

Article

The Effect of Heat Treatment and Different Degrees of Deformation on the Microstructure and Mechanical Properties of Pure Mo Sheets

Wenjing Chen ^{1,2}, Lina Gu ^{1,3}, Jiayu Han ^{1,3}, Songwei Ge ^{1,3}, Xingjiang Hua ^{1,3}, Ping Hu ^{1,3,*}, Run Bai ^{1,4}, Wen Zhang ^{4,*}, Tian Chang ⁴ and Kuaishe Wang ^{1,3}

¹ School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China

² Xi'an Aeronautical Polytechnic Institute, Xi'an 710089, China

³ National and Local Joint Engineering Research Center for Functional Materials Processing, Xi'an University of Architecture and Technology, Xi'an 710055, China

⁴ Northwest Institute for Non-Ferrous Metal Research, Xi'an 710016, China

* Correspondence: huping@xauat.edu.cn (P.H.); gwenzh@163.com (W.Z.)

Abstract: Molybdenum has a broad application and good prospect in the field of nuclear energy, aerospace, electronics, etc., due to its high melting point, high hardness, corrosion resistance and other excellent performances. In this paper, an isothermal and isochronous annealing heat treatment, at the temperature of 800–1300 °C for 0.5–2 h, was applied to pure molybdenum (PM) sheets with deformation of 70%, 80%, 90%, and 95%. The initial deformation of the PM sheet was increased from 70% to 95%. After annealing at 900–1200 °C for 1 h, the recrystallized grain size gradually decreased. The Goss texture ($\{110\}\langle 001 \rangle$) was always present in the pure molybdenum sheet with 95% deformation during heat treatment, but its strength decreased with the increase of the temperature. The copper texture ($\{112\}\langle 110 \rangle$) deflected to a cubic texture, and its orientation changed from $\{001\}\langle 110 \rangle$ to that of cube texture $\{110\}\langle 100 \rangle$. With the increase of the temperature, the cubic texture was obtained more easily in the pure molybdenum sheet. The recrystallization nucleation mechanism of the pure molybdenum sheet with 95% deformation was mainly in situ nucleation and orientation nucleation. The Avrami index of the pure molybdenum sheet with 95% deformation was calculated by the JMAK equation and found to be 3.6.

Keywords: pure molybdenum; recrystallization; microstructure; deformation; texture



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1. Introduction

Molybdenum, a refractory metal, is a typical body-centered cubic (bcc) metal, which is widely used in the industry for its comprehensive and excellent performance, such as good thermal shock resistance, high-temperature resistance, and corrosion resistance. In addition, its high melting point, low cross-section of thermal neutron capture, and heat resistance allow molybdenum to be used in the construction of nuclear reactors for outer space and other applications [1–5]. With the development of the economy and the advancement of technology, the demand of the market and the improvement of the service conditions of materials have promoted the production of pure molybdenum plates with increased sheet width [6]. For example, these plates are used in the fields of crucibles for sapphire growth, sputtering a target material, and semiconductors.

Molybdenum has a high melting point. Considering the economic value and the homogeneity of the structure of molybdenum products, sintering blanks are usually fabricated by powder metallurgy, and then pure molybdenum sheets are made by rolling deformation. Compared with smelting, the composition of materials can be better controlled, and the loss of cutting can be reduced through powder metallurgy. Usually, during the rolling process, the pure molybdenum slab not only needs to experience a geometric shape change,

but also completes the transformation from the sintered state to the processed state, thus changing the mechanical properties and process performance of the slab and laying a good foundation for subsequent processing. For molybdenum sheets, the texture is a vital factor for anisotropy during the rolling process. Moreover, the transformation of the plastic–brittle transition temperature and microstructure will have an improved impact on the subsequent processes such as drawing and punching.

C. Bonnekoh, et al. [7] elucidated the mechanisms of controlling the brittle-to-ductile transition in pre-deformed, textured, polycrystalline bcc metals by the example of cold rolled tungsten. The toughness tests showed that the DBT temperature decreased with an increasing degree of deformation (83.5%, 91.8%, 95%, 96.7%, and 98.3% in the technical notation) from 115 ± 15 °C to -65 ± 15 °C. After a large plastic deformation, the most simple and effective method to eliminate the working hardening and reduce the residual stress in a pure molybdenum sheet is heat treatment. Overheating after processing, restores the plastic deformation capacity of the sheet, even its chemical composition, and its microstructure and improves the performance of the composite.

