Study on the microstructure and properties of a phosphor copper ball during its formation process

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Abstract

Microcrystalline phosphor copper balls with a diameter of 28 mm were prepared via continuous extrusion upsetting. Optical microscopy and electron backscatter diffraction were used to study the microstructural evolution of phosphor copper balls during the formation process. In addition, the hardness distribution and tensile properties were tested. The results show that fine dynamic recrystallisation grains and twins were formed after continuous extrusion and that the grains were further refined after upsetting. After continuous extrusion upsetting, there were typical $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ fibre textures, and the proportions of these three textures in the individual samples were different. The change in microhardness was affected by the microstructure. The increase in the hardness value from casting and continuous extrusion upsetting was owing to pronounced grain refinement. The grain sizes from the centre to the edge were similar, and the grain refinement was more uniform. Notably, the grain size of the extruded rod was still fairly uniform from the centre to the edge in the radial direction. It can be concluded that the continuous extrusion-upsetting phosphor copper anode is more conducive to the formation of black film, that is, it is more suitable for electroplating anode material.

1. Introduction

Pure copper and its alloys have good properties, such as high electrical conductivity, high thermal conductivity, and high formability and machinability, and they are some of the most attractive metals in industry \cite{1,2}. Phosphor copper is made via the addition of 0.04% to 0.065% phosphorus to pure copper. In recent decades, with the rapid development of the electronics industry, phosphor copper, as a soluble anode raw material for copper sulphate electroplating, has been increasingly studied in the hardware decoration and printed circuit board (PCB) industries \cite{3}. However, the microstructures of phosphor copper balls prepared by casting have defects such as segregation and coarse grains, which cause a thicker phosphorous film to be produced during the electroplating process, as well as a weaker bonding force, higher required phosphorous content, and poor subsequent machining properties \cite{4}.

As one of the most important ways to change the microstructure and mechanical properties of coarse-grained materials, grain refinement has attracted widespread attention from researchers worldwide \cite{5,6}. There are many commonly used methods of grain refinement, such as equal-channel angular pressing (ECAP) \cite{7,8}, cyclic extrusion-compression (CEC) \cite{9}, high-pressure torsion (HPT) \cite{10,11} and accumulative roll-bonding (ARB) \cite{12}. The ECA, HTP, CEC, and ARB processes are used to prepare various materials, such as copper \cite{13,14}, magnesium alloys \cite{15}, aluminium \cite{16}, tantalum \cite{17}, titanium \cite{18}, and magnesium aluminium alloys \cite{19}, and the cracks on the edges of the aluminium strips are eliminated \cite{20}. Through the above-mentioned grain refinement process, the microstructure can be recrystallised, thereby producing more equiaxed crystals and finer grains so that certain mechanical properties are optimised. However, many of the above...
refinement methods have shortcomings, and their high cost is not suitable for all industrial materials that require certain characteristics. Additionally, the extrusion and forging processes are suitable for the indoor grain refinement of some materials. Therefore, there have been related studies that combine these two traditional processes in a conventional direct extrusion and free forging cycle process, namely, repetitive extrusion and free forging (REFF). Compared to other refinement methods, the REFF method has higher cyclic strain, more shear surfaces, and a better crushing effect [21]. Similar to other refinement methods, the repetitive extrusion-upsetting (REU) technology consists of a continuous cycle of traditional direct extrusion and upsetting. Relevant studies have shown that it also has a high cyclic strain, more shear surfaces, and good crushing effects, along with other advantages [22]. Although some materials processed by REU can meet the needs of industrial applications, the process is complicated, and for the electroplating industry, the crystal grains of the phosphor copper balls are too fine, which increases the production cost. In particular, when the grain size of the phosphor copper ball is less than 10 μm, the optimal requirement for electroplating is reached, and previous studies have shown that a recrystallised structure is optimal [23]. Some studies have shown that the extrusion-upsetting (EU) process is a simple and severe plastic deformation (SPD) method that can refine grains and modify textures. Notably, the above method was applied to magnesium alloy bars [24]. The continuous extrusion-upsetting (CEU) process used in this study includes continuous extrusion forming (CEF) and upsetting. CEF is an SPD technique that is considered to increase the strength without a decrease in conductivity [25]. Therefore, in this study, microcrystalline phosphor copper balls were fabricated via continuous extrusion upsetting, and the microstructure evolution and mechanical properties of the phosphor copper during the EU process were studied.

2. Experimental method

2.1. CEU process and mechanical properties

A phosphor copper rod with a diameter of 20 mm cast using the up-drawing continuous casting method was employed as the test material. The chemical compositions are listed in Table 1. Figure 1 shows a schematic of the CEF process. The casting phosphor copper rod was extruded using TLJ-400 continuous extrusion equipment at room temperature. The extrusion rate was 10 mm s$^{-1}$, and the diameter of the extruded phosphor copper rod was 18.5 mm. After extrusion, the obtained extruded phosphor copper rod was processed into a 28 mm diameter phosphor copper ball by passing the rod through an upsetting mould, as shown in Figure 2; an upsetting rate of 3 mm s$^{-1}$ and a compression ratio of 1.36 were used. A Wilson VH1102 automatic micro-Vickers hardness

| Material component | Material composition (%) | Impurity content (%) |
|--------------------|--------------------------|----------------------|
| Rod Cu             | 99.9474                  | 0.0442               |
| Phosphorus Sn Pb Zn Ni Fe As | ≤0.00010 ≤0.00058 <0.00060 0.00045 0.00098 0.00059 |

Figure 1. Schematic diagram of the CEU process.
The hardness tester was used to measure the hardness distribution of the three sample sections (load: 1.96 N, pressure holding time: 10 s, test point spacing: 0.5 mm). In the tensile test, according to the GBT228.1-2010 standard for testing metal at room temperature, the cast rod and extrusion rod samples were cut along the longitudinal direction (ED or UD) to obtain dog bone samples with a standard length of 25 mm and a diameter of 5 mm. The phosphorus copper ball was cut along the upsetting direction to obtain dog bone samples with a standard length of 12 mm and a straight diameter of 3 mm. ED and UD refer to the extrusion and upsetting directions, respectively. The sample was subjected to tensile testing on a Shimadzu series electronic universal testing machine, and the strain rate at room temperature was 10–3/s. Each mechanical test was repeated three times.

2.2. Microstructure characteristics
To study the evolution of the microstructure and texture of up-drawing continuous casting copper bars after CEU, specimens were cut from the cast and extruded. Phosphor copper ball sections perpendicular and parallel to the ED or UD. ED and UD represent the extrusion and upsetting directions, respectively. After mechanical polishing, the cast rod sample was corroded with a solution of FeCl3 (3.5 g), HCl (12.5 ml), and ethanol (85 ml), and its microstructure was observed by optical microscopy (OM, Axio Scope A1). Electron backscatter diffraction (EBSD) analysis was performed using an FEG-450 thermal field emission scanning electron microscope equipped with an HKL Channel 5 system. The scanning step length of the upper casting rod was 20 μm, that of the continuous extrusion rod was 0.2 μm, and that of the upsetting ball was 0.12 μm. Each specimen was scanned in three different areas to measure the average grain size. The EBSD sample was placed in an electrolyte containing 50% phosphoric acid, 25% distilled water, and 25% ethanol, and mechanical grinding was performed at a DC voltage of 6.5 V. Then, the sample was chemically polished at 273 K for 7 s before the HKL Channel 5 software was used to perform the EBSD data analysis. A minimum orientation angle of 2° between two adjacent pixels was used to identify the grain boundaries, thereby identifying continuous closed grain boundary grains with at least a 2° grain boundary angle. The crystal grain orientation is defined as the average value of the pixel orientations constituting the crystal grain, and these average values were used to obtain the misalignment angle between adjacent crystal grains [18]. A critical misorientation angle of 15° was used to divide the low-angle grain boundaries and high-angle grain boundaries and analyse the misorientation angle distribution.

2.3. Electroplating of phosphor copper anode
The currents and times used in this experiment were 0.9 A, 4 h and 1.5 A, 2 h, respectively, and the corresponding current densities were 0.86 A dm⁻² and 2.16 A dm⁻², respectively. A CEU microcrystalline phosphor copper anode and a cast phosphor copper anode were used for electroplating. The samples of the CEU phosphor copper anode were numbered as 1 and 2, and the samples of the cast copper anode were numbered as 3 and 4. Samples 1 and 3 were electroplated with 0.9 A/4 h electroplating parameters, and samples 2 and 4 were electroplated with 1.5 A/2 h electroplating parameters. The basic sulphate copper plating solution (200 g/L CuSO₄ · 5H₂O + 60 g H₂SO₄ + 120 mg HCl) was used to eliminate the influence of other factors. A constant temperature of 25 °C was maintained in a constant-temperature water bath, and the other experimental conditions were consistent.
3. Results and discussion

3.1. Microstructure during the formation process

The microstructure of the upper casting rod is shown in figures 3(a) and (b). Because of the strong thermal conductivity of copper, the entire section of the phosphor copper rod demonstrated a high cooling rate; thus, the solidification was relatively uniform, and columnar crystals developed. The microstructure consisted of columnar and equiaxied crystals. The edge of the bar was a coarse columnar crystal, and the centre was a small equiaxed crystal [26]. After EBSD scanning, the number of grains was found to be 22, and the average grain size was $248 \pm 3 \mu m$. From figures 3(b) and (c), it can be seen that the low-angle grain boundaries in the up-drawn casting rod account for the main proportion. The contrast in the same grain is almost the same, but the contrast in different grains is very large. This result shows that there is no lattice distortion in the same crystal grain during the solidification process, but the grain boundary orientation difference in adjacent crystal grains is relatively large.

Figure 4 shows the microstructure of the centre, one-half radius, and edge of the upper casting rod after continuous extrusion, as well as the CEU sample (there is a colour-coded triangle in the lower right corner). Different contrasts in the figure indicate different orientations (composed of different Euler angles). In the figure, the yellow line represents low-angle grain boundaries (LAGBs), where the misalignment angle of the low-angle grain boundaries is between $2^\circ$ and $15^\circ$, and the black line represents high-angle grain boundaries (HAGBs). Regarding the grain boundaries, the value of the HAGBs was greater than $15^\circ$. Owing to the strong...
shear deformation and extrusion deformation of the upward casting rod during the continuous extrusion process, the original coarse columnar crystal grains were clearly broken. After continuous extrusion, the samples from the centre, half radius, and the edge show that the average grain size of the crystals decreases sharply from the initial 248 μm to 2.3 μm, 2.4 μm, and 2.7 μm, respectively; notably, the grain refinement is relatively uniform. As shown in figures 4(a)–(c), the refined grains were mainly composed of a large number of sub-grains and a small amount of recrystallised and deformed grains. Owing to the strong shear and extrusion deformations during the continuous extrusion process, a large amount of deformation and frictional heat was generated, which provides the driving force and temperature conditions for dynamic recrystallisation and causes the metal to recrystallise and undergo crystal grain refinement [27, 28]. However, similar to the continuous extrusion process of a CuCrZr alloy, our samples do not undergo complete DRX [25]. From figures 4(a)–(c), it can be seen that the phosphor copper rod sample after continuous extrusion produced a large number of twins from the centre to the edge area of the grain. After the phosphor copper rod obtained by continuous extrusion is upset, the average grain sizes from the centre to the edge of the sample were further refined to 1.2 μm, 1.5, and 1.7 μm. This grain refinement is still relatively uniform. As shown in figures 4(d)–(f), all sub-grains disappear after upsetting, and the grains after further refinement are mainly composed of many low-angle deformed grains and a small number of large-angle recrystallised grains. The twins within the grains almost disappeared, and a large number of LAGBs appeared inside the grains. The grains from the middle to the edge of the upsetting sample tended to recover nearly equiaxed grains and moved closer to the middle area so that the recovery degree increased; in contrast, the grains at the edge tended to bend. Because of the strain path from the initial continuous extrusion to the final upsetting, both the amount of strain and direction of strain are reversed; thus, the grains tended to return to an isometric shape. Furthermore, the upsetting process is typically explained by the slip line field. Owing to the discontinuity of the velocity, tangential stress is generated, which causes the sub-grains or grains to bend and shear, further refining the grains. This mechanism is similar to the evolution of the grain structure of industrially pure aluminium after the first cycle [22].

Figure 5 shows the histogram of the grain boundary orientation distribution in the centre, half radius, and edge area of the continuous extrusion rod and phosphor copper ball. As shown in figures 5(a)–(c), after continuous extrusion, the HAGBs of the centre, half radius, and edge area of the phosphor copper rod were 74%, 66%, and 58%, respectively. The proportion of HAGBs above 15° after CEF increased, and the newly formed grain boundaries in the deformation process appeared as sub-grain boundaries or HAGBs with larger orientation differences. This result is similar to the results obtained by ECAP extrusion after more than two passes. Because the effective strain in continuous extrusion is more than twice that of typical ECAP and conventional extrusion [29], a certain amount of HAGBs is produced under this stress. In addition, in
figures 5(a)–(c), it can be seen that the grain boundary distribution has a peak intensity at 60°. This result shows that a large number of twins with a \(\{111\}\) orientation angle of 60° were produced in the new grains, which conforms to the characteristic grain boundary structure of \(\Sigma 3\). Some researchers believe that because of the different orientations of crystal grains, when under a specific external force, the shear stress of the twin system in different crystal grains is also different, and the time and number of slips appearing during deformation are also different; furthermore, the strength of the interaction between dislocations, the interaction strength between dislocations, and the distribution of orientation differences in the grains are all different \([30]\). Thus, grains with a favourable orientation twin first and form a strong substructure in the preferred orientation. The results show that HAGBs decrease from the centre to the edge, which is caused by the different shear and deformation stresses in the different regions of the phosphor copper rod during continuous extrusion. As shown in figures 5(d)–(f), after the extruded rod was upset, LAGBs dominated the grains. The twin crystals and recrystallised structures disappear, resulting in a sharp decrease in the HAGBs.

The mechanism of grain refinement differs between continuous extrusion and upsetting. The grain refinement mechanism in the continuous extrusion process is grain dynamic recrystallisation \([25]\), while the grain refinement in the process of upsetting is grain breakage caused by the maximum shear stress on the slip line \([22]\).

Figure 6 shows the \{100\}, \{110\}, and \{111\} pole figures of the up-drawn cast rod, the continuous extrusion rod, and the phosphor copper ball, where X0 represents the normal direction (ND) (perpendicular to the extrusion direction) and Y0 represents the extrusion direction ED. It can be seen from these figures that there were medium-strength unannealed textures in the raw materials, and the texture dispersion was large. After continuous extrusion, these unannealed textures disappeared, the texture strength was weakened, and there was no pronounced grain orientation preference phenomenon. After passing the continuous extrusion rod through
upsetting, the texture orientation and strength of the samples were clearly different. The texture produced during continuous extrusion is parallel to the ND direction and parallel to the UD direction after upsetting. In the CEU process, the force acting on the specimen in the final stage is opposite to the ED direction, which may cause grain rotation and cause the texture of the coarse pier sample to become inclined from the radial direction to the ED direction. This mechanism is similar to the texture mechanism of the alloy bar after extrusion upsetting [24].

Table 2 lists the proportions of the main components in the EBSD orientation imaging statistics. The statistical results showed that the Goss-oriented grain content increased after continuous extrusion and upsetting, indicating that there were more grains after grain refinement, and there were many $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 100 \rangle$ fibre textures in the casting rod, continuous extrusion rod, and upsetting ball, which is consistent with the conclusion that copper wire contains a typical fibre texture [31]. Figures 7(a)–(c) shows the EBSD orientation distribution function (ODF) cross-sections for the upward casting rod, continuous extrusion rod, and phosphor copper ball, respectively. The colour from light to dark indicates a gradual increase in strength. This figure shows

| Samples   | Cube  $\langle 001 \rangle \langle 100 \rangle$ | Goss $\langle 011 \rangle \langle 100 \rangle$ | Brass $\langle 011 \rangle \langle 211 \rangle$ | S $\langle 123 \rangle \langle 634 \rangle$ | Fibre texture $\langle 111 \rangle$ | $\langle 110 \rangle$ | $\langle 100 \rangle$ |
|-----------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|-------------------|-------------------|-------------------|
| Initial   | 6.2%                                        | 0%                                          | 0.179%                                      | 21.3%                                      | 35%                           | 43%                           | 8.95%                          |
| CEF       | 12.2%                                       | 0.738%                                      | 1.75%                                       | 10.2%                                      | 14.4%                         | 40.7%                         | 19.7%                          |
| CEU       | 8.9%                                        | 6.6%                                        | 0.57%                                       | 18.1%                                      | 18.7%                         | 26.8%                         | 21%                            |

Figure 7. ODF diagram of phosphor copper: (a) upward casting rod, (b) continuous extrusion sample, and (c) upsetting ball.
that the main components of the upward casting rod texture have a strong (110) texture and weak (111) and (100) fibre textures. After continuous extrusion, the (100) texture was significantly strengthened, and the (111) and (110) textures were significantly weakened. As reported in [32, 33], the (111) and (110) fibre orientations develop in extruded and drawn face-centred cubic (FCC) crystals. After extrusion rod upsetting, the texture strengths of the (110) and (111) fibres increased, while the texture strength of the (100) fibre decreased. Hibbard concluded that the strength of the (100) fibre texture decreases with an increase in strain, and thus, that the (111) fibre texture is the most stable texture component in an FCC metal [34]. During compression, the (110) fibre orientation develops in FCC metals [35].

3.2. Formation Performance of the Phosphor Copper Balls
3.2.1. Microhardness
As shown in figure 8, the microhardness distribution from the centre to the edge section of the upward casting rod, continuous extrusion bar, and CEU sample is shown. As shown in figure 8(a), the hardness distribution of the upward casting rod was relatively uniform; thus, the low hardness accounted for the main proportion with a value of approximately 65 HV. From figure 8(b), it can be clearly seen that the hardness value of the upward casting rod increases significantly after continuous extrusion. This larger hardness value accounts for the main proportion. Notably, the hardness distribution was relatively uniform, with a value of approximately 75 HV. As shown in figure 8(b), the microhardness value of the continuous extruded rod increased further after upsetting, and the distribution was still relatively uniform in the radial direction; however, the hardness value of the central area was extremely high in the height direction. The hardness values of the upper and lower ends were low, with a value of approximately 110 HV. The change in microhardness was affected by the microstructure. The continuously increasing hardness of the sample from the casting rod to the continuous extrusion rod and then to the upsetting phosphor copper ball was due to severe grain refinement. The grain sizes from the centre to the edge were close to each other, and the grain refinement was more uniform. However, the grain size of the continuous extrusion rod was still close to the edge of the radius direction after upsetting.

3.2.2. Tensile performance
Figure 9 shows the true stress-strain curves of the upward casting rod, continuous extrusion rod, and upsetting phosphor copper ball specimen at room temperature. The results are shown in table 3. After the continuous extrusion of the original sample, the ultimate tensile strength (UTS) increased significantly from 236 MPa to 257 MPa, the yield strength (YS) increased slightly from 109 MPa to 114 MPa, and the elongation decreased from 46% to 36%. The change in the YS can be explained by the Hall-Petch equation [36]. The grains of the initial sample were refined after continuous extrusion, so the YS increased. This result is most likely due to the increase in dislocation density during the deformation process; thus, the tensile strength increased. A certain degree of work hardening occurred during the continuous extrusion process, which decreased the elongation of the sample. However, figure 9 and table 3 show that when the continuous extrusion rod underwent upsetting, the UTS increased sharply from 257 MPa to 414 MPa, the elongation increased slightly, and the YS decreased sharply from 114 MPa to 64 MPa. According to the Hall-Petch equation, the grain size of the continuous extrusion sample is further refined after upsetting, and the upsetting sample should have a higher YS. However, the experimental results of this study were the opposite. Therefore, not only is the Hall-Petch equation needed to explain this result, but the texture evolution results also need to be used in the explanation. In other words, the different textures of the continuous extrusion sample and upsetting sample need to be part of the explanation [24].
Compared to the continuous extrusion sample, the increase in the elongation of the sample after upsetting was due to the decrease in the work hardening rate when the stress increased, which facilitated the formation of the phosphor copper ball.

To study the rapid necking behaviour of phosphor copper casting slabs under different processes, scanning electron microscopy (SEM) was used to analyse the fractures; the results are shown in figure 10. The results show that a relatively flat area can be observed near the dimples of phosphor copper, which is a typical fracture characteristic of copper. As shown in figure 10(a), the tensile fracture of the upward casting rod had a large number of dimples and an uneven size distribution. This is due to defects such as deep dimples and shrinkage holes, which are caused by the processing of materials, such as casting. This result shows that there is a relatively large plastic deformation before upward casting rod fracture occurs [37]. After continuous extrusion upsetting, the dimple size decreased, and the dimple became shallow, which was due to the decrease in the average grain size. This result is similar to that reported in [38]. From the point of view of dimple change, although the toughness of the sample decreases, the overall feature is still plastic fracture, which corresponds to the previous elongation change [39].

| Samples | Yield strength, MPa | Ultimate strength, MPa | Elongation, % |
|---------|---------------------|------------------------|--------------|
| Initial | 109 ± 2              | 236 ± 1                | 46 ± 3       |
| CEF     | 114 ± 4              | 257 ± 2                | 36 ± 1       |
| CEU     | 64 ± 2               | 414 ± 1                | 38 ± 0.9     |

Figure 9. Stress-strain of phosphor copper sample after undeformed, continuous extrusion and CEU.

Figure 10. SEM images of (a) upward casting rod, (b) continuous extrusion, and (c) fracture of upsetting specimen.

Table 3. Mechanical properties of three samples.
3.3. Effect of phosphor copper anode on electroplating

3.3.1. Current and resistance in electroplating process

The change rule for the current and voltage in the electroplating process can be obtained directly from the DC power supply of the BH-Hastelloy cell tester, and the ratio of voltage to current is the change rule of the corresponding resistance, as shown in figure 11. It can be seen from figure 11(a) that when the electroplating parameter is 0.9 A/4 h, the current of the CEU phosphor copper anode is stable before 2 h, indicating that the electroplating process is very stable, and the anode is not passivated; between hours two and three, the current decreases, and then it is stable after 3 h, and the current is 0.8 A, indicating that the anode is slightly passivated, and then normal electroplating begins. This passivation has no pronounced effect on electroplating. The current of the cast phosphor copper anode rapidly decreased to 0.6 A in a few minutes, stabilised at 0.6 A between 30 min and 2 h, and then began to decrease to 0.5 A until the end of electroplating. This shows that the passivation of the cast phosphor copper anode occurs easily during the electroplating process, which affects the electroplating effect. Regarding the change in resistance, the resistance of the CEU phosphor copper anode was in a stable state before 2 h, which indicated that the black film formed evenly and stably and increased after 2 h, indicating that the black film continued to form, and the resistance of the cast phosphor copper anode increased at the beginning of the electroplating process, and then decreased suddenly after 30 min, indicating that the black film formed on the anode surface fell off locally, and then decreased again. The black film began to increase, indicating that the black film continued to form, in order to supplement the black film to maintain the plating process, and finally make the plating in a stable state, the black film formed in this process is not uniform. Figure 11(b) shows that both types of phosphor copper anodes will be passivated rapidly, but the final stable current of the CEU phosphor copper anode was higher than that of the cast phosphor copper anode. From the point of view of resistance, the black film on the cast phosphor copper anode continued to form, but it decreased suddenly after 1 h until the end of electroplating, which indicated that the black film on the cast phosphor copper anode would fall off suddenly during the continuous formation of the black film during electroplating, and it would fall off until the end of electroplating; however, although the resistance of CEU phosphor copper anode decreased at a certain time, the resistance increased again later, which indicated that the CEU phosphor copper anode had high resistance. The black film on the phosphor copper anode falls off at a certain time during the process of electroplating, but the black film will continue to form until the end of electroplating. In conclusion, the electroplating effect of the CEU phosphorous copper anode was better than that of the cast phosphorous copper anode under the two electroplating parameters. The reason for this phenomenon is that the grain size and structure of the phosphor copper anode significantly influence the adhesion of the black film formed on the anode surface during the plating process. The smaller the grain size, the greater the adhesion of the black film [23].

3.3.2. Black film on phosphor copper anode surface

Previous studies have shown that the main composition of black film is, [40] so only the microscopic morphology of the black film after the electroplating of different phosphor copper anodes is discussed here. SEM was used to detect the microscopic morphology of the black film, as shown in figure 12. Figures 12(a) and (b) indicate that when the electroplating parameter was 0.9 A/4 h, the black film produced in the CEU phosphor copper anodic plating process was compact and uniform, and no shedding holes were present. However, in the process of casting phosphor copper anodic plating, the black film was partially shed, the surface holes were
larger, there were more cracks, and the binding force was insufficient. According to the formation mechanism of the black film, the disproportionation reaction may occur locally, which leads to an increase in the coating roughness. It can be seen from figures 12(c) and (d) that the black film on the CEU phosphor copper anode formed relatively densely during the electroplating process, but partial shedding, many cracks in the black film, and insufficient adhesion were present. However, the black film formed during the electroplating of the cast phosphor copper anode exhibited pronounced shedding behaviour, which also provides evidence that the resistance declined starting at a certain point in the process of electroplating. In summary, the influence of different phosphor copper anodes on electroplating is mainly through affecting the formation of black film, which will further affect the performance of electroplating. Meanwhile, it can be concluded that the CEU phosphor copper anode is more conducive to the formation of black film, that is, it is more suitable for electroplating anode material.

4. Conclusion

After the continuous extrusion of the edge columnar crystals and central equiaxed crystals of the up-drawn casting rod, the grain size largely decreased, a recrystallised structure and twin crystals formed, and the grains were refined. With the continuous extrusion of the rod through upsetting, the grain size continued to decrease; thus, the crystal grains were better refined and met the refinement requirements.

The grain refinement mechanism differed between the continuous extrusion and upsetting. Continuous extrusion produced a large amount of deformation and friction heat, which recrystallised the metal and refined the grain. In contrast, upsetting caused grain breakage owing to the generation of the maximum shear stress on the slip line.

After continuous extrusion upsetting, there were typical \( \{111\} \), \( \{100\} \), and \( \{110\} \) fibre textures, and the proportions of the three textures in individual samples were different. The change in microhardness was affected by the microstructure. The continuous increase in coarse hardness from casting to extrusion and then to
upsetting was due to pronounced grain refinement, the grain sizes from the centre to the edge were close to each other, and the grain refinement was more uniform. Notably, the grain sizes in the upsetting sample from the centre to the edge of the radius direction were still close to each other.

Under all of the parameters in the experiment, the black film produced in the process of CEU phosphorous copper anodic plating was uniform and dense, and there was either no peeling or partial peeling. However, in the process of casting phosphor copper anodic plating, the black film substantially fell off, the surface holes were larger, more cracks occurred, and the bonding force was insufficient. It can be concluded that the CEU phosphor copper anode is more conducive to the formation of black film, that is, it is more suitable for electroplating anode material.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflicts of interest

The authors declare no conflicts of interest.

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