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Grain Refinement of Hypereutectic Immiscible Cu-50Cr Alloy during Rapid Melting and Solidification Induced by High Power Density Laser Beams

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Abstract: The microstructure of hypereutectic immiscible Cu-50Cr alloy (wt%) was effectively refined and homogenized by a high power density Nd:YAG continuous laser beam (power density 10^4 – 10^5 MW/m²). The average grain size of Cr was effectively refined from ~100 μ m to ~1 μ m, and some of the Cr particles even decreased to a few hundred nanometers. The high cooling rate (7.29×10^6 K/s) effectively inhibited the coarsening effect on Cr particles during liquid phase separation (LPS). The spherical Cr particles were preferably dispersed in the melt layer, and the thickness of the layer was up to ~150 μ m. The refinement and dispersion of the Cr phase contributed to improving the interruption capability of the Cu-Cr contacts. Compared with the untreated samples, the arc duration and the withstanding voltage of the laser surface melting (LSM) treated contacts with refined microstructure increased to 21% and 33%, respectively. The results demonstrated that the LSM method was an effective approach to optimize the microstructure of Cu-Cr alloy, which made it a promising modification method for Cu-Cr vacuum contact applications.

Keywords: Cu-Cr immiscible alloy; laser surface melting (LSM); liquid phase separation (LPS); grain refinement; rapid solidification; interruption capability

1. Introduction

Hypereutectic Cu-Cr alloys with high Cr content (Cr mass ratio from 20–60%) have been widely accepted as electric contact materials in nearly all the high voltage commercial vacuum interrupters (VIs) [1]. Recent investigations revealed that the performances of Cu-Cr alloy are significantly affected by the grain size and distribution of the Cr phase. Especially, when refined Cr spherical particles are dispersed uniformly in the Cu matrix, it was helpful to reduce chopping currents, sustain high voltage breakdown strength capacity, and effectively avoid failures during switching off operations [2–5]. However, traditional preparation methods for Cu-Cr alloys, including powder metallurgy, casting, and arc melting, often fail to control the size of the Cr phase effectively and avoid microstructural segregation [6].

Therefore, some small-scale rapid solidification methods, for example melt spinning [7], gas atomization [8], electromagnetic levitation with splat-quenching [9], and selective laser melting [10], were applied to refine the microstructure. Similar to other Cu-X (X = Fe, Mn, Co, etc.) liquid immiscible alloys, where X indicates body centered cubic (bcc) crystal transition metals, when the Cu-Cr melt was

undercooled below the miscible metastable gap, the Cu-Cr melt separated into two mutual insoluble Cu-rich and Cr-rich liquids due to liquid phase separation (LPS) [11–13]. Sun et al. found that the size of Cr particles in $\text{Cu}_{72}\text{Cr}_{18}\text{Zr}_6$ was refined to ~ 100 nm in the process of LPS [14]. Gao et al. stated that the size of the Cr phase was inversely proportional to the cooling rate [15]. These techniques are only suitable for fabricating small-sized samples, so their applicability is limited. The surfaces of the Cu-Cr alloy contacts are the sites where failures frequently originate, so attention has been attracted to surface modifications [16–20]. Among various surface treatment techniques, laser surface processing stands out for its fast processing speed, high controllability, and minimum thermal distortion. The laser beam acted as a controllable heat source to generate a dynamic temperature field on the alloy surface, followed by rapid solidification. Zhang et al. [21] reported that a Cu-25Cr (wt%) cladding layer without large-scale macroscopic separation was produced by laser cladding (LC) with a CO_2 laser with power density of $\sim 10^2$ MW/m², whose microstructures were composed of Cr dendrites (~ 50 μm) and several hundred micron-scale Cr phases embedded in the Cu matrix due to insufficient LPS. Hirose et al. [22–24] attempted laser surface alloying (LSA) of Cr powders onto a Cu substrate by a CO_2 laser with a laser power density of $\sim 10^3$ MW/m² to obtain Cu-Cr alloyed layers, and the size of Cr particles decreased to ~ 5 μm , which presented an inhomogeneous Cr concentration from the surface to the bottom.

Laser surface melting (LSM) is capable of large-scale industrial production, which is more reliable and economical efficient due to the absence of elements' additions or changes of chemical compositions. However, LSM of Cu-Cr alloy was challenging because of the high thermal conductivity and high reflectance of Cu-X alloys for an infrared wavelength laser. The grain size of Al-based alloys with high thermal conductivity was refined to the sub-micron scale using a laser power density of $\sim 10^3$ MW/m² [25]. Besides, Silva et al. [26] discovered that Cu-Al-Ni-Mn alloy could be refined to 23 ± 5 μm with laser power density up to $\sim 10^4$ MW/m². The grains were refined with a high power density laser by LSM, and it could be expected that a finer microstructure of immiscible Cu-Cr alloy could be obtained similarly. In this paper, the Cu-50Cr (wt%) contacts were firstly melted on the surface by a high power density (10^4 – 10^5 MW/m²) laser beam aiming at refining and uniformly distributing the Cr phase. The grain refinement kinetics in a hypereutectic Cu-Cr alloy subjected to a high density laser beam and the influence of grain refinement on withstanding voltage and the interruption capability of Cu-Cr contacts were studied. This paper provides a novel approach to improve the properties of Cu-Cr electrical contacts and is of great potential to future industrial applications.

2. Experiments

2.1. Material and Methods

The investigated commercially-available Cu-50Cr (wt%) alloys were prepared by powder sintering. The chemical composition, density, ad mechanical and physical properties are listed in Table 1. The process involved a vacuum-sintered matrix of Cr and then mixed with Cu powers, and the processing temperatures (900–1000 K) were below the melting points of both Cu (1356 K) and Cr (2133 K). Meanwhile, the maximum solubility of Cu in Cr and Cr in Cu is 0.0077 and 0.0008 (mole fraction) at eutectic temperature, respectively. Therefore, Cu-Cr alloy is a pseudo alloy composed of Cr particles embedded in Cu matrix.

Table 1. Chemical composition and mechanical and physical properties of Cu-Cr alloy.

Material	Chemical Element (wt%)				Density (g/cm ³)	Hardness (HB)
	Cr	Cu	O	N		
Cu-Cr(50)	47–52	Bal.	≤ 0.05	≤ 0.05	≥ 7.90	≥ 80

The absorptivity of the material was calculated by the Hagen-Ruben equation (1) [27]:

$$A = 0.365 \times \left(\frac{\eta}{\lambda} \right)^{\frac{1}{2}} \quad (1)$$

where A is the absorptivity of the samples for laser, λ (m) is the wavelength of the laser, and η ($\Omega \cdot \text{m}$) is the conductivity of pure Cu [28]:

$$\eta = (0.0078T - 0.7502) \times 10^{-8} \quad (2)$$

As shown in Figure 1, the absorption of Cu for infrared wavelength laser is extremely low (less than 0.02). Obviously, the absorption of Cu for the YAG laser with a 1.064- μm wavelength is higher than that of a CO₂ laser with a 10.6- μm wavelength. The schematic diagram of the experimental setup for the LSM process is given in Figure 2, and the experiments were conducted with a continuous 1 kW Nd:YAG laser. The focal length was 125 mm, focus spot diameter 0.1 mm, focal spot position kept as 0, and the laser beam combined onto an optical fiber with a diameter of only 100 μm to obtain a high laser power density up to $\sim 10^5$ MW/m². Irradiated by the high density laser beam, the surface can be heated rapidly, and the laser absorption can be greatly improved (Figure 1). On the basis of these factors, the temperature of the alloy surface can be rapidly heated to above the liquidus line. In order to get a higher temperature cooling rate and prevent deformation due to thermal stress, a water cooling device was used to cool the back of the Cu-Cr contact. A high cooling rate contributes to the grain refinement of Cu-Cr alloy during liquid phase separation. Furthermore, the deformation caused by thermal stress was avoided, since deformation will greatly affect the contact resistance of the Cu-Cr contact. After LSM, the contacts can be directly used in commercial interrupters without secondary processing. The temperature of the back of the sample was maintained at 15 °C to get a higher cooling rate from the surface to the bottom. The LSM process was protected in an atmosphere protection device filled with argon (gas content: O₂ < 50 ppm, H₂O < 100 ppm).

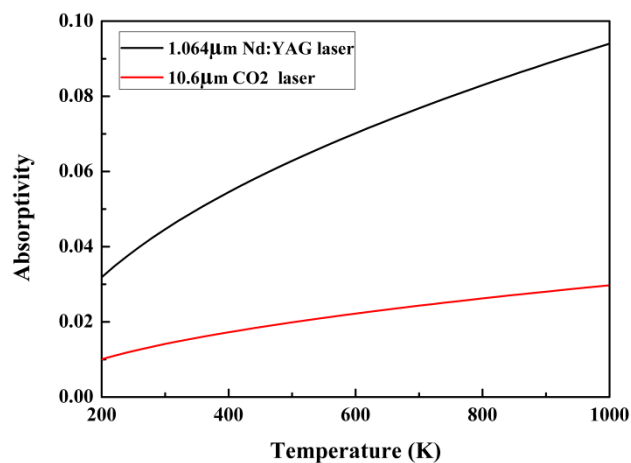


Figure 1. Absorptivity of Cu for the CO₂ and Nd:YAG laser.

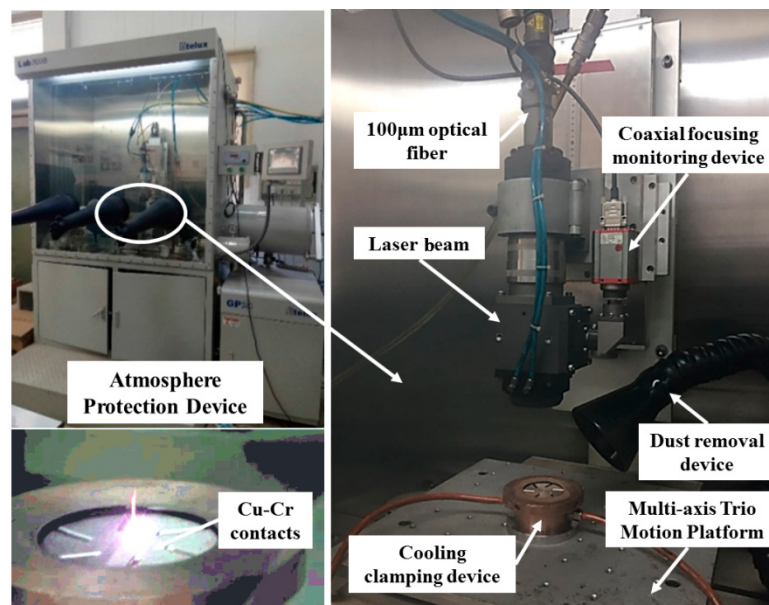


Figure 2. Schematic diagram of laser surface melting process for Cu-50Cr (wt%) alloy.

The laser power density Q (W/m^2) is expressed by Equation (3); the interaction time t (s) between laser beam and Cu-Cr alloy is calculated by the following Equation (4), and the laser energy density E (J/m^2) is described by Equation (5) [29]:

$$Q = \frac{P}{\pi r_B^2} \quad (3)$$

$$t = \frac{2r_B}{v} \quad (4)$$

$$t = \frac{2r_B}{v} \quad (5)$$

where P (W) is laser power, r_B (m) is the radius of the laser spot, and v (m/s) is the laser scanning speed. In an effort to establish the range of optimal laser processing parameters, a series of experiments have been carried out at laser power densities from $5.0 \times 10^4 \text{ MW}/\text{m}^2$ – $8.5 \times 10^4 \text{ MW}/\text{m}^2$ and laser scanning speed from 6 m/min–10 m/min. The interval between each scanning tracks was 80 μm , and the surface was continuously scanned in lines that were equal to the length of the samples.

2.2. Characterization

The laser-treated samples were cut perpendicular to the laser scanning direction with electrical discharge wire cutting. Then, the samples were mechanically polished by the usual metallographic procedure and etched in an acidic water solution ($\text{HNO}_3:\text{H}_2\text{O}$ equal to 3:10 in volume). The microstructure was observed by SEM (ZEISS EVO18, scanning electron microscope, Heidenheim, Germany) equipped with an EDS (energy dispersion spectrometer, Oxford Instruments, Oxford, UK). The phase constituents of the surfaces of the samples were analyzed by XRD (SMART LAB 9X, X-ray diffractometer, Rigaku, Tokyo, Japan, with Cu $K\alpha$ radiation) operating at 40 kV and 120 mA. About 30–50 images were used to measure the diameter of the Cr phase. The mean diameter of the Cr particles was measured and calculated by Image-Pro software, the average length of diameters measured at 2-degree intervals and passing through the object's centroid. The steps were as follows. First, the original images were segmented with false color, then the binary images were obtained, and at last, the diameter of the Cr grains was measured. The pixel portion of the measurement was 5% higher than that of the average strength of the selected object, so the systematic error of Image-pro was around 5%.

2.3. Interruption Capability and Withstanding Voltage Tests

In order to test the service performance of the laser-treated Cu-Cr contacts, pairs of untreated and LSM-treated contacts with the same processing parameters were symmetrically assembled in 6 vacuum interrupters (Vis, Shanxi Baoguang Vacuum Electric Device CO., LTD., Baoji, China). The withstanding voltages of these VIs were tested with the contact gap of 2 mm. The lightning voltages were applied to the contacts by an up-and-down method until the contacts broke down. The maximum value of the voltage was cited as the withstanding voltage. The number of tests was limited to 15 times to minimize the damage caused by standard lightning impulse voltage.

Parameters for the switching down tests were as follows: voltage 23 kV, contact gap 11 mm; transient recovery voltages (peak up to 22 kV, 4100 Hz) were standardized to correspond to the values guided by IEC 62271-100 [30]. At the beginning of the experiment, the contacts were closed. During the high current range, the current exhibited a sinusoidal characteristic up to a maximum high current, between 5 and 10 kA. The contacts were separated at a velocity of 0.2 m/s. After arc ignition, the current was conducted until the current decreased to zero.

3. Results

3.1. Microstructure

The microstructure of the Cu-50Cr (wt%) alloy is shown in Figure 3. Light elements (low atomic number) have darker contrast than heavy elements (high atomic number) in a BSE image. This is known as the atomic number or Z-contrast of backscattered electrons. In this study, the atomic number of Cr ($Z = 24$) was significantly lower than that of Cu ($Z = 29$). Therefore, the Cu phases were brighter in a BSE image compared with the Cu phases. Dark round or elliptical Cr particles were enveloped by the bright Cu phases. The average size of the Cr phase, which acted as the key parameter for Cu-Cr alloy, was approximately 85.7 μm . The XRD results are given in Figure 3 to prove that the Cu-Cr50 (wt%) alloy was composed of face-centered cubic (fcc) ϵ -Cu with peaks at (111), (220), (200) and body-centered cubic (bcc) α -Cr with peaks at (110), (211), (200). It can be seen from the XRD results that there was no peak corresponding to any new phase or metallic compounds, indicating that phase transformation did not occur during LSM of Cu-Cr alloy.

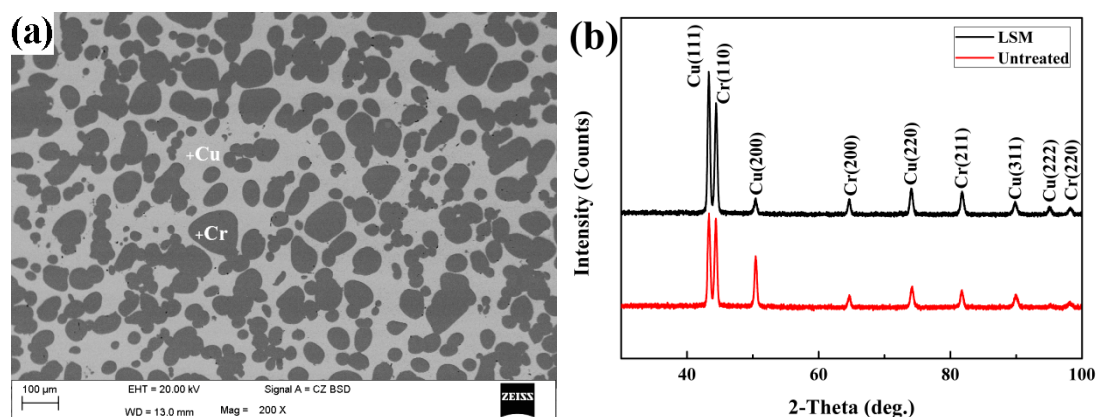


Figure 3. (a) Microstructure of Cu-50Cr alloy (backscattered electron image) and (b) XRD measurement results of the raw-material and after LSM.

Figure 4a shows the cross-sectional microstructure of Cu-50Cr alloy after laser surface melting with $Q = 7.0 \times 10^4 \text{ MW/m}^2$, $E = 43.8 \text{ MJ/m}^2$. The microstructure of the melt layer was significantly different from that of the substrate, and a clear interface between the melt and the unmelt layers could be recognized. The thickness of the melt layer was $85 \pm 30 \text{ }\mu\text{m}$. The Cr phase in the melt layer was refined, and massive small Cr particles and some big Cr particles coexisted in the melt layer. However, the presence of un-dissolved Cr bands (marked by A) indicated that the laser power was not enough to ensure adequate melting of the Cr phase, thus resulting in insufficiently refined Cr particles.

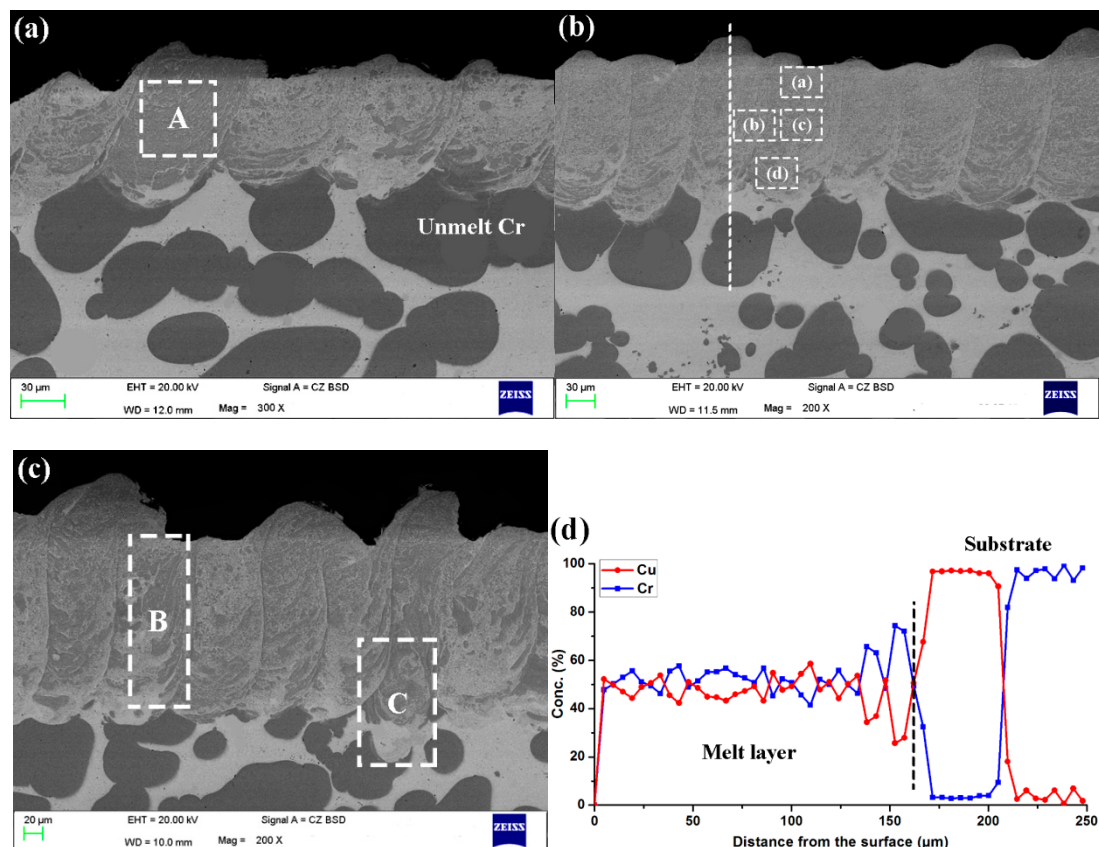


Figure 4. Microstructure of the melt layer under various laser energy densities: (a) $E = 43.8 \text{ MJ/m}^2$; (b) $E = 52.5 \text{ MJ/m}^2$; (c) $E = 66.3 \text{ MJ/m}^2$; and (d) EDS line scanning along the black dotted line in Figure 4b.

Figure 4b presents the cross-sectional microstructure of Cu-50Cr alloy after laser treatment with $Q = 7.0 \times 10^4 \text{ MW/m}^2$, $E = 52.5 \text{ MJ/m}^2$. The average thickness of the melt layer was $150 \pm 30 \text{ }\mu\text{m}$. Large quantities of refined spherical Cr particles were dispersed in the melt layer, while only a small number of Cr sheets were observed at the bottom of the melt pool. A typical element distribution of the surface melt layer is given in Figure 4d. Since there existed only two components in the alloy, the elements' distribution in the melt layer reflected the distribution of the two phases. Based on the line analysis results, it was clearly seen that the elements in the melt were uniformly mixed and distributed in the melt layer, while in the substrate, the two constituents showed a tendency to segregate. Closer to the bottom of the melt layer, the content of Cr was relatively higher because of the appearance of a few larger Cr sheets at the bottom of the melt pool. This sample is called LSM contacts in the following study to further study the refinement of the Cu-Cr alloy and its related properties.

Figure 4c illustrates the cross-sectional microstructure of Cu-50Cr alloy after laser surface melting with $Q = 7.0 \times 10^4 \text{ MW/m}^2$, $E = 66.3 \text{ MJ/m}^2$. The thickness of the melt layer was $200 \pm 40 \text{ }\mu\text{m}$. In the melt layer, there existed two shapes of refined Cr phases. One of them corresponded to small Cr spheres, and the other was large Cr sheets with strong swirled and elongated patterns (marked by B). The elongation directions of the sheeted Cr phases were towards the upper side of the melt pool. Since the two phases could be discriminated by contrast, it could be seen that the composition in the melt layer was non-uniform. The influence of strong stirring effect caused by convection on the phase separated liquids could be seen (marked by C), which showed the strong swirling flow patterns with larger Cr sheets. Figure 4c evidenced the effect of excessive laser power, resulting in the formation of a large number of Cr sheets because of intense melt flow.

Figure 5a shows that numerous spherical Cr particles with the average diameter of $\sim 0.44 \text{ }\mu\text{m}$ (Figure 5e) were dispersed within the Cu matrix on the top of the melt pool (marked (a) in Figure 4b). In the middle of the melt pool, there also existed massive Cr spheroids homogeneously distributed in the Cu matrix (marked (b) in Figure 4b). The average diameter was relatively larger, $\sim 0.58 \text{ }\mu\text{m}$ (Figure 5f). Figure 5c displays the overlapping zone (marked (c) in Figure 4b). The mean diameter of Cr grains in this zone was $\sim 0.61 \text{ }\mu\text{m}$ (Figure 5g). The refined Cr particles were preferably distributed in the Cu matrix with a sphere or near sphere morphology. Additionally, a gathering tendency for the Cr spheroids to form bigger Cr clusters was observed on the fusion line in the overlapped zone. Figure 5d depicts the refined Cr phases at the bottom of the melt pool; many Cr spheroids and a few large Cr sheets were observed in the region (marked (d) in Figure 4b). According to the micrographs and the statistics of Cr grain size, the size of refined Cr particles increased with the increasing distance from the surface to the bottom of the melt pool, and the majority of the Cr particles all had an almost round shape to minimize individual surface energy. A few Cr sheets were observed only at the bottom of the melt pool. The diameter of the Cr particles varied from several hundreds of nanometers to almost $\sim 10 \text{ }\mu\text{m}$, and the average diameter of Cr particles near the surface was less than $1 \text{ }\mu\text{m}$.

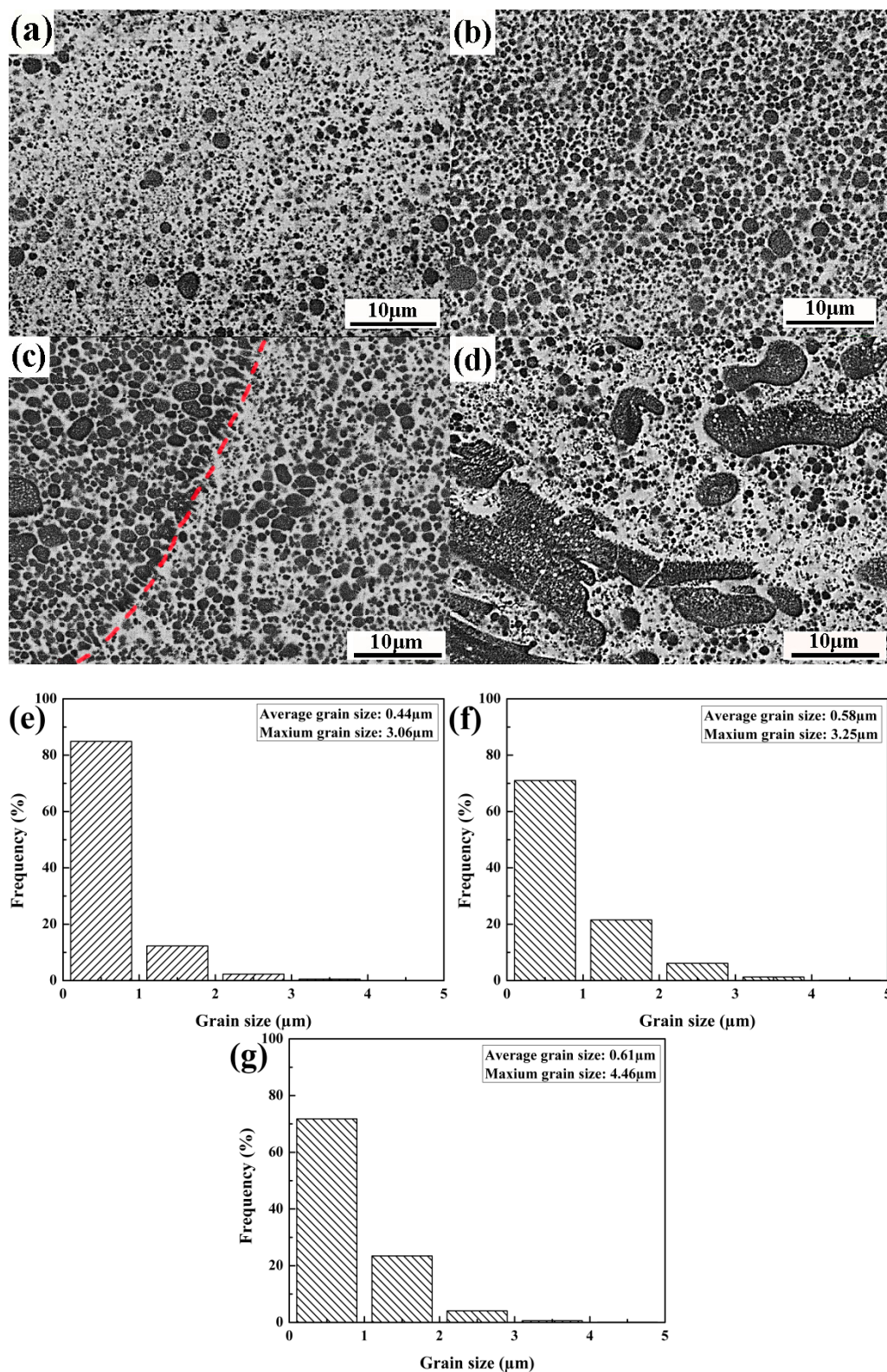


Figure 5. Magnified backscattered electron image of the morphologies of Cr particles in Figure 4b: (a) top of the melt pool, (b) middle of the melt pool, (c) overlap zone of the melt pool, (d) bottom of the melt pool, (e) the grain size distribution of Cr particles in (a), (f) the grain size distribution of Cr particles in (b), and (g) the grain size distribution of Cr particles in (c).

Figure 6 displays the magnified image of Cr-rich clusters on the overlapping zone in Figure 5c and their corresponding EDS analysis. As denoted by D in Figure 6a, many nano-sized Cu particles precipitated into a Cr spheroid. The EDS analysis demonstrated that the Cr content in the particle was similar to that of $\text{Cu}_{36}\text{Cr}_{64}$ (in mass ratio), as shown in Figure 6b. Figure 6c shows the sheeted Cr particle with an irregular shape (marked by E) containing a supersaturated Cr (66 wt%) (Figure 6d). Therefore, the Cr cluster was actually a Cr-rich cluster in the present study. The microstructure of the refined Cr phase dispersed in the melt layer had three kinds of morphological characteristics: the Cr spheroids, Cr-rich clusters, and Cr-rich sheets.

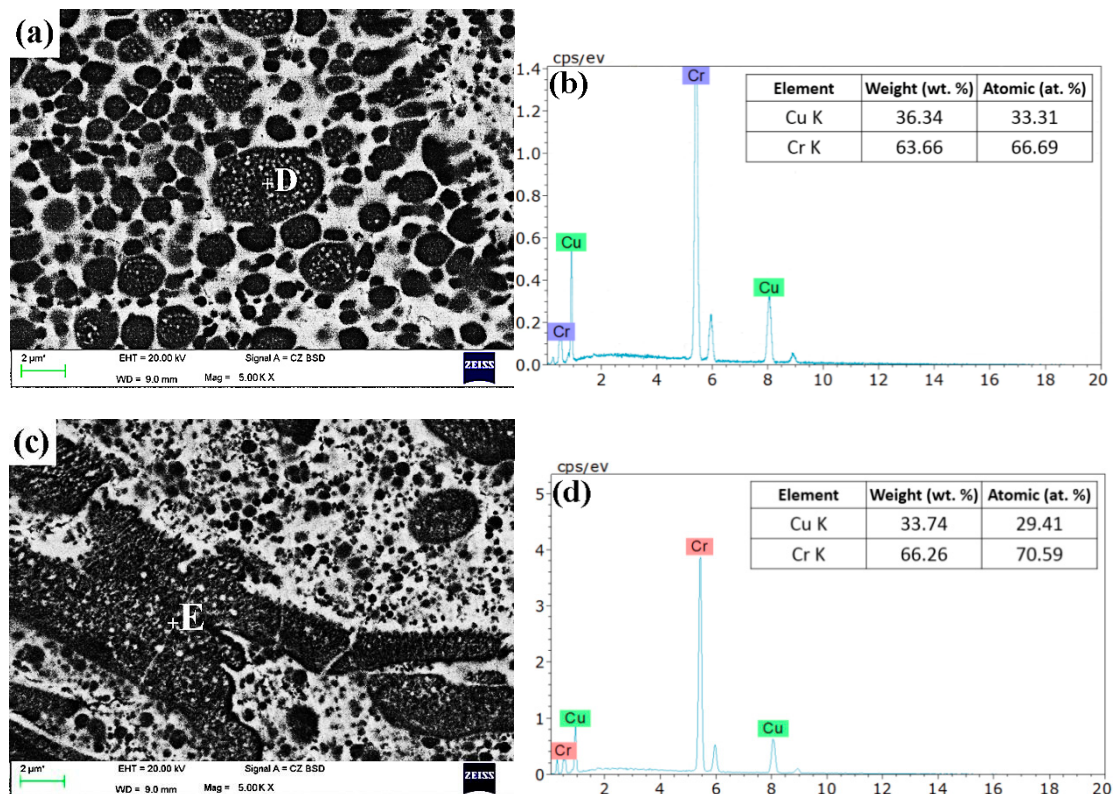


Figure 6. (a) Magnified image of the Cr-rich cluster in Figure 5c, (b) the corresponding EDS analysis of Point D, (c) magnified image Cr-rich sheet in Figure 5d, and (d) the corresponding EDS analysis of Point E.

3.2. Parametric Results

Figure 7a presents the influence of Q on the thickness of the refined layer: the higher the power density, the thicker the refined layer. With the same Q , the longer the interaction time, the more energy irradiated the surface during LSM. It was apparent that the thickness of the refined layer was directly related to the interaction time within the appropriate range of Q given here. However, the properties of Cu-Cr alloy not only depended on the depth of the refined melt layer, but also on the size and distribution of the Cr phase. As the grain refinement of Cu-Cr alloy depended both on the interaction time and laser power density, the effect of E on the melt layer is given in Figure 7b. On the basis of repeated experiments, it has been found that the optimal range of E is very narrow, between 43 MJ/m^2 and 56 MJ/m^2 . Generally, when E was lower than that of the optimal range, it was not sufficient to completely melt the Cr phase, leading to un-dissolved bulk Cr phase, illustrated in Figure 4a. In turn, when E was higher than 56 MJ/m^2 , the intense melt flow resulted in the formation of large quantities of Cr-sheets, which enlarged the size of Cr particles shown in Figure 4c. As shown in Figures 4b and 5, when E was 52.5 MJ/m^2 in the optimal range, most of the Cr particles had a sphere or near sphere shape dispersed on the surface of the melt layer, and only a few Cr-sheets may appear at the bottom.

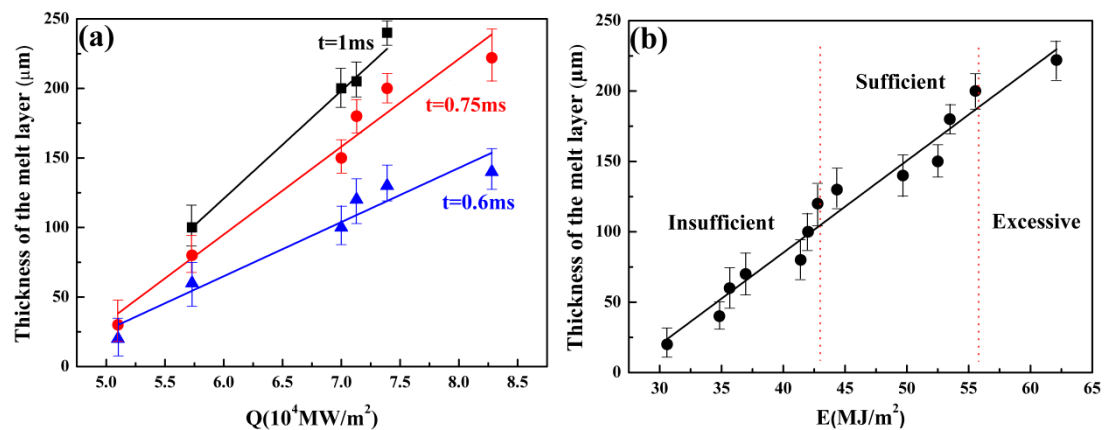


Figure 7. (a) The influence of laser power density and (b) laser energy density on the thickness of the melt layer of Cu-50Cr alloy.

3.3. Property

3.3.1. Withstanding Voltage

Figure 8 displays the overall view of the untreated and LSM-treated Cu-50Cr contacts. Large-scale surface modification was achieved on the surface of the contact. Figure 9 shows the withstanding voltage values of these contacts. The contacts treated by LSM with a refined layer exhibited a higher withstanding voltage (125 KV) than the untreated sample (103 KV), which was 21% higher than the untreated contacts. The results were in accordance with the expectations because LSM treatment provided grain refinement in the surface, which was responsible for the higher withstanding voltage observed.

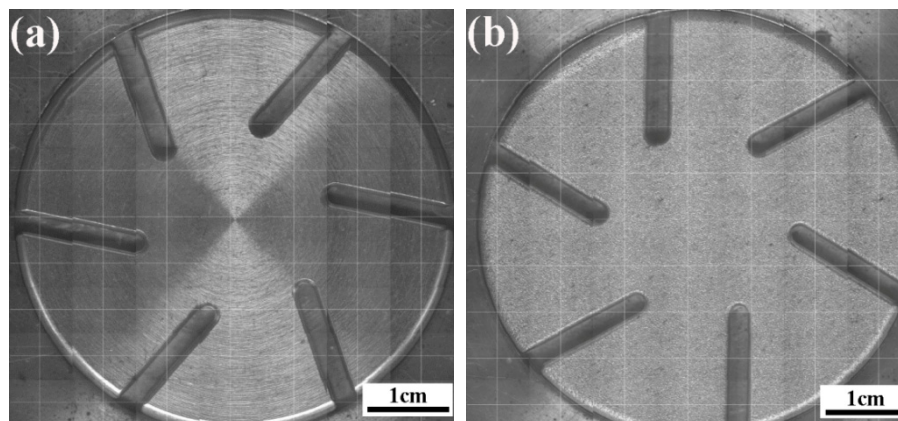


Figure 8. Top-view of (a) untreated and (b) LSM-treated Cu-50Cr contacts.

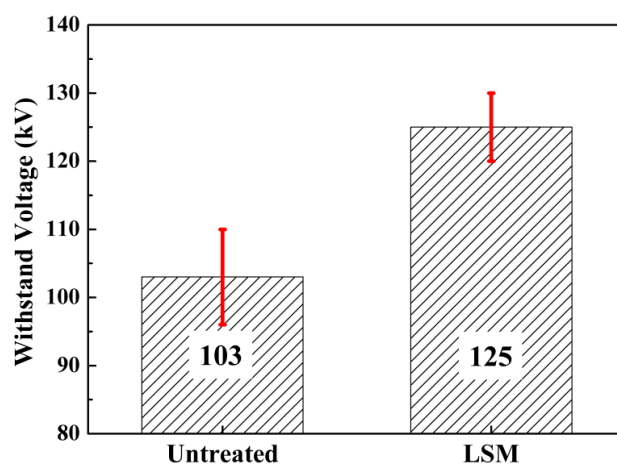


Figure 9. Withstanding voltage values for the untreated and LSM-treated contacts.

3.3.2. Interruption Capability

To testify to the influence of grain refinement on the switching performance of VIs, a direct comparison of the interruption capability of untreated and LSM-treated contacts was carried out. As shown in Figure 10, the LSM contacts passed all 15 successive tests, while the untreated contacts failed four times. The average arc duration of the LSM sample (5.6 ms) increased up to 33% higher than that of the untreated samples (4.2 ms), and both the max and min arc duration of LSM sample were higher than the untreated (Table 2). The arc duration of LSM contacts remained relatively stable, which fluctuated slightly around 5.6 ms. However, the arc duration of the untreated contacts differed greatly.

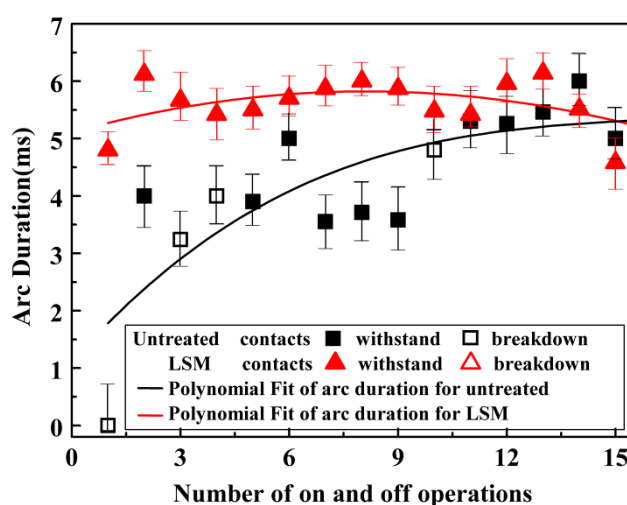


Figure 10. Arc duration measured by each switching off operation of the vacuum interrupters (VIs).

Table 2. Arc duration features of different samples.

Sample	Ave, Arc Duration (ms)	Max, Arc Duration (ms)	Min, Arc Duration (ms)	Standard Deviation of Arc Duration
Untreated	4.2	5.5	0	1.4
LSM	5.6	6.2	4.6	0.4

4. Discussion

4.1. Parametric Study

The thermal conductivity of Cu (394 W/m·K) is quite high, so it needs to consume more laser power to form a stable melt pool on the surface of Cu-Cr alloy. Therefore, the Q acted as a threshold, which determined whether the alloy surface could be melted. E is the energy input per unit time, which decided the depth and the microstructure of the melt layer. When insufficient E was adopted, the temperature in the melt layer was above the melting point of Cu and below the melting point of Cr. The adjacent Cr phase absorbed the latent heat released from the solidified Cu phase, so only the edges of the Cr phase were dissolved (denoted by Arrow A in Figure 4a). When excessive Q was adopted, the maximum temperature of the melt pool increased, and there existed a sharp temperature gradient from the melt surface to the substrate. As depicted by Arrow B in Figure 4c, it revealed the occurrence of deep laser beam penetration around the center of the laser track, and the temperature at the bottom of the melt pool was almost to the boiling point of Cr. Accordingly, it took more time to cool the melt pool, and the convection in the pool became more intense. The longer time the solidification cost, the more complete the liquid phase separation and the larger the Cr size would be. The appearance of the spherically-shaped Cr particles was beneficial for the improvement of the properties of Cu-Cr alloy, while the large Cr sheets with irregular shapes were harmful to the performance of Cu-Cr contacts. An appropriate selection of Q and t was essential to obtain a dispersed and refined microstructure. In this study, the derived value of laser energy E was given (Figure 7b). Only in the laser energy density range, the temperature of the Cu-Cr melt could be heated rapidly above the miscible metastable gap, then followed by sustainable inter-diffusion and rapid solidification, so the LPS was suppressed to obtain the desirable dispersive microstructure.

4.2. Microstructure Evolution

According to the Cu-Cr binary diagram proposed by Jacob demonstrated in Figure 11a, the mole Gibbs free energies (G_{mix}) of the Cu-Cr alloy at different temperatures are calculated in Figure 11b, and G_{mix} (J/mol) is defined as follows [31]:

$$G_{\text{mix}} = RT(X_{\text{Cu}} \ln X_{\text{Cu}} + X_{\text{Cr}} \ln X_{\text{Cr}}) + \Omega_{\text{Cu-Cr}} X_{\text{Cu}} X_{\text{Cr}} \quad (6)$$

where X_{Cu} and X_{Cr} are the molar fractions of Cu and Cr, $R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the gas constant, T (K) is the temperature of the melt, and $\Omega_{\text{Cu-Cr}}$ is the interaction coefficient of the two components [27]. As shown in Figure 11b, when the temperature is high, the value of ΔG_{mix} is always negative, indicating that the two melts, i.e., $L_{\text{Cu-rich}}$ and $L_{\text{Cr-rich}}$, can spontaneously mix with each other, and the single melt is miscible. G_{mix} tends to be positive when the temperature decreases, and whether the mixing of $L_{\text{Cu-rich}}$ and $L_{\text{Cr-rich}}$ can spontaneously proceed depends on the composition of the alloy and the temperatures of the system, while the two liquids are immiscible under certain conditions. Using the calculated results in Figure 11b, ΔG_{mix} of supercooled Cu-Cr melt at 1550 K was taken as an example in Figure 11c. According to the following equation [14,32],

$$\frac{\partial G_{\text{mix}}}{\partial X_{\text{Cr}}} = 0 \quad (7)$$

at Points a and e in Figure 11c, ΔG_{mix} has a minimum value, and at Point c, ΔG_{mix} has a maximum value. At Point b and Point d, the following expression could be obtained [14,32],

$$\frac{\partial^2 G_{\text{mix}}}{\partial X_{\text{Cr}}^2} = 0 \quad (8)$$

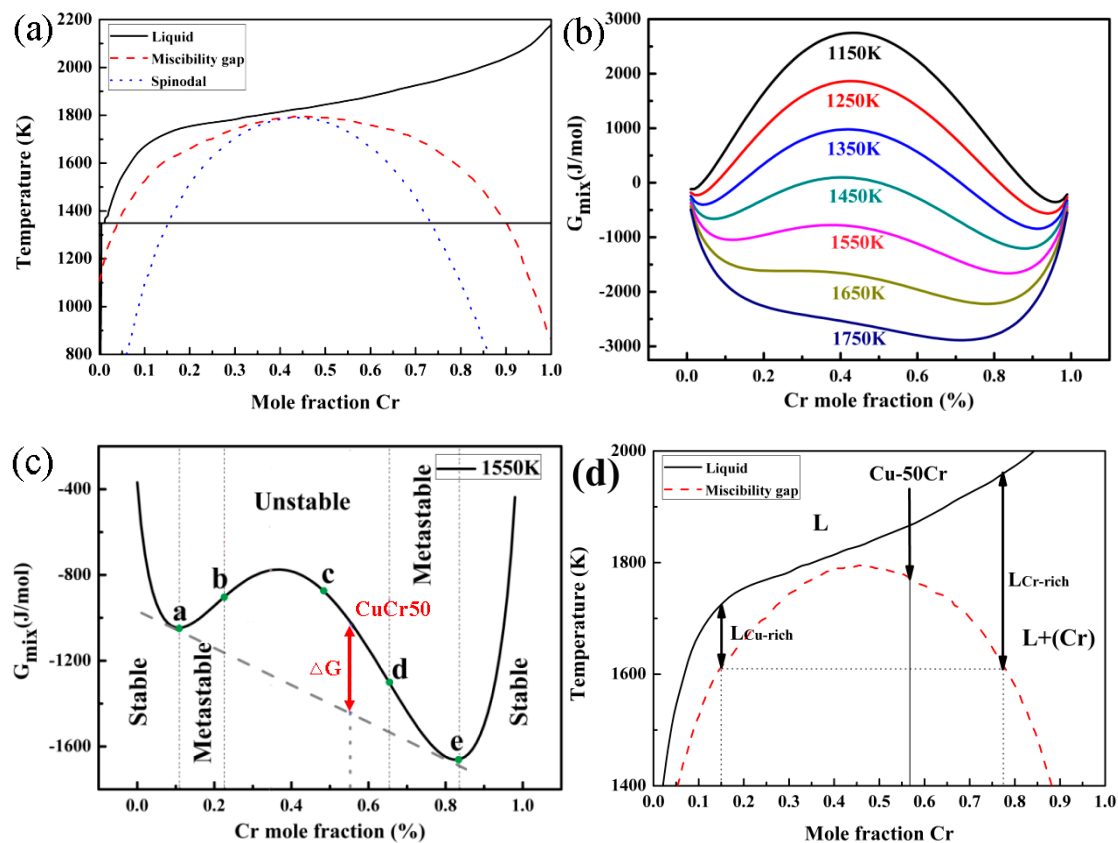


Figure 11. (a) Binary diagram of Cu-Cr alloy with a metastable gap predicted by thermodynamic data from Reference [31], (b) calculated mole Gibbs free energy (G_{mix}) of Cu-Cr alloy at different temperatures, (c) relationship between G_{mix} and the composition of Cu-Cr alloy, and (d) liquid phase separation under rapid cooling conditions.

(1) When the content of Cr is between a and b and d and e, the value of $\frac{\partial^2 G_{\text{mix}}}{\partial X_{\text{Cr}}^2}$ is positive, and the system is thermodynamically metastable; liquid phase separation can be carried out only when the degree of undercooling continues to increase. (2) When the composition of Cr is between Points b and d, the system is thermodynamically unstable. If the melt was undercooled, the Cu-Cr melt would be separated spontaneously to decrease the G_{mix} of the system. (3) Liquid phase separation does not occur in the melt of Cu-Cr alloy with the composition beyond Points a and e, where the system is thermodynamically stable. As for the Cu-50Cr wt% alloy, the composition is between b and c, where Cu-Cr melt can demix spontaneously when it was supercooled. As shown in Figure 11c, the driving force for liquid phase separation was $\Delta G = 445.9$ J/mol.

Cu and Cr existed as two independent phases in Cu-Cr alloy, and the two components will not undergo a solid-liquid phase transition at the same temperature, so the process of melting and solidification happened at their respective melting points. At 1355 K, the Cr phase was in the solid state, and the latent heat was only part of Cu. When the temperature rose to 2133 K, the Cu phase was all melted, and only the latent heat of Cr was considered at this temperature. In the temperature between 1355 K and 2133 K, the melt was in the state of the mixture of solid and liquid. As shown in Figure 4b, obviously, the Cr phase was completely fused in the Cu matrix. The latent heat of the solid-liquid phase transition in the melt zone at different temperatures is listed in Table 3. The cooling rate for the LSM samples was calculated by Equation (9) [33],

$$\frac{dT}{dt} = -\frac{2\pi K(T - T_0)^2}{A\left(\frac{q}{v}\right)} \quad (9)$$

where K (W/m·K) is the thermal conductivity of the alloy, T (K) and T_0 (K) are the melting temperature and room temperature, A is the absorptivity for the laser beam, v (m/s) corresponds to the laser scanning velocity, and q' (W) is the energy that can be used to raise the temperature of the remaining solid. The value of q^* is obtained by Equation (10) [33], and the value of A is obtained by Equation (11) [22],

$$q^* = q - 2r_B Z_m v L \quad (10)$$

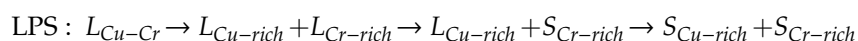
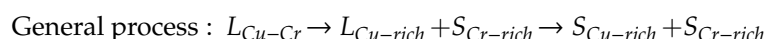
$$A = \frac{2\pi K r_B T}{1.77q} \quad (11)$$

where L (J/m³) is the latent heat of melting, q (W) is the laser power, r_B (m) is the radius of the laser beam, and Z_m (m) is the average thickness of the melt layer. For the calculation of the cooling rate, the laser scanning speed, and the thickness of the melt layer and their respectively laser power, $K = 244$ W/m·K, $r_B = 50$ μ m, $T_0 = 288$ K, $v = 0.13$ m/s, $q = \pi r_B^2 = 550$ W, $T_m = 2133$ K, $Z_m = 150$ μ m, and $L = 1.45 \times 10^9$ J/m³ were taken as input parameters. The calculated cooling rate was 7.29×10^6 K/s.

Table 3. Latent heat of the Cu phase, Cr phase, and Cu-Cr alloy, respectively.

Material	Density (10 ³ kg/m ³)	Latent Heat of Melting/(J·m ⁻³)
Cu	8.9	1.82×10^9
Cr	7.2	2.89×10^9
Cu-50Cr	7.9	1356 K: $0.5 \times 1.82 \times 10^9$
		2133 K: $0.5 \times 2.89 \times 10^9$

According to the calculation above, the cooling rate is on the order of $\sim 10^6$ K/s, which can lead to a considerable dynamic supercooling of ~ 150 K [34]. Generally, the supercooling of the Cu-Cr immiscible alloys with 50 wt% Cr content is less than 98 K during the process of liquid phase separation (LPS) [15]. As shown in Figure 11d, the Cu-Cr melt was supercooled into the metastable liquid miscible gap (MG) during LSM and then decomposed into mutual insoluble $L_{Cu-rich}$ and $L_{Cr-rich}$. Once the LPS started, the solidification of primary crystals stopped, as the Gibbs free energy of a liquid and a solid was larger than that of the coexistence of two liquids. The two distinct solidification procedures are described below:



The Cr particles with a spheroidal morphology dispersed in the Cu matrix with an average diameter of ~ 1 μ m evidenced the process of LPS, as shown in Figure 5. The whole solidification process lasted only tens of milliseconds; even if the time for liquid cooling was neglected, such a short time could not allow nano-sized nuclei of a solid solution to grow to Cr particles with a diameter up to a few microns due to slow diffusion kinetics in the solid state. However, if the micron-sized Cr particles were nucleated from a supersaturated Cu-Cr melt through the LPS, they would be able to reach a size even of several micros within a few seconds due to a faster convection kinetics, as well as collision-assisted coagulation in the liquid state.

As presented in Figures 5b and 6, the collisions and coalescences between Cr particles occurred frequently, resulting in an agglomeration trend to form Cr-rich clusters. The Cr particles were not stationary; instead, they were affected by various convection forces and gravity during LPS. The velocity of Marangoni motion (v_m) and Stokes motion (v_s) are the two competitive factors. The velocities of the Cr particles controlled by Marangoni motion due to temperature gradient and Stokes motion due to gravity are described as follows [11]:

$$v_m = \frac{2}{3} \cdot \frac{G}{3\eta_d + 2\eta_m} \cdot \frac{\partial \sigma}{\partial T} \cdot r \quad (12)$$

$$v_s = \frac{2}{3} \cdot \frac{(\eta_d + \eta_m)g}{\eta_m(3\eta_d + 2\eta_m)} \cdot \Delta\rho \cdot r^2 \quad (13)$$

where $r = 0.5 \mu\text{m}$ is the radius of the Cr droplet, and $G(\text{K/m})$ is the temperature gradient of the melt pool; the viscosity of Cr-rich phase μ_d and the viscosity of Cu-rich phase μ_m ($T = 1550 \text{ K}$) was estimated to be 3.5cP and 4cP, respectively. $\frac{\partial\sigma}{\partial T}$ is the interfacial energy with the value of $2.4 \times 10^{-4} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $g = 9.8 \text{ m}\cdot\text{s}^{-2}$, and $\Delta\rho = 1.2 \times 10^3 \text{ kg/cm}^3$ [35]. Therefore, the ratio of v_m/v_s was calculated to be 0.022G. Since the cooling rate of the melt layer was $7.29 \times 10^6 \text{ K/s}$, the G in the melt pool was up to $\sim 10^5 \text{ K/m}$, indicating that Stokes motion could be ignored. Generally, the temperature gradient at the bottom of the melt pool was larger than that at the other region. Obviously, the increase in temperature gradient can result in the increasing of v_m . Thus, the probability of collision and coalescence between the Cr-rich spheroids increased correspondingly. Consequently, the average diameter of Cr-rich particles in the Cu matrix increased with an increase in the distance away from the surface, as shown in Figure 5. Especially, at the bottom of the melt pool where the G was largest, the Cr-rich sheet appeared because of the fierce collisions and accumulation between Cr-rich spheroids.

Presented in Figure 5c is the overlapping zone of the melt pool. The left side is outlined by red dashed line, which was heated twice, and the size of the Cr particles was larger than that of the right side, which was heated only once. On the fusion line of the overlapping zone (the red dashed line), a large number of Cr spheroids can be observed to aggregate along the direction perpendicular to the overlapping line, which reflects the direction of solidification. Figure 6a shows an enlarged image of the Cr-rich spheroids in the reheated zone. Figure 6b shows the EDS element analysis of the Cr-rich particle, showing that the Cr phase is a Cr-rich sphere containing supersaturated Cu (36.34 wt%). The Cr-rich sites were also found in an electron beam-irradiated Cu-30Cr alloy, which were attributed to the formation of some $\text{Cu}_x\text{-Cr}_{1-x}$ compounds [36]. However, in theory, the formation enthalpy was positive on the whole composition range, implying that there was little possibility for the existence of such compounds. A more reasonable explanation for the formation of Cr-rich clusters was the solute trapping; a second liquid phase separation occurred for the Cu-rich phase inside the Cr-rich sphere, in which a large number of Cu-rich phases precipitated during second liquid-liquid phase transition. Therefore, a “hollow sphere” structure, which is shown in Figure 6, was formed. The overlapping area underwent a second heat input before the first heating process had completely cooled down. In the solidification process, the liquid-liquid transition was not complete, so the Cu-rich phase in the spheres could not completely separate from the Cr-rich phase. On the right side, which was heated once, it can be seen that the interface of the Cu phase and Cr phase was clearer and the edge of Cr spheres was more regular. This is because the area without reheating had higher undercooling and faster cooling speed, which not only resulted in a smaller size of the Cr phase, but also inhibited the occurrence of solute trapping.

4.3. Withstanding Voltage and Interruption Capability

The withstanding voltage and the interruption capability of Cu-Cr contacts depended on the size, distribution, and morphology of the Cr phase. The microstructure of the contact material dominated the motions of cathode spots during the switch off operations. When a vacuum interrupter was turned off, a vacuum arc was induced, and then, the cathode spots stimulated by the arc moved randomly on the contact surface to control the arc characteristics. The electron emission current remarkably increased with the decrease of the work function at constant electric field intensity. The maximum work function of the close-packed plane Cr (110) was 0.13 eV smaller than that of Cu (111) [37]. Therefore, the electrons were more easily emitted from the Cr phase, so the cathode spots preferred to ignite on Cr particles. This is in accordance with previous experimental results that the first breakdown occurred on the dielectrically-weak Cr phase [38]. The Cr particle size of the untreated alloy was $\sim 100 \mu\text{m}$, which was about 20 times bigger than that of the conventional recognized cathode spot size of $\sim 5 \mu\text{m}$ [39]. The near spherical cathode spots tended to restrict or jump over the coarse Cr phase during the process of arcing, which resulted in deep and large cathode craters. After the LSM treatment, the Cr particles

on the surface were refined to a smaller average size ($\sim 1 \mu\text{m}$) and a similar morphology to those of the cathode spots. Thus, the spot migration pattern was transferred to fast continuous moving, which led to a longer arc trace route and a higher velocity of spot motions, resulting in the uniform distribution of arc energy on the contact surface. As a result, the surface of the contacts was able to withstand a higher voltage (125 kV).

Grain refinement was also helpful to mitigate serious partial ablating of the surfaces and reduce the possibility of failures in switching off operations. As shown in Figure 10, all the failures of untreated contacts occurred with relatively lower arc duration, proving that the arc duration affected the success or failure of each switching off operation. The vacuum arc was supplied only by metal vapor evaporated from the contact surface material. Consider the critical metal vapor as an ideal gas: the effect of particle size on the metal vapor pressure is given by Kelvin's equation [40]:

$$RT \ln \frac{P(r)}{P(\infty)} = \frac{2\gamma \cdot V}{r} \quad (14)$$

where $P(r)$ is the vapor pressure on the condition that the radius of spherical Cr particles is r , $P(\infty)$ is the vapor pressure on the surface of coarse-grained Cu-Cr alloy (Cr size is about $\sim 100 \mu\text{m}$), which equals $5.0 \times 10^5 \text{ Pa}$ [41], $r = 0.5 \mu\text{m}$ is the radius of the Cr particle, and γ is the surface tension. Since the Cu-Cr alloy can be considered as a kind of mechanical mixture of the two phases, the value of γ is half from the Cu phase and half from the Cr phase, which is calculated to be $1.64 \text{ J}\cdot\text{m}^{-2}$ [40]. $T = 3000 \text{ K}$ is the temperature. V is the mole volume $7.15 \text{ cm}^3\cdot\text{mol}^{-1}$, and $R = 8.31 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ is the gas constant [27]. The relationship between saturated vapor pressure and Cr size was calculated, as illustrated in Figure 12. The vapor pressure $P(r)$ increased with the decrease in the Cr grain size. When the radius of Cr spheroids decreased to $\sim 0.5 \mu\text{m}$, the vapor pressure was $6.1 \times 10^6 \text{ Pa}$, which is 12 times that of the coarse-grained Cu-Cr alloy. The higher the vapor pressure, the longer time it could provide the metal vapor necessary for the arc to maintain stable currents. Hence, fine-grained contacts obtained more stable and longer arc duration (increased by 33%), so LSM contacts succeeded in passing the twenty successive switch-off operations, as shown in Figure 10.

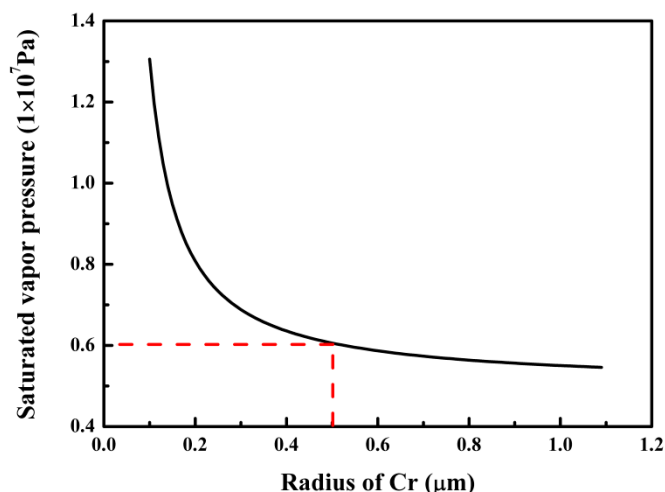


Figure 12. Relationship between saturated vapor pressure and the radius of Cr particles in Cu-Cr alloy.

5. Conclusions

A high power density laser beam (10^4 – 10^5 MW/m^2) was used to modify Cu-Cr vacuum electrical contacts, which were fabricated through the PM process. A homogeneous melt layer with thickness was produced by laser surface melting, and the microstructure of the layer was characterized by the refined spherical Cr spheroids and Cr-rich sites embedded in Cu matrix. The withstanding voltage

and the interruption capability were tested to investigate the effect of grain refinement on the electrical properties of Cu-Cr contacts. The following results were obtained:

1. The average diameter of the Cr phase was effectively refined from $\sim 100\ \mu\text{m}$ to $\sim 1\ \mu\text{m}$ and dispersed in the melt layer with a thickness of up to $150\ \mu\text{m}$.
2. In order to obtain a dispersed and refined microstructure, the optimal laser energy density was from $43\ \text{MJ}/\text{m}^2$ to $56\ \text{MJ}/\text{m}^2$.
3. The gathering tendency for the Cr spheroids induced by LPS was suppressed by the high cooling rate ($7.29 \times 10^6\ \text{K/s}$) during the LSM process.
4. The withstanding voltage of the LSM contacts increased to 125 kV, which was 21% higher than the untreated. The arc duration increased by 33%, resulting in 15 successful successive switching off operations.

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