the maximum effective value of the current is 40 kA. The main closing switch is a vacuum circuit breaker equipped...
with a spring-operating mechanism. The sample was placed in the vacuum arcing chamber. A monostable permanent magnet operating mechanism was used to adjust the opening speed and distance of the contacts. During the experiment, the vacuum was maintained at $1 \times 10^{-4}$ Pa.

Figure 3. X-ray diffraction spectrum of the CuCr alloy film.

Figure 4. Low-magnification and high-magnification (upper right corner) scanning electron micrographs of the surface morphology of the deposited and annealed CuCr and CuCrMo films, (a) CuCr film as deposited, (b) CuCr film annealed at 773 K, (c) as-deposited CuCrMo film, and (d) CuCrMo film annealed at 773 K.
3. Experimental results

3.1. Structure and morphology
Compare to the CuCr film, the CuCrMo film has smoother morphology and blur grain boundary with larger lattice distortion according to the x-ray diffraction spectra, scanning electron micrographs and the transmission electron micrographs.

Figure 3 shows the x-ray diffraction spectra of the CuCr and CuCrMo films. In the deposited state, the CuCr film and CuCrMo film are both BCC structures. After doping with 10 at% Mo, the diffraction peak shifts significantly to the left. Because the atomic radius of Mo is 190 pm, which is larger than the atomic radii of Cu (145 pm) and Cr (166 pm) [18], the doping of Mo causes the lattice constant to increase and the diffraction peak to shift to the left. According to the free energy of supersaturated solid-solution CuCr alloys with different Cr atom contents, when the Cu and Cr atomic ratio is approximately 60:40, the BCC structure of the CuCr and the CuCrMo film has the lowest free energy [19]. Therefore, the CuCr and CuCrMo films are both single-phase BCC structures. The full width half maximum (FWHM) of (110) diffraction peak of CuCr and CuCrMo film is 0.577

Figure 5. Transmission electron micrographs of the as-deposited and annealed CuCr films at 770 K, (a) bright-field and electron diffraction images (bottom right) of the as-deposited CuCr films, (b) bright-field and electron diffraction images (bottom right corner) of the CuCr films after annealing, (c) dark-field image of the BCC structure (110) crystal plane of the CuCr film after annealing, and (d) dark-field image of the FCC (111) crystal plane of the CuCr film after annealing.
Figure 6. Transmission electron micrographs of the as-deposited and annealed CuCrMo films at 770 K: (a) bright-field image and electron diffraction of the as-deposited CuCrMo films (bottom right corner), (b) BCC structure (110) crystal planes of the as-deposited CuCrMo films (dark-field image), (c) bright-field and electron diffraction of the CuCrMo film after annealing (bottom right corner), (d) BCC structure (110) crystal plane dark-field image of the CuCrMo film after annealing, (e) high-resolution image of the deposited CuCrMo thin film, and (f) high-resolution image of the CuCrMo thin film after annealing.
and 0.591. The FWHM of CuCrMo film slightly increase because of larger lattice distortion introduced by doping of Mo.

After annealing at 773 K, the CuCr film becomes two-phased, and diffraction peaks of the FCC and BCC structures emerge. After annealing, the diffraction peaks of the BCC (110) crystal plane of the CuCrMo film are broadened, and weak FCC (200) crystal plane diffraction peaks appear. The FWHM of (111) diffraction peak and (110) diffraction peak in annealing CuCr film is 0.452 and 0.380, and the FWHM of (110) diffraction peak in annealing CuCrMo film is 0.803. After annealing, the FWHM of diffraction peak from CuCr film is decreasing but the FWHM of diffraction peak from CuCrMo film is increasing.

Figure 4 shows the surface morphologies of the CuCr and CuCrMo films before and after annealing. Upon comparing the CuCr film before and after annealing, it was evident that the surface of the deposited CuCr film was smooth, and the granular morphology could be seen in the high-magnification image (figure 4(a)). After annealing, as shown in figure 4(b), white particles were precipitated on the surface, energy spectrum analysis shows that it is a Cu-rich phase; moreover, several fractal-like cavities appear. The cavities are formed because of the effect of the interface energy of the grain boundary and that of the interface energy between the substrate and the deposited surface, and the granular morphology appears subtle in the high-magnification image. The incorporation of Mo effectively inhibits the precipitation of Cu-rich white particles and the formation of voids.