The melting point of molybdenum is 2620 °C, and the theoretical recrystallization temperature is ~1048 °C. Tungsten, a refractory metal, is of the same VIB family in the periodic table of the chemical elements as molybdenum, thus exhibiting similar properties compared with molybdenum. Yu et al. [8] studied the isothermal annealing hardness change of a hot-rolled pure tungsten plate with 90% deformation in the temperature range of 1200–1350 °C. It was considered that 90% of the deformed tungsten plate was at a temperature of 1200 °C to 1350 °C. The recrystallization in the range was controlled by the same activation energy as the grain boundary diffusion. The apparent activation energy of the semi-recrystallization of 90% the hot rolled tungsten plate was calculated to be 203 kJ/mol. On this basis, Wang et al. [9] analyzed the recrystallization behavior of the isothermal annealing of pure tungsten plates with deformations of 50%, 67%, and 90% at 1350 °C, combining the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model and the hardness test, examining the recrystallization dynamics of pure tungsten and the nucleation and growth types of recrystallized grains in the tungsten plate.

Oertel et al. [10] studied the microstructure, texture, and mechanical properties of molybdenum plates produced by different rolling processes through scanning electron microscopy, X-ray diffraction, and tensile tests. A low-deformation molybdenum sheet obtained by unidirectional rolling produced α -fibers, $\{100\}\langle 110 \rangle$. At higher deformations, the texture deflected, reaching $\{112\}\langle 110 \rangle$ and adding $\{100\}\langle 110 \rangle$ texture to cross-rolling. The anisotropy of the plasticity of the molybdenum plate was explained qualitatively using the “Taylor–Bishop–Hill” theory.

Primig et al. [11] analyzed the recrystallization behavior of a molybdenum plate with 5–68% deformation, during heat treatment at a temperature of 900–2500 °C, with a heating time of 20 min, holding heat for 1 h, and cooling the pure molybdenum plate in the furnace. The recrystallization structure of the deformed material was characterized by a metallographic microscope. The relationship between the deformation degree, annealing temperature, and grain size of the molybdenum plate can be understood directly and quickly. Hünsche et al. [12] studied the effects of deformation and annealing temperature on the microstructure of plates. In their study, the recrystallization kinetics calculated using JMAK indicated a reduced Avrami coefficient from 2.5 to 1.1 as the temperature increased. The activation energy reached 5 eV, which is consistent with the volume self-diffusion coefficient. Zhang et al. [13] showed that the heat treatment temperature of the molybdenum target material with a deformation amount of 80% increased from 1050 °C to 1300 °C, and the grain size gradually increased from 43 μm to 60 μm .

Researchers previously focused on differences in the rolling process resulting in different textures of pure molybdenum sheets. The heat treatment research of pure molybdenum sheets mainly focuses on the calculation of grain size, texture change, and recrystallization kinetics of pure molybdenum sheets with rolling deformation of less than 80%. However,

the study of the microstructure evolution of a pure molybdenum plate with large plastic deformation under heat treatment is lacking.

In this work, the recrystallization behavior, microstructure characteristics, and texture evolution of pure molybdenum were investigated. Four different reductions of deformed molybdenum samples were selected for heat treatment and investigated by some characterization methods after heat treatment. The data were analyzed and summarized, indicating the structure–activity relationship of pure molybdenum samples under heat treatment deformation through different heat treatment systems.

2. Materials and Methods

The molybdenum powder for the experiment was supplied by Jinduicheng Molybdenum Group Co., Ltd. (Xi'an, China). The chemical composition of the pure molybdenum powder was analyzed, and the results are presented in Table 1. The purity of the experimental molybdenum powder was 99.95% wt%. Pure molybdenum sheets were prepared using powder metallurgy. The process was as follows: the pure molybdenum powder was subjected to cold isostatically pressing at 180 MPa and then sintered at high temperature at 800 °C, 1200 °C, 1600 °C, and 1880 °C to obtain sintered billets. The sintered billets were hot-rolled (20–30% per pass), warm-rolled (10–20% per pass), and cold-rolled (within 10% per pass) to obtain pure molybdenum sheets with 70%, 80%, 90%, and 95% deformation, respectively. The specimens used in this experiment were taken from the middle of the cold-rolled molybdenum sheet with different deformation amounts (7 × 10 mm) to avoid rolling defects such as uneven tissue or cracking at the edges.

Table 1. Chemical composition of the pure Mo powder.

Element	Mo	W	O	C	P	Pb	Al	Si
(wt.%)	Bal.	0.01	0.025	0.004	≤0.001	≤0.005	≤0.0015	≤0.0015

The pure molybdenum sheets were subjected to heat treatment in a slide-rail tube furnace (NBD-CMT1200X) (Nobody Materials Science And technology Co., Ltd., Zhengzhou, China) with a hydrogen atmosphere for oxidation protection. The isothermal and isochronous heat treatment was carried out at different temperatures in the temperature range from 800 to 1300 °C. The parameters of the annealing treatments were as reported in Table 2.

Table 2. Heat treatment parameters used in the annealing process.

