Abnormal grain growth in thin copper foils during high-temperature annealing

J Guo¹*, C L Zhang², X Li³⁴, T L Huang¹, G L Wu⁵, H F Shi³⁴, D Juul Jensen⁶ and X X Huang¹

¹International Joint Laboratory for Light Alloys (MOE), College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China
²Department of Mechanical Engineering, National University of Singapore, 117581, Singapore
³Chongqing Key Laboratory of Multi-Scale Manufacturing Technology, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, P.R. China
⁴University of Chinese Academy of Sciences, No.19(A) Yuquan Road, Shijingshan District, Beijing, 100049, P.R. China
⁵Beijing Advanced Innovation Center for Materials Genome Engineering, University of Science and Technology Beijing, Beijing, 100083, P.R. China
⁶Department of Civil and Mechanical Engineering, Technical University of Denmark, Kgs. Lyngby DK-2800, Denmark

*Corresponding author (Email: guo_jing@cqu.edu.cn)

Abstract. We investigate grain growth at 1000 °C, a critical temperature for abnormal grain growth in copper foils. By ex-situ annealing experiments at 1000 °C, it is found that abnormal grains grow through the entire sample thickness, forming a polycrystalline structure with a single layer of grains. The migration of the boundaries surrounding the abnormally large grains are characterized by optical microscopy and electron backscatter diffraction. The migration rates are found to vary significantly from place to place, which is analysed based on boundary characteristics, i.e., misorientation and boundary curvature, and the size distribution of the neighbouring grains.

1. Introduction
Stimulated by the recent development of electronic technologies, the research on two-dimensional materials is becoming more and more popular. In this context, graphene has attracted much attention due to its excellent performance [1-4]. Graphene is commonly manufactured by chemical vapor deposition (CVD) on metal substrates [5,6]. Copper foils are frequently used as such substrates [7-9] because of its low dissolution of carbon [10] and low cost. A single crystal substrate is preferred to obtain graphene with no/fewer boundary defects [11-13]. Currently, annealing of cold rolled copper foil is typically applied to prepare single-crystal copper substrates [14]. Yet, it is not clear if and how abnormal grain growth occurs. We have therefore studied the microstructure and texture evolution of copper foils at different annealing temperatures [15]. It is found that abnormal grain growth occurs in copper foils within a polycrystalline recrystallized structure with a strong cube texture during annealing.
at ultra-high temperatures (>1000 °C) [16-18], i.e., near the melting point of copper. The aim of the present work is to study in detail the grain growth at 1000 °C, a temperature close to the transition from normal to abnormal grain growth.

2. Material and experimental details
A 46 μm thick copper foil (Chalco Shanghai Copper Co., Ltd., 99.94%) was used in this study. X-ray diffraction measurements revealed that the initial texture was a typically rolled texture [15] consisting of S{123}<634> (34.6%, volume fraction), Brass{011}<211> (19.7%), Cu{112}<111> (16.6%) and Goss{011}<001> (5.8%).

A rectangular-shaped sample, 80 mm in length (in the transverse direction) and 30 mm in width (in the rolling direction) was cut out of the Cu foil by a paper cutter, as illustrated in Figure 1. The sample was placed on a flat quartz plate. Thereafter, the quartz plate with the sample was placed in the heated region of the furnace with the rolling direction perpendicular to a furnace tube axis and annealed ex-situ at 1000 °C for intervals of 5 min. The whole annealing process was carried out in a protective gas environment of 500 standard cubic centimetre per minute (sccm) argon gas [19].

![Figure 1](image_url)

The annealed copper foil was imaged using a Keyence VHX-6000 optical microscope. Then, a Zeiss scanning electron microscope (SEM) equipped with an Oxford Instruments Aztec electron backscatter diffraction (EBSD) detector, at the voltage and current of 20 kV and 15 mA, respectively. The EBSD data was processed by the HKL-Channel 5 software and MTEX toolbox [20]. The sample was carefully handled to avoid folds or scratches during the whole experiment.

3. Results and Discussion
The average grain size in the polycrystalline region after annealing for 10 min is about 93 μm, which is larger than the thickness of the sample (46 μm).

To monitor the boundary migration of the abnormal grains, ex-situ EBSD observation was carried out and the results are shown in figure.2. There are four abnormal grains (grain A, B, C, and D) observed at the edge of the sample, which are likely stimulated by the additional deformation during the sample cutting. However, this is not critical for the present study because the initial locations of the abnormal grains are largely irrelevant.

Substantial boundary migration is found for grains B and D along the direction marked by yellow arrows during the annealing step from 10 to 15 min, after which no notable boundary migration is observed (as shown in figure 2f). The lack of further growth is likely to be due to thermal grooving. Grain A grows slightly during the annealing while the boundary surrounding grain C barely moves during the whole annealing process. It is worth noting that the abnormal grains grow into a columnar fully recrystallized microstructure with almost 100% of the grains having cube orientation (see the right side of the EBSD maps in figure 2).