Figures 5 and 6 show TEM images of the CuCr and CuCrMo films before and after annealing, respectively. In figure 5(a), the electron diffraction of the CuCr film before annealing shows that the CuCr film has a single-phase BCC structure, while the bright-field image in figure 5(a) shows that the deposited film has a columnar crystal structure and that the cross-sectional size of the columnar crystal is approximately 30–50 nm. After annealing, the electron diffraction pattern in figure 5(b) shows a dual-phase structure composed of Cu-rich FCC and Cr-rich BCC, which was also observed by Raghaavan [13]. In the bright-field image, it is evident that the columnar crystal structure has virtually disappeared. In the dark-field images of the BCC (200) crystal plane and FCC (220) crystal plane in figures 5(c) and (d), it can be seen that after annealing, the film has a nanocrystalline structure with sharp grain boundaries. The grain size of the Cr-rich phase in the BCC structure is only a few nanometres, while that of the Cu-rich phase in the FCC structure is between a few nanometres to tens of nanometres. According to the result of x-ray diffraction and Transmission electron micrographs, after annealing at a temperature of 773 K, a similar spinodal decomposition phenomenon occurs in CuCr film, and a dual-phase structure of Cu-rich FCC and Cr-rich BCC is formed. Although grain size and Cr-rich particles size decrease, the Cr atom precipitated and interstitial atoms reduction during annealing could be reason of the FWHM of x-ray diffraction peak decreasing.

Figure 6(a) shows that the as-deposited CuCrMo film only has BCC diffraction rings and is a single-phase BCC structure which is identical to the x-ray result. The bright-field phase indicates that the film has a columnar crystal structure. The 20-nm-thick film between the CuCrMo film and the substrate is a Ti film, which acts as a diffusion barrier. The dark-field image shown in figure 6(b) shows that the size of the columnar crystals of the as-deposited CuCrMo film is approximately 20–40 nm, which is slightly smaller than that of the CuCr film.
Moreover, Mo doping suppresses the growth of columnar crystals to a certain extent. After annealing, the bright-field image in figure 6(c) reveals that the columnar crystal structure disappears. In the electron diffraction pattern, FCC diffraction rings appear. Figure 6(d) shows dark-field images of the BCC (110) and FCC (111) crystal planes. Unlike in the dark-field image of the CuCr film after annealing (figure 5(d)), the grain size of the CuCrMo film in figure 6(d) is comparable to that of the CuCr film, although the grain boundaries are blurred. The nanocrystalline nature of the CuCrMo film after annealing broadens grain boundaries compared with those of the CuCr film. In the high-resolution images of the annealed CuCr and CuCrMo films, shown in figures 6(e) and (f), the crystal lattice of the CuCrMo film after annealing is severely distorted. The larger lattice distortion of the CuCrMo film after annealing make diffraction peak broaden in figures 3 and 6(c) and is reason of that diffraction peak of FCC(111) is indistinguishable from that of BCC(110) in figure 3.

### 3.2. Hardness and modulus

Figures 7 and 8 show the elastic modulus and nanoindentation hardness of the deposited and annealed films, respectively. The elastic moduli of CuCr is almost same as that of CuCrMo no matter if film is deposited or annealing. After annealing, the elastic moduli of both the CuCr and CuCrMo films increased; however, the hardness of the CuCr film decreased, whereas that of the CuCrMo film increased.

During the film deposition process, owing to atomic sputtering, the deposited film contains more vacancies and interstitial atoms. After annealing, the number of point defects is reduced due to the diffusion of atoms and the recombination of vacancies and interstitial atoms, the elastic modulus of film increases [21].
The decrease in the hardness of the CuCr film after annealing is related to the spinodal decomposition. Before annealing, the CuCr film is a single-phase BCC solid solution with a small film grain size; moreover, solid-solution strengthening and fine grain strengthening are the main strengthening mechanisms. After annealing, the film undergoes a similar spinodal decomposition phenomenon, and the effect of solid-solution strengthening decreases. However, owing to the formation of the FCC and BCC dual-phase structures and the smaller grain size, the density of the phase interface and grain boundary increases, which enhances the grain-boundary strengthening effect. The two effects nullify each other, resulting in a slight decrease in hardness. In the

Figure 10. Cu contact and as-deposited CuCr, CuCrMo film vacuum ablation morphology, (a) and (b) Cu-based contact ablation morphology and 3D morphology, (c) and (d) CuCr film ablation morphology and 3D morphology, (e) and (f) CuCrMo film ablation morphology and 3D morphology.
CuCrMo film, the broadening of the grain boundary increases the density of the grain boundaries. The larger lattice distortion inhibits dislocation slipping. More solute atoms are dissolved in the crystal lattice of the CuCrMo film than in that of the annealed CuCr film, and the solution strengthening effect is higher. Therefore, the hardness of the CuCrMo film increases after annealing because of grain-boundary strengthening, dislocation strengthening, and solid-solution strengthening.

3.3. Resistivity
Figure 9 shows the resistivity of the as-deposited and annealed films. The resistivities of the deposited CuCr film and CuCrMo film are higher than those of Cu (resistivity: 1.68 mW · cm) and Cr (resistivity: 12.9 mW · cm), and the resistivity of the CuCr film doped with Mo is lower than that of the undoped CuCr film. After annealing, the resistivity decreased; however, the resistivity of the CuCr film was still higher than that of Cu, and the resistivity of the CuCrMo film was also higher than that of the CuCr film. The supersaturated solid-solution atoms and point defects in the deposited film scatter the electrons, which leads to the high resistivity before annealing. After annealing, the spinodal decomposition and the reduction in the number of point defects caused by atomic diffusion are the main reasons for the decrease in resistivity. The CuCrMo film has more solid solute atoms and a larger lattice distortion, which increases the probability of electron scattering; thus, the resistivity of the CuCrMo film is higher than that of the annealed CuCr film.

3.4. Vacuum arc ablation experiments
A metallographic picture of the as-deposited film after one breakdown vacuum arc ablation experiments is shown in figures 10 and 11. After ablation, the depth of the ablation pits are essentially the same for the Cu contact and the deposited film. The CuCrMo film has a slightly larger ablation area with the smoothest morphology, and the dispersion arc ablation spots are uniformly distributed.
To Cu contacts, the arc ablation is concentrated in an approximately circular area in the centre. In the arc ablation experiment, the tungsten tip of the cathode is a round tip, the work function is the same everywhere on the surface of Cu contacts because of the larger grain size and uniformity of composition. The max electron emission current locates at the max electric field strength which is between tungsten tip and the Cu contacts, according to the Fowler-Nordheim electron emission equation (equation (1)) [22–24]:

\[
j = \frac{aE^2}{\phi t^2} e^{-\frac{b\sqrt{\phi t}}{E}}
\]

where a and b are constant, v and t are elliptic functions.

So, the arc ablation is concentrated in the centre, the black and light black area, as shown in figure 10(a). The black and light black area in the centre is the ablation pit with clear edges. The ablation pits in the 3D morphology of figure 10(b) is the yellow region which deeper than the green region. The Rv, Ra and RΔq of ablation pits can be obtained from figure 10(b). In table 2, the Rv increase to 39 μm which means there is a deeper ablation pit. The Ra increase to 7 μm which mean more rougher surface after ablation. The root mean square slope of profile(RΔq) increases to 9 μm after ablation which mean the deeper arc pits.

The ablation of deposited CuCr film is also mainly concentrated in the central area. In figure 10(c), there is an aggregate with distinct boundary. In figure 10(d), the aggregate, the blue region is higher than the edge, the yellow region, which could be due to the splashing of liquid metal under the action of arc force [25]. The splashing of liquid metal happens when the arc concentrated and arc root shrink, the surface at arc root on the contacts is overheated by the increasing of current density of arc root.

The ablation of deposited CuCrMo film is not concentrated in the central area. In figure 10(e), the light black area without clear boundaries is ablation area. In figure 10(f), the centre area with blue colour is surrounded by yellow colour region which lower than the blue colour region. Compare figures 10(e) and (f), there is no larger and deeper ablation pit on the surface of annealing CuCrMo film, the small ablation pits scatter on the surface. The Rv, Ra and RΔq are 21 μm, 2 μm and 2 μm which are smaller than that of the Cu contacts before ablation. That means the arc is not concentrating in a certain position and randomly move around at the surface of Cu contacts.

| Table 2. The surface roughness. | Rv/μm | Ra/μm | RΔq/μm |
|--------------------------------|-------|-------|--------|
| Cu contacts                    | 24    | 4     | 5      |
| vacuum ablation of Cu contacts | 39    | 5     | 9      |
| vacuum ablation of As-deposite CuCr35 film | 20 | 4 | 7 |
| vacuum ablation of CuCr35 film after 773 K annealing | 22 | 3 | 6 |
| vacuum ablation of As-deposite CuCrMo film | 21 | 2 | 2 |
| vacuum ablation of CuCrMo film after 773 K annealing | 19 | 1 | 2 |

Figure 12. CuCrMo film deposited on the CuCr contact after the 40 kA arc control experiment: (a) macroscopic optical image and (b) partially enlarged scanning electron microscopy image of CuCr contact-deposited CuCrMo film after arc control.
contacts, and the ablation pits are shallow and the surface roughness is smooth, the ablation resistance of Cu contacts with deposited CuCrMo film is increasing.

Figure 11 shows the results of the ablation experiment on the films after annealing. The ablation resistance of the CuCr film and CuCrMo film both increased significantly and the CuCrMo film after annealing has best ablation resistance among them. In figure 11(a), The ablation area of annealing CuCr film has no clear boundaries. In figure 11(b), the ablation pits with yellow colour or orange colour which is deeper than the yellow colour region scatters around blue and green area on the surface. The $R_v$, $R_a$, and $R_{\Delta q}$ are 22 $\mu$m, 3 $\mu$m and 6 $\mu$m respectively. The ablation resistance of annealing CuCr film is better than that of the Cu contacts, but worse than that of the deposited CuCrMo film. In figure 11(c) the colour of annealing CuCrMo film is almost unchanged, and in figure 11(d) the ablation region with yellow region is broader and dispersed. The $R_v$, $R_a$ and $R_{\Delta q}$ are 19 $\mu$m, 1 $\mu$m and 2 $\mu$m which mean the dispersed shallow ablation pits shown on the surface of this film. The increase in the smooth ablation area and the decrease in the ablation depth indicate that the arc cathode spots are more prone to migration on the CuCrMo film surface rather than concentrate on some certain area.

Figure 12 shows a CuCrMo film with a thickness of 5 $\mu$m deposited on the surface of the CuCr contact through the same process as presented in table 1. After annealing at 773 K, it was subjected to a 40 kA vacuum arc for 9 ms. In the photograph shown in figure 11(a), the colour of CuCr contact remains the same and there are no evident ablation pits on the surface of the CuCrMo film. In the scanning electron micrograph shown in figure 11(b), it can be seen that the uniformly distributed molten morphology and the white spherical droplet morphology correspond to the molten metal and condensed copper vapour during the movement of the cathode beam spot, respectively. The experimental results indicate that the annealed CuCrMo film exhibits strong arc ablation resistance against large currents.

4. Analysis and discussion

According to the ablation result, the ablation of Cu-based contacts is concentrated in the central area. The surface roughness of Cu-based contacts increases after ablation. The ablation resistance of Cu-base contacts with film increase and the ablation pits is dispersive and shallow. The ablation resistance of film after annealing increase and the ablation pits is more dispersive and shallower. The annealing CuCrMo film has best ablation resistance.

The cathode spot generation and motion have a strong correlation with the electron emission [26]. According equation (1), the electron emission current is inversely proportional to the work function of cathode materials suppose an electric field distribution is given. The work function of polycrystalline has related to the atomic number Z, grain boundaries and lattice distortion. For example, the work function of polycrystalline Cr, Mo and Cu are 4.5, 4.6 and 4.65, respectively [27]. The traditional CuCr bulk alloy has a dual-phase structure composed of Cu and Cr. The cathode spot is first formed on the low-work-function Cr phase, which has a higher melting point than the Cu phase. The priority ablation of the Cr phase endows the CuCr alloy with excellent performance. In a study on nanocrystalline W and Ni, it was found that the nanocrystalline structure can reduce the work function value is also related to the lattice constant. The lattice constant reducing induced by the lattice strain, the work function increases linearly.

Although, the as-deposited CuCrMo films have uniform single-phase structures, the boundaries of fine nanosized grain has a lower work function, so the cathode spot can quickly move in a direction far away from the initiating ignition site which have been proved in the research of Zhimao Yao etc by a digital high-speed video camera. The ablation area dispersed in a small region and the cathode spot migration lead to the concentrated ablation decreasing; thus, the surface roughness decreases and arc ablation resistance increase.

After annealing, the CuCr and CuCrMo films exhibit a dispersed Cr-rich phase BCC structure and a Cu-rich FCC structure, respectively. The lower work function of the Cr-rich phase is smaller and fine grain boundaries increasing; thus, the fine dispersion of the Cr-rich phase and grain boundaries significantly expands the migration of the cathode arc spots, this results in an increase in the ablation area and a decrease in the surface roughness and ablation pits depth.

In the CuCrMo film doped with elemental Mo, the nanocrystalline grain boundaries are more blurred than those of the CuCr thin film, and severe lattice distortions are observed in the nanocrystalline structure. Therefore, for the annealed CuCrMo film, the broadened grain boundary reduces the work function of the film as well as the energy of the field emission electrons. Moreover, the severe lattice distortion makes the lattice constant is disturbed rather than constant; hence, the work function also presents an uneven distribution which the location of lower work function more uniformly distribute on the surface rather than on the grain boundaries or Cr phase. The cathode arc spots easily migrate to farther areas, and thus, the arc ablation area considerably increases, the ablation pits are considerably decrease, the surface roughness is smoother. After the
40 kA arc ablation for 9 ms, the surface ablation of the CuCrMo film was very shallow, the film was still perfect, and the uniformly distributed molten area on the surface showed that the arc migrated smoothly on the surface. Moreover, there was no evident intense ablation caused by concentrated arc energy. Uniform small condensation droplets were observed, indicating that no arc splash erosion had resulted from concentrated arc energy. This proves that the CuCrMo film has a better arc ablation resistance.

5. Conclusions

CuCr and CuCrMo films prepared via magnetron sputtering with Cu and Cr atomic ratios close to 60:40 are all single-phase BCC structures in the deposited state, and the CuCrMo film increase the ablation resistance of Cu-based contacts. After annealing at 773 K, the CuCr film become a dual-phase structure composed of Cu-rich FCC and Cr-rich BCC owing to spinodal decomposition. After annealing, the grain sizes of the CuCr film become fine, and the grain boundaries become sharp. Moreover, the elastic modulus of the film increases, although the hardness and the resistivity decrease. After vacuum arc ablation, the ablation area increases. For the annealed CuCrMo film, the surface is smooth, the grain sizes are fine, the grain boundaries are blurred, the lattice distortion is severe, the elastic modulus and hardness of the film increase, and the resistivity decrease. After vacuum arc ablation, the ablation area is larger, the surface roughness is smooth, and the ablation pits are very shallow. After vacuum arc ablation with a 40 kA current for 9 ms, the CuCrMo film exhibits a strong arc ablation resistance.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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