Heat Treatment Temperature (°C)	800	850	900	950	1000	1050	1100	1150	1200	1250	1300
	800	850	900	950	1000	1050	1100	1150	1200	1250	1300
Holding Time (h)	800	850	900	950	1000	1050	1100	1150	1200	1250	1300
0.5	•		•		•		•		•		
1	•	•	•	•	•	•	•	•	•	•	•
2	•		•		•		•		•		

The heat-treated sample was ground by emery paper with grit from 80 to 3000 and etched by the Murakami's etchant solution (a solution of 1 g of potassium ferricyanide in 10 mL of distilled water mixed with 1 g of sodium hydroxide dissolved in 10 mL of distilled water). The microstructure of the sample was observed by an Olympus GX51 optical microscope (OM) (Olympus Corporation, Tokyo, Japan). The contaminants and residual stresses on the sample surface were removed by electropolishing. An EBSD sample was prepared by polishing with a solution of sulfuric acid (H₂SO₄) and methanol (CH₃OH) at a ratio of 1:3, polishing 20 s at a voltage of 18 V. After electropolishing, the microstructure of the sample after heat treatment was analyzed by the electron backscatter diffraction technique (EBSD). The scanning electron microscope used in the experiment was Gemini

300 (Carl Zeiss AG, Oberkochen, German). The EBSD data were processed using the HKL technology system (Channel 5 software) (Oxford Instruments, UK).

3. Results and Discussion

3.1. Microstructure Evolution

Figure 1 shows the microstructure of the original rolled pure molybdenum sheets with four different deformations. According to Figure 1a, the grain of the pure molybdenum sheet with a deformation of 70% extended along the rolling direction, which was larger than that of the sample in Figure 1b, with a deformation of 80%. With the increasing degree of deformation, the morphology of the grains deviated from the approximately spherical sintered state, and the grains of the deformed sheet gradually extended along the rolling direction. When 95% of severe plastic deformation was reached, the grains were deformed to a greater extent, and the morphology showed a fibrous “pancake” shape, as shown in Figure 1d. When analyzing the grains’ aspect ratio in Figure 1, it was concluded that the deformation of the pure molybdenum sheet increased from 70% to 95%, and the corresponding grain aspect ratio increased from 2.4 to 10.3.

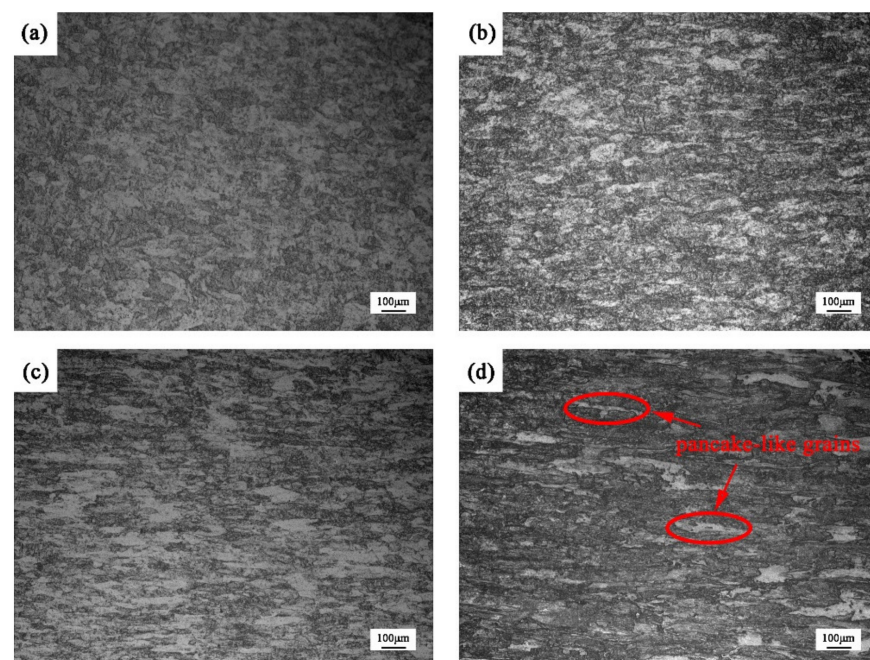


Figure 1. Microstructure of the as-received PM sheets. (a) 70%; (b) 80%; (c) 90%; (d) 95% deformation.

After heat treatment at 900 °C for 1 h (Figure 2a), since the temperature was lower than the theoretical recrystallization temperature, no fine recrystallized grains were observed in the metallographic microstructure diagram, and the microstructure morphology of the rolled state was maintained. The annealing temperature was raised to 1000 °C (Figure 2b), reaching a higher temperature than the starting temperature of theoretical recrystallization of pure molybdenum. The narrow structure of the deformed molybdenum sheet appeared mixed with extremely fine recrystallized grains; as the annealing temperature continued to increase, the recrystallized grains continued to grow. Gradually, the grains in the structure became uniformly equiaxed. As shown in Figure 2d, the grain size in most of the structure of the pure molybdenum sheet with deformation of 90% was $19.2 \pm 8.0 \mu\text{m}$ when recrystallization was completed.