As shown in figure 2, the orientations of the four abnormal grains are different. There are large-sized twins in both the growing grains, B and D. Grain B consists of a (323 - along ND) oriented matrix (labeled as B1) and its (103) oriented twin (labeled as B2), and the grain boundary segment of the former (indicated by the upper yellow arrow in figure 2a)) migrates significantly. Grain D has three parts...
because of twining, labeled as D1, D2, and D3, oriented as (217), (259) and (324) respectively. In contrast to grain B, the grain boundaries of both twins D1 and D3 migrate significantly during the annealing. It is interesting to note that there is no twin relationship between D1 and D3.

Figure 2. a)-e) Optical micrographs and inverse pole figure (IPF) coloring orientation maps (ND colored) of the regions within the red boxes of the microstructure after different annealing times; a) 10 min, b) 15 min, c) 20 min, d) 25 min, and e) 45 min. The four large grains are labelled by A-D, respectively. White dashed lines reveal the grain boundary positions. The yellow arrows indicate the directions of grain boundary migration. f) Boundary position evolution as a function of annealing time from 10 min to 45 min. g) Optical micrographs and corresponding EBSD results of local magnification for the sample after 10 min annealing.

To investigate possible reasons for the significant difference in boundary migration, an analysis of the boundary characteristics was carried out. Figure 3b) - e) show the misorientation axes and angle distributions of the grain boundaries of grains A - D, respectively. Both the migrating grain boundaries of grains B and D and the stationary grain boundaries of grain A and C have misorientations close to 50°/<537> (as shown by dark blue bars and white dots in the IPF in figure 3b) - e)). It means that some boundary segments migrate while others don’t, even though they are of the same boundary type.
Similarly, the misorientation axes and angle distribution of the stationary boundary segments of grain B (shown by the light blue bars and black dots in IPF in figure 3c)) and the migrating D1 boundary (shown by the light blue bars and black dots in IPF in figure 3e)) both have the boundaries close to 20°/<100>. This suggests that the migration of grain boundaries during abnormal growth is not determined by the grain boundary type in our case.

Figure 3. Morphologies and characteristics of boundaries of grain A - D. a) Inverse pole figure (IPF) coloring orientation maps (ND colored) after annealing for 20 min. b) - e) Misorientation axis and angles distributions of the boundaries between the different abnormal grains and the polycrystalline recrystallized matrix. b) grain A, c) grain B (the light blue column and black dots correspond to twin B2); the dark blue column and white dots correspond to twin B1), d) grain C, and e) grain D (the light blue column and black dots correspond to twin D1 and dark blue column and white dots correspond to twin D3).

As shown in figures 2 - 4, the polycrystalline matrix is composed of many small <001> oriented grains (shown in red) with low-angle grain boundaries between. The microstructural evolution in this polycrystalline region is followed during the annealing and as shown in figure 4, the orientation and microstructure remain stable during the annealing.
Figure 4. a) Inverse pole figure (IPF) coloring orientation maps (ND colored) of the same polycrystal region after annealing for different times. b) Distribution of misorientation angles of grain boundaries in this polycrystalline region.

It is well known that larger gains grow at the expense of small grains during grain growth[21,22]. In the present work, the grain size distributions of the polycrystalline matrix within similar distances from the boundaries of the four abnormal grains after annealing for 10 min are therefore characterized. The results are shown in figure 5. The regions through which the grain boundaries migrated during the 10-15 min annealing period are marked by shadows in figure 5b). Depending on whether the boundary segments migrate or not, they are classified as motion (white lines) and no-motion (red line) boundaries (see figure 5a). The polycrystalline regions in front of the abnormal grains are classified accordingly. It should be noted that for grain C, the adjacent polycrystalline regions are also adjacent to grain B and grain D, so there is an overlap in the classification, however, we have done the classification as consistently as we could. As shown in figure 5c), the regions through which significant boundary migration occurs, have more small grains with sizes in the 0-0.1 mm range; such as region 1 and regions red ① and red ②. Also the frequency of grains with 0-0.1 mm sizes in region white ②, where less but still some boundary migration is observed, is slightly higher than that within the regions not transversed by boundary migration. This indicates that the boundary migration tends to occur preferentially into polycrystalline regions with small grains, i.e., the spatial distribution of grains with different sizes plays an important role for the migration of grain boundaries surrounding the abnormally growing grains.
Figure 5. a) Optical micrograph of the sample after annealing for 10 min. White and red lines indicate migrating and non-migrating grain boundaries, respectively; the blue boxes mark regions in which the grain sizes were measured. b) Optical micrograph for the sample after annealing for 15 min. The shadow indicates the region swept by grain growth during the annealing period from 10 min to 15 min. c) The grain size distribution within regions marked by blue boxes in a).

4. Summary
Ex-situ observations of a cold-rolled copper foil during annealing at ultra-high temperature annealing (1000 °C) showed that abnormal grain growth occurred mainly within the first 15 min. The analysis revealed that the migration of the grain boundaries depends critically on the spatial distribution of grain sizes in front of the abnormally growing grains, while the type of grain boundaries and misorientation distribution are of less importance. A smaller grain size, i.e., a higher boundary energy density distribution, in front of the grain boundary, facilitates grain boundary migration.

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