Effect of Cryogenic Treatment on Extruded Copper Structures

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Abstract. To improve the quality of electroplated copper anodes and reduce the amount of anode mud, it is necessary to further refine copper grains. In the electronics industry, this is typically accomplished by either extrusion or cryogenic treatment. In this study, samples were subjected to different cryogenic treatment periods, and SEM, EDS, XRD, and hardness tests were performed. It was confirmed that a sub-grain boundary was formed due to the disappearance of vacancies and an increase in dislocations after the cryogenic treatment of extruded copper, which improved the grain refinement and hardness. At longer treatment times, the combination and entanglement of dislocations reduced the strengthening effect, and the copper diffraction peaks changed. However, the distribution of trace phosphorus did not change with the grain refinement distribution. Therefore, the results confirm that cryogenic treatment can be used to refine the grains of extruded copper.

1. Introduction

Cryogenic treatment is currently widely used to improve the organization of materials or eliminate stress in steel and non-ferrous metals. Much research has been performed on steel processing, including the treatment of retained austenite [1-3] in high-speed steel [4] and other steels to improve the service life of tools. Some researchers have used this technique for cemented carbide [5-7] to improve the mechanical properties of materials, and much research has been performed on copper and aluminum alloys [8-13]. It has been noted that cryogenic treatment makes the structure of copper alloys compact, changes the stress, and rotates and refines the grains. As electronics technology has developed, the requirements for electroplating anode copper have become increasingly stringent. It is necessary for the dissolution of copper to be even and controllable during electroplating. A lower amount of anode mud is preferred, and only in this way can a higher-quality circuit board be prepared. In order to solve this problem, phosphorus and refining crystal grains are often added to copper [14-17]. The industry currently requires 0.04-0.065% of phosphorus to ensure the even distribution of copper. Phosphorus forms a gel-like Cu3P anode film on the surface of copper during electroplating, which can completely prevent copper particles from falling off and also helps slow the dissolution of copper. However, the distribution of phosphorus in copper varies according to the different processes used. If crude phosphorus in the original structure is concentrated at the grain boundary, and other impurity element in copper are simultaneously enriched at the grain boundary, during electroplating, copper will first dissolve at the grain boundary. The internal dissolution speed of the crystal grains is slower than...
at the grain boundary, and the undissolved crystal grains enter the solution in the form of anode mud, which increases the consumption of anode copper. More importantly, the anode copper will nodulate and roughen the cathode during its migration. Even if undissolved copper is present when the crystal grains are small, the Cu$_3$P gel-like anode film can prevent the cooper from detaching and entering the anode mud. Therefore, grain refinement is an important way to improve the quality of phosphor copper. In this respect, the grains can be refined during continuous casting, but this method is rarely used. Deformation can occur during subsequent processing steps to achieve grain refinement. Much work has been performed in this field, and have shown good results. In order to achieve refine the grains, cryogenic treatment was performed after the extrusion deformation of cooper. This technique is inexpensive, simple to operate, does not damage the workpiece, has no pollution, and has a low energy consumption.

2. Research methods
In this research, an upward continuous casting cooper rod with a diameter of 20mm was used, with a phosphorus content of 0.04-0.065%. After deformation extrusion, the diameter was 18.5 mm, and the cut 20mm was held in liquid nitrogen at -196°C to cryogenically treat samples for 0h, 2h, 6h, 8h, and 20h. After the cryogenic treatment, the deformation, structure, and grain change of samples were analyzed using a D/max-2004 X-ray diffractometer. The distribution of phosphorus and copper in the structure was analyzed using a JSM-7000F scanning electron microscope (SEM). And an HV-1000DT microhardness tester was also used.

3. Test Result and Analysis

3.1 Effect of Different Cryogenic Treatment Periods on Deformed Copper Structure
Samples exposed to different cryogenic treatment periods were observed, and the obtained structures are shown in Figures 1-6.

Figure 1. Deformation without cryogenic treatment is the same as (a, b, c).

Figure 2. Deformation after 1 h cryogenic treatment is the same as (a, b, c).
Before the cryogenic treatment of copper samples, internal stresses and crystal defects were present due to extrusion deformation. After extrusion deformation, the surface cooled first, followed by the core, which led to the generation of surface compressive stress and core tensile stress in the samples. During the cryogenic treatment of cooper samples, due to heat transfer, the surface temperature decreased before the core temperature. During the cryogenic process, the core tensile stress decreased.
at the beginning and increased again after reaching a certain time, resulting in new deformations and slip dislocations. At this time, the stress state included both surface compressive stress and core tensile stress. When the sample was removed at room temperature, the surface of the sample eventually reached room temperature, followed by the core. During this process, the stress changed to surface tensile stress and core compressive stress. In terms of the crystal structure, metal plastic deformation theory holds that metal plastic deformation at normal and low temperatures mainly occurs by slip and twinning. Therefore, the change in the type of stress affects the change in the slip and twinning of the extruded copper samples. The grain orientation varied between different grains, and samples with different grains had different slip directions.

After copper extrusion deformation, many crystal defects, vacancies, and dislocations appeared in the grain, as well as a small number of twins as shown in Figure 1a and 1b. In terms of grain size, a large number of fine grains was formed among the bulk grains as shown in Figure 1c. When the extruded copper was subjected to cryogenic treatment, the temperature decreased from room temperature 20°C to 196°C (a temperature difference of 216°C), which produced a large shrinkage pressure in the samples. Under this shrinkage pressure, the crystal defect vacancies caused by deformation disappeared, and dislocation parts merged to form new dislocations and sub-boundaries. It can be seen from Figure 2a and 2b that there were slip lines and twins in the structure. The appearance of twins may be the main reason for the formation of sub-boundaries, which can refine the grains to a certain extent, as shown in Figure 2c. It can be seen from Figure 2c that the large crystal grains in Figure 1c substantially disappeared, and the crystal grains were refined. When the cryogenic period was extended to 2h and 6h, crystal defect vacancies and dislocations continued to merge to form new sub-grain boundaries, dislocations, or dislocation entanglements and disappearances. The grains were further refined, and many slip lines and twins (sub-grain boundaries) were formed inside the grains as shown in Figures 3a, 3b, 4a, and 4b. Additional grain refinement was the result of crystal deformation due to a prolonged cryogenic period, as shown in Figures 3c and 4c. As the cryogenic period was extended to 10h and 20h, the slip line (sub-grain boundary) in the grain had a tendency to merge and decrease, as shown in Figures 5a, 5b, 6a, and 6b. The effect of grain refinement was reduced, as shown in Figures 5c and 6c. In addition, as the cryogenic treatment time was prolonged, new corrosive spots appeared inside the grains, which may be the result of dislocation entanglement during movement. The entangled points have high energy, making them subject to corrosion. The resulting corrosion points are shown in Figures 6a and 6b.

It can be seen that the deformation stress and the stress generated by cryogenic shrinkage in the extruded cooper caused changes in vacancies, dislocations, slip lines, and twins. This resulted in the formation of sub-grain boundaries and grain refinement.

### 3.2 XRD Analysis
The XRD analysis of continuous casting copper and extruded copper samples are shown in Figure 7 and Figure 8.
Figure 7. XRD pattern for continuous casting cooper.
Figure 8. XRD patterns for different cryogenic periods.

As can be seen from Figure 7 and Figure 8, the extrusion deformation and the cryogenic treatment did not cause diffraction peaks to appear after the copper phase transformation. The position and intensity of the diffraction peaks in Figure 7 and Figure 8 were measured, and the results are shown in Table 1. As can be seen from Table 1, the strength of (200) and (222) faces of face-centered cubic copper increased, while the strength of the (220) and (311) faces showed relative decreases due to the extrusion deformation of copper.

According to the principle of expansion and contraction, the crystal material generated compressive stresses which reduced the volume during cryogenic treatment. In this way, the crystal material generated internal stress. Due to the action of the high internal stress, the dislocation-prone crystal plane firstly slipped, and the preferred orientation of the grain rotated obviously. The strength of the (200) and (222) faces in the extruded copper sample after the cryogenic treatment were generally larger than that of the extruded copper. The (220) surface was enhanced only before 2 hours and continued to decrease after the enhancement. The (311) surface continued to increase during the cryogenic process, while the strength at the beginning of cryogenic treatment was greater than during the extruded state. In short, the change in the peak strength was due to the disappearance of vacancies and the rearrangement of dislocations caused by the cryogenic treatment. The cryogenic treatment caused a significant change in the relative intensity of the XRD diffraction peak of copper on the main diffraction crystal plane.
Table 1. Peak ratio of diffraction intensity at different cryogenic periods.

| Diffraction Peak | Continuous Casting State | Extrusion State | 1h | 2h | 6h | 10h | 20h |
|------------------|--------------------------|----------------|----|----|----|-----|-----|
| \(I_{(111)}\)    | 100.0                    | 100.0          | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| \(I_{(200)}\)    | 39.1                     | 46.5           | 75.2 | 61.4 | 67.6 | 72.7 | 77.0 |
| \(I_{(220)}\)    | 28.6                     | 9.8            | 9.5  | 13.3 | 7.5  | 7.0  | 4.2  |
| \(I_{(311)}\)    | 18.4                     | 16.0           | 17.2 | 16.1 | 16.4 | 12.7 | 10.8 |
| \(I_{(222)}\)    | 3.7                      | 6.9            | 7.9  | 8.9  | 8.4  | 7.3  | 9.1  |

In order to further determine the effect of cryogenic treatment on grain refinement, the grain size was calculated from the Scherrer formula according to the XRD curve:

\[
D_{hkl} = \frac{K \lambda}{\beta \cos \theta}
\]

where \(D_{hkl}\): is the grain size (nm) perpendicular to the hkl crystal plane, \(\beta\) (20) is the diffraction caused by grain refinement peak broadening (radian), \(\lambda\) is the X-ray wavelength (nm), \(\theta\) is the diffraction angle (degree), and \(K\) is a constant value (if \(\beta\) takes half height and width, \(K = 0.89\)).

For samples with different cryogenic treatment periods, \(D_{hkl}\) of the diffraction peaks (111), (200), (220), (311), and (222) were calculated, and the average values were obtained as shown in Table 2. It can be seen that at longer cryogenic treatment times, grain refinement tends to occur between 0h and 6h, and decreases between 10h and 20h, during which the grain size tends to increase. This is basically the same trend as the results of the previous studies.

Table 2. Trends of grain sizes at different cryogenic treatment periods.

| Cryogenic Period (h) | 0 | 1 | 2 | 6 | 10 | 20 |
|----------------------|---|---|---|---|----|----|
| Grain Size (μm)      | 0.628 | 0.614 | 0.598 | 0.576 | 0.579 | 0.630 |

3.3 EDS Analysis

a. Untreated.  
b. Cryogenic treatment for 1h.
In order to study the change of the alloying element phosphorus during the cryogenic treatment of extruded copper, surface scans were used to analyze the phosphorus distribution in the copper.

As can be seen from the results in Figure 9, although the grain size of copper was refined by cryogenic treatment, the distribution of phosphorus hardly changed. During the casting process, because phosphorus was almost completely segregated and concentrated on the grain boundary, the phosphorus distributed on the grain boundary after extrusion deformation was redistributed due to the fracture of the crystal grains. This made it difficult to re-enter the solid crystal grains, and it was redistributed at the newly formed high-energy sub-grain boundaries. During the cryogenic treatment, the kinetic energy was insufficient because of the diffusion of phosphorus atoms, so that the phosphorus in the crystal grains or at the grain boundary could not diffuse to the newly formed sub-grain boundary. Even with prolonged grain refinement, it was difficult for the small phosphorus atoms to diffuse to the sub-grain boundaries with insufficient kinetic energy. Therefore, the distribution of phosphorus showed nearly no changes, as shown in Figure 9a-d.

In addition, a point analysis was conducted at the points of phosphorus enrichment in the samples subjected to different cryogenic treatment periods, and the results are shown in Figure 10. It can be seen that the phosphorus content in the precipitated phase was 0.1%. Therefore, it can be concluded that although the cryogenic treatment refined the grains of the extruded copper, it had little effect on the distribution of phosphorus.
3.4 Effect of Cryogenic Treatment on Hardness

The change of hardness can be observed by measuring the hardness of samples for different cryogenic periods, as shown in Figure 11.

As can be seen from Figure 11, at longer cryogenic treatment times, the hardness of the core and edge of the samples continuously increased. The hardness increased greatly from 0h to 2h, and then only slightly increased thereafter. From another aspect, grain refinement was weakened. The hardness of the core and the edge increased between 12.3 and 12.5 (HV). Therefore, it can be concluded that the grain refinement of the core and the edge was consistent during the cryogenic treatment, and the grain size after the cryogenic treatment was affected by extrusion deformation.

4. Conclusion

After analyzing the extruded copper samples, the following conclusions were obtained:

1) The stress generated by the cryogenic treatment of extruded copper resulted in vacancies, dislocation redistribution, and new dislocations, which formed sub-grain boundaries. This caused the copper crystals to shrink and then grow within the test time range. The grain refinement effect decreased at longer test times.

2) The copper crystals had different orientations in grains, the slip degree of each grain was different, and the diffraction peak intensities of higher planes were also different.

3) The phosphorus in extruded copper did not change during the cryogenic treatment, and the distribution of phosphorus was not redistributed due to the cryogenic grain refinement, and copper
phosphide did not decompose.

4) During the cryogenic treatment, the hardness of each position of the sample was essentially the same, and the effect of the cryogenic treatment on the grain refinement of the copper sample was small. These two results are consistent with each other.

References
[1] Kalsia N S, Sehgalb R, Sharma V S, (2010) Materials & Manufacturing Processes, Cryogenic Treatment of Tool Materials: a Review, 25(10): 1077.
[2] Stewart H A, (2004) Forest Products Journal, Cryogenic Treatment of Tungsten Carbide Reduces Tool Wear when Machining Medium Density Fiberboard, 54(2): 53.
[3] ZHANG Hejia, XU Yonggang, MA Hongying, LI Zhengtuan, WANG Wenguang, (2018) Microstructure of Ultrafine-Grained Cemented Carbides with Deep Cryogenic Treatment, Chinese Journal of Rare Metals, Vol.42 No.11, 1149-1155.
[4] LI Xiong, LI Shiyan, ZHANG Hongbing, RUAN Xue, (2002) Microstructure of 6W-5Mo-4Cr-2V High Speed Steel after Cryogenic Treatment, Journal of Shanghai Jiaotong University, Vol.36 No.7, 905-907,910.
[5] Yong A Y L, Seah K H W, Rahman M, (2007) International Journal of Advanced Manufacturing Technology, Performance of Cryogenically Treated Tungsten Carbide Tools in Milling Operations, 32(7-8): 638.
[6] Wei J W, Tang L L, Li S H, Wu X C, (2012) Transactions of Nonferrous Metals Society of China, FEM Simulation and Experimental Verification of Temperature Field and Phase Transformation in Cryogenic Treatment, 22(10): 2421.
[7] Gill S S, Singh R, Singh H, Singh J, (2009) International Journal of Machine Tools & Manufacture, Wear Behavior of Cryogenically Treated Tungsten Carbide Inserts under Dry and Wet Turning Conditions, 49(3-4): 256.
[8] Teng Jie, LIU Fang, JIANG YONG, CHEN Jian, CHEN Ding, (2008) Heat Treatment of Metals, Red Cooper Processing, Vol.33 No.4, 49-51.
[9] LU Qiuong, ZHAO Weisong, SUI Manting, LI Douxing, (2006) Acta Metallurgica Sinica, Study on Nano Twin Cooper Produced by Dynamic Plastic Deformation at Liquid Nitrogen Temperature, Vol.42 No.9, 909-913.
[10] WANG Sixian, GU Kaixuan, WANG Junjie, ZHANG Hong, GUO Jia, (2013) Chinese Journal of Rare Metals, Effect of Cryogenic Treatment on Microstructure and Properties of Pure Copper, Vol.37 No.2, 230-235.
[11] JIANG Junliang, (2013) Jiang Junliang, Influence Mechanism of Cryogenic Treatment on the Microstructure and Electrical Conductivity of Cu alloys, School of Materials Science and Engineering, Tianjin University, 38-40.
[12] WANG Qiucheng, KE Yinglin, (2003) Journal of Zhejiang University (Engineering Science), Relief of Residual Stresses in 7050 Aluminum Alloy by Cryogenic Treatment, Vol.37 No.6, 748-751.
[13] SHI Hongsong, PENG Qiumei, WANG Xing, ZENG Xiaoshu, YUAN Qiuong, (2016) Hot Working Technology, Study on Microstructure and Properties of Copper Wire in Process of Cryogenic Deformation, Vol.45 No.21, 66-68,73.
[14] GAO Yan, WANG Xin-ping, HE Jingjiang, LIU Hong-bin, JIANG Xuan, JIANG Yuhui, (2011) China Integrated Circuit, Phosphorized Copper Anode in ULSI and Studies on Related Problems, 64-67.
[15] FENG Shengping, (2003) Inspect of Copper Anode Quality, Printed Circuit Information, 31-34.
[16] ZHANG Lilun, Electroplating and Decoration, Discussion on Factors Affecting Quality of Phosphorized Copper Anode used for Acidic Copper Electroplating, 35-38.
[17] JIN Rendong, WANG Baoyu, YAN Shi-gong, HU Zhenghuan, (2004) Journal of Baotou University of Iron and Steel Technology, Experiment of Anodic Phosphor Copper Deformation Resistance, Vol.23 No.4, 332-334.