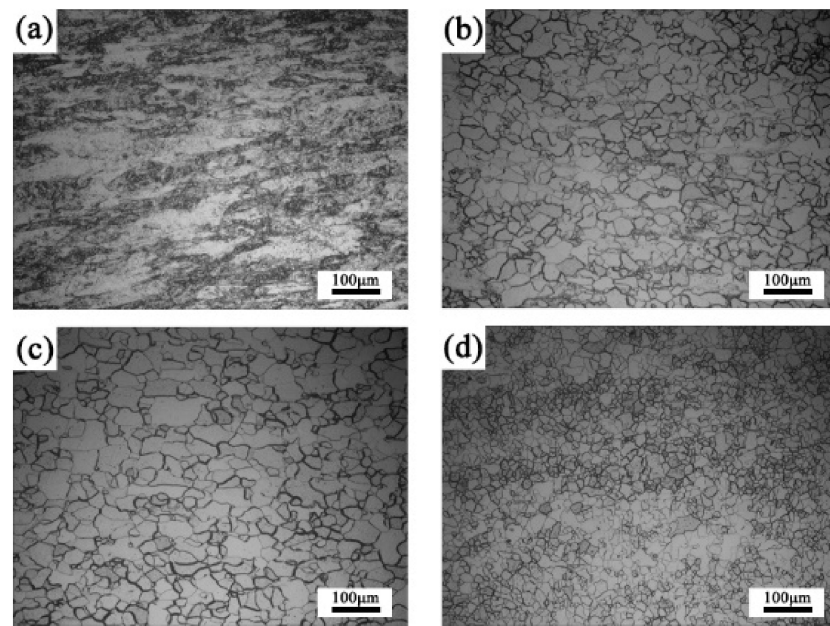


Figure 2. Microstructure of a pure molybdenum sheet with 90% deformation after heat treatment at 900–1200 °C for 1 h. (a) 900 °C; (b) 1000 °C; (c) 1100 °C; (d) 1200 °C.

In Figure 3a, a pure molybdenum sheet with 95% deformation was heat-treated at 900 °C. New recrystallized grains, which were small and roughly circular, preferentially appeared between two long, narrow, and fibrous grains or were concentrated at the tip of the grains and around broken grains (as indicated by the arrows in Figure 3a). The temperature was increased at intervals of 50 °C to continue the isochronous heat treatment. The number of recrystallized nuclei increased. The gradually recrystallized grains can be observed in Figure 3b. During the process, the “pancake”-like rolling structure gradually faded and was replaced by a uniform structure with small equiaxed grains. The grain size of a pure molybdenum sheet with a deformation of 95% was about 12.68 μm when recrystallization was almost completed (Figure 3f).

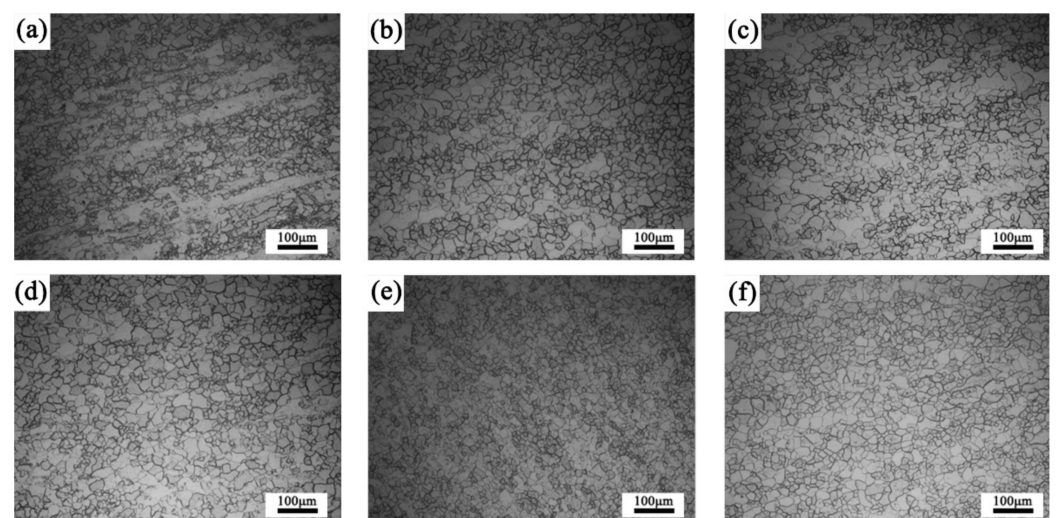


Figure 3. Microstructure of a pure molybdenum sheet with 95% deformation after heat treatment at 950–1200 °C for 1 h. (a) 950 °C; (b) 1000 °C; (c) 1050 °C; (d) 1100 °C; (e) 1150 °C; (f) 1200 °C.

Compared with Figures 2 and 3, it was found that the higher the heat treatment temperature, the larger the proportion of recrystallized grains in the structure. The aver-

age mobility $\bar{m}$ at the grain boundaries is proportional to $e^{-\frac{Q_m}{RT}}$ according to Arrhenius formula [14] (1):

$$\bar{m} = m_0 e^{-\frac{Q_m}{RT}} \quad (1)$$

Here, m_0 is related to the diffusion constant, Q_m is the grain boundary migration activation energy, R is the perfect gas constant, $8.314 \text{ J}/(\text{mol} \cdot \text{K})$, and T is the heat treatment temperature. When the amount of deformation of the pure molybdenum sheet is constant, the atomic diffusion energy Q_m is a fixed value. The higher the temperature, the more the energy provided for atomic motion. The faster the mobility of the grain boundaries, the faster the macroscopic growth of the recrystallized grains, and the larger their proportion in the structure. In addition, the pure molybdenum sheet with a larger deformation had smaller grains after recrystallization for a period of time, which was certainly related to the grain size of the original rolled sheet. In the 900°C annealing below the recrystallization temperature, recrystallized grains first appeared in the pure molybdenum sheet with a large amount of rolling (Figure 2d). Comparing Figure 2a,d, the degree of recrystallization was higher in pure molybdenum sheets with a large deformation.

3.2. Texture Evolution

The formation mechanism of rolling texture is mainly related to the stress analysis of Dillamore and Roberts [15]. It is also useful to study the orientation of rolling texture by means of local orientation, that is, the free rotation of a certain angle around a fixed axis. A $\{110\}$ //RD-TD texture, $\{110\}<110>$ formed in pure molybdenum sheets with different deformation amounts, together with weak $<100>\{211\}$, $<001>\{211\}$, and $\{211\}<110>$ texture [16].

For the study of pure molybdenum sheet rolling texture evolution behavior during the process of annealing in this paper, the EBSD method was used to characterize the large plastic deformation after annealing. Using the Bunge method [17], the Euler coordinate system was established, involving the Euler angle (φ_1 , Φ , φ_2) texture orientation. The ODF diagrams were determined by the Euler angle (φ_1 , Φ , φ_2). In the ODF diagram, the Miller index $\{ND\}<RD> = \{hkl\}<uvw>$ can be known from the Euler angles (φ_1 , Φ , φ_2) of the texture. The analysis of the typical texture type of a cubic-structure metal in this paper used a section of $\varphi_2 = 45^\circ$, and the standard texture ODF diagram of $\varphi_2 = 45^\circ$ is shown in Figure 4. The texture of a sample of 95%-deformed pure molybdenum sheet after recrystallization annealing at $800\text{--}1300^\circ\text{C}$ for 1 h was studied. The orientation density of the recrystallized texture components with the annealing system is shown in Figure 5.

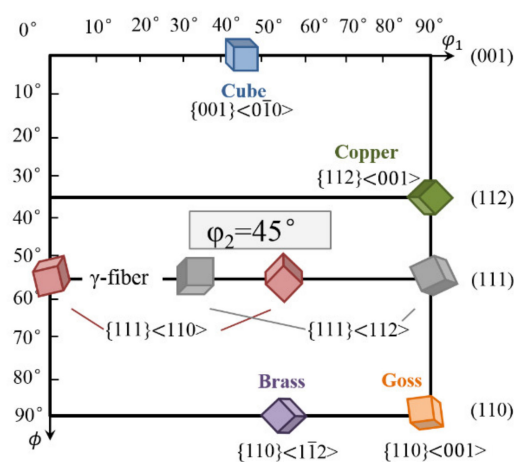


Figure 4. Standard texture ODF map ($\varphi_2 = 45^\circ$).

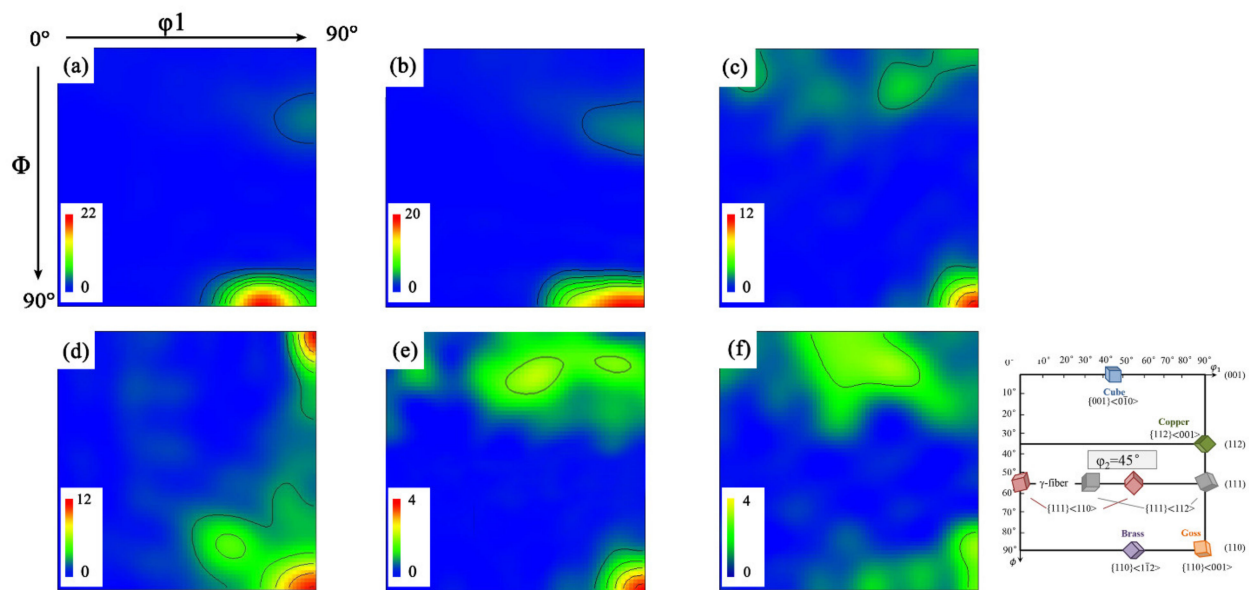


Figure 5. ODF diagram of a 95%-deformed pure molybdenum sheet heat-treated at 800–1300 °C for 1 h. (a) 800 °C; (b) 900 °C; (c) 1000 °C; (d) 1100 °C; (e) 1200 °C; (f) 1300 °C.

Combining the Euler angle and the Miller index in Figure 4, it can be seen that the pure molybdenum sheet with a deformation amount of 95% in Figure 5a mainly contained a strong Brass texture, a weak Copper texture, and a weak Goss texture after annealing at 800 °C for 1 h. During the rolling process, due to the sliding movement of dislocations, the orientation change caused by the dislocations during deformation was such that the sliding surface tended to be parallel to the rolling direction. The body-centered cubic structure metal would cause stable Goss texture formation due to shear forces. During the rolling process, the $\{110\}<001>$ texture appeared first, parallel to the rolling direction $\{110\}$. Under the action of shear stress, two stable plastic deformation textures, Goss and Goss Twin, formed [18]. In this paper, the rolling texture components of the pure molybdenum sheet without recrystallization and the deformed pure molybdenum sheet were basically consistent. Ideally, these alignment lines always correspond to high-intensity regions of the orientation distribution, but the maximum region for any given ODF map may deviate from the ideal position.

In Figure 5b, the Goss texture, Brass texture, and Copper texture are present in the microstructure of the pure molybdenum sheet with a deformation of 95% at 900 °C. In Figure 5c, the structure of the pure molybdenum sheet after annealing at 1000 °C includes Goss texture and $\{001\}<001>$ oriented texture. The annealing temperature continued to increase to 1100 °C, and a strong Goss texture remained in the structure. There were only two component textures in the annealed structure at 1300 °C, which were Goss texture and cubic texture. It is known that the type of texture in a sheet changes as the heat treatment temperature is increased. The Goss texture always exists, and the orientation of other weak textures changes. In our sample, the Copper texture changed to $\{001\}<001>$ as the heat treatment temperature increased, and then turned to cubic texture $\{001\}<0\bar{1}0>$. The $\{001\}<0\bar{1}0>$ texture was the main texture component after recrystallization was completed. The texture composition in Figure 5a–f shows a change in intensity, with the Goss texture decreasing from 21.99 to 2.67, and the cube texture appearing and increasing in intensity from 0 to 2.77, with no new texture types appearing during recrystallization. This indicated that during the recrystallization process, the grains with $\{001\}<0\bar{1}0>$ texture in the deformed structure might undergo “directional nucleation”. The mechanism of texture recrystallization is considered to be related to a dislocation movement in the microstructure. Increasing the heat treatment temperature can provide energy for grain boundary movement during recrystallization, which can affect the change in orientation

of some weaving structures. The annealing time was extended by an hour, and the 95%-deformed pure molybdenum sheet was heat-treated for 2 h at 900–1300 °C, as shown in Figure 6.

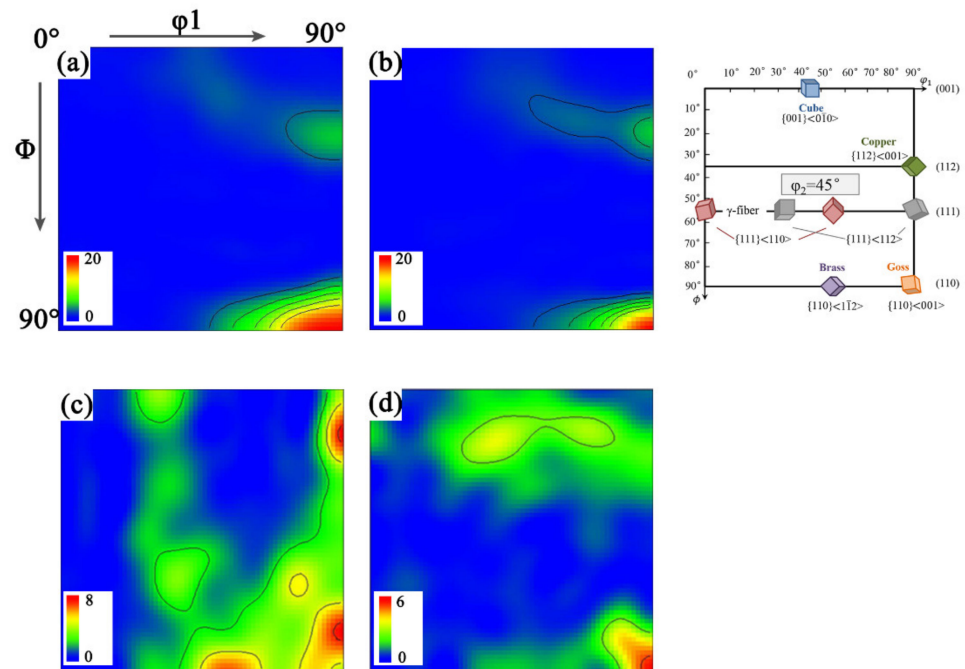


Figure 6. ODF diagram of a 95%-deformed pure molybdenum sheet heat-treated at 900–1200 °C for 2 h. (a) 900 °C; (b) 1000 °C; (c) 1100 °C; (d) 1200 °C.

When extending the annealing time, as shown in Figure 6a–d, the intensity of the Goss texture, the major texture component in the pure molybdenum sheet, decreased from 19.69 to 4.36. After annealing at 1000 °C for 2 h, the Copper texture $\{112\}<111>$ had a tendency to transition to the plane (113). After annealing at 1100 °C for 2 h, the Copper texture was transformed into the cube texture, and the path passed from $\{001\}<110>$ to $\{110\}<100>$. As shown in Figure 6c, the reason for the weakening of the Goss texture strength was that the orientation of the Goss texture was converted to γ -fiber, which transitioned from $\{110\}<100>$ to $\{111\}<112>$. In order to examine the texture transformation, the texture components in Figure 6 were statistically analyzed (Figure 7).

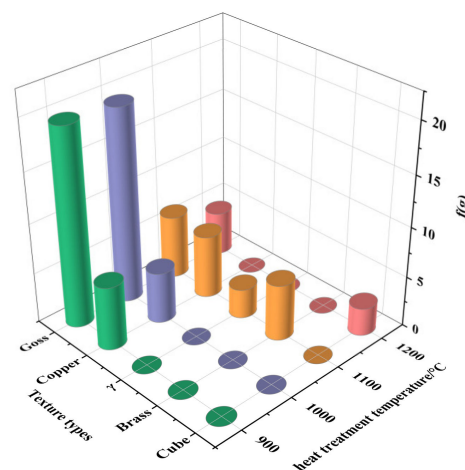


Figure 7. Texture distribution after heat treatment at 900–1200 °C for 2 h.

In Figures 5c and 6b, the recrystallization texture at 1000 °C is slightly different. It is possible that the area measured by EBSD was under a relatively concentrated stress, in relation to the orientation distribution of stress caused by anisotropic density in the system. Previous researchers [19] explained that when the direction of the minimum elastic modulus of recrystallized grains coincides with the direction of the largest absolute value of stress in a deformed matrix, the released strain is the largest. At this time, the driving force provided to the recrystallization is also the largest. The crystalline grains grow rapidly, forming a recrystallized texture that is associated with a specific orientation of the deformed matrix.

Figure 7 shows the texture distribution after heat treatment at 900–1200 °C for 2 h. Table 3 shows the strength of each texture type. The pure molybdenum sheet with a large plastic deformation still had a deformation texture after heat treatment. It is highly possible that the recrystallized texture of the pure molybdenum sheet had the same orientation as its rolling texture. The strength of the Goss weave weakened and tended to shift in the direction of γ -fiber, and the Copper weave deflected in the direction of the cubic weave during heat treatment-induced recrystallization of molybdenum plates with a large plastic deformation.

Table 3. Strength of each texture type after heat treatment at 900–1200 °C for 2 h.

Texture Type \ T/°C	T/°C			
	900	1000	1100	1200
Cube	0	0	0	2.77
Brass	0	0	5.61	0
γ	0	0	2.94	0
Copper	6.34	5.09	6.29	0
Goss	19.69	19.38	6.32	4.36

This phenomenon is inextricably linked to the process of recrystallization nucleation and grain growth, which weakens the deformation fabric anisotropy. The evolution of the recrystallization texture is complex and affected by many factors; therefore, it is difficult to study the formation and evolution mechanisms of the recrystallization texture. Therefore, the formation of the recrystallization texture can be discussed from the perspective of recrystallization nucleation and orientation change during grain growth.

3.3. Change of the Grain Boundary

Figure 8 shows a characteristic distribution diagram of EBSD grain boundaries after a 95%-deformed molybdenum sheet was heat-treated at 800–1300 °C for 1 h. Dislocations proliferated and became entangled during rolling deformation, and their distribution was not uniform. The local low-angle grain boundaries (LAGB) were dense, as shown in Figure 8a. The LAGB/subgrain boundaries are represented by green lines. The grain boundaries were still tightly distributed between the grains. When annealing was performed at a lower temperature (900 °C), a recovery process of the molybdenum sheet structure occurred, and the dislocation density inside the metal decreased. In conjunction with Figure 1c, when recovery occurred and large-area recrystallization did not occur, the microstructure of the sample was mainly composed of broken grains interspersed with extended grains after rolling, and most of the pancake-like high-angle grain boundaries (HAGB) (red lines) were still maintained; the migration of dislocations within the structure led to the consolidation and slippage of the subgrains, which made the substructure polygonal, forming grain boundaries, and the number of green LAGB was larger. This observation is similar to those reported in other studies [20].

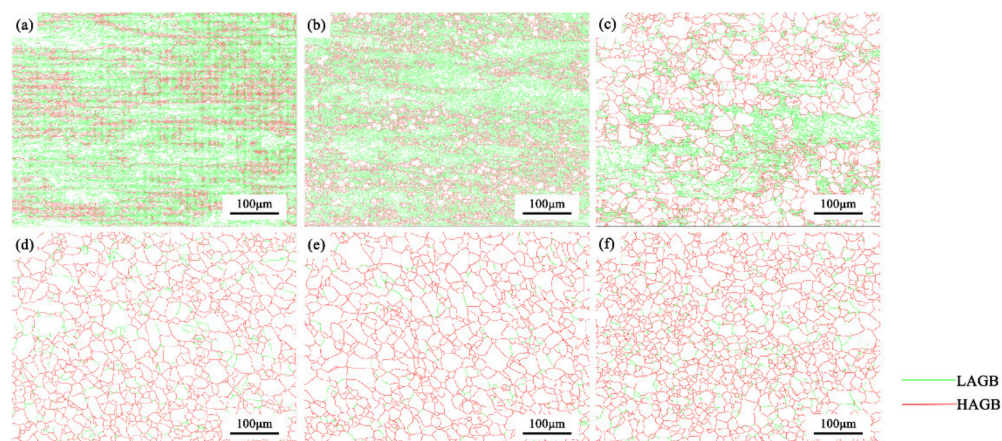


Figure 8. Misorientation angle distribution in 95%-deformed pure Mo samples annealed for 1 h at various temperatures. (a) 800 °C; (b) 900 °C; (c) 1000 °C; (d) 1100 °C; (e) 1200 °C; (f) 1300 °C.

As the annealing temperature increased (Figure 8d), with the completion of the recovery recrystallization process, the proportion of HAGB in the microstructure increased significantly. With the increase of the temperature, along with the increasing degree of recrystallization, until complete recrystallization (1200 °C) occurred, the LAGB were gradually transformed into HAGB during the recrystallization process, and high-angle grain boundary almost occupied all grain boundaries. It is worth noting that even if the corresponding boundary had high energy and mobility, its contribution would not disappear. During grain growth, some of these boundaries disappear, but others form because they are needed to maintain orthorhombic sample symmetry [21].

The characteristic distribution of the LAGB (misorientation angle (θ) between 2° and 15°) and HAGB (misorientation angle (θ) higher than 15°) boundaries was found to be influenced by the rolling and the annealing processes. To avoid artifacts in the local misorientation data, the misorientation angles lower than 2° were removed, which might have caused experimental fluctuations between adjacent pixels within a single grain.

As shown in Figure 8a, in the grain boundary distribution diagram of the 95%-deformed pure molybdenum sheet treated at 800–1300 °C for 1 h, fine HAGB existed between adjacent elongated rolled fibrous tissues and surrounded the rolled broken grain. If these substructures aggregated, the LAGB did not have high mobility and did not easily grow into recrystallization nuclei due to the small difference in orientation between the substructure and the deformed substrate. In Figure 8, it can be observed that recrystallization occurred preferentially in the vicinity of certain regions with the same characteristics, i.e., these regions were substructures and deformed grains with very different orientations and high mobility and could be rapidly transformed into recrystallized nuclei. The evolution of the dislocations can be seen in the TEM results.

Figure 9 shows the direct observation of the dislocation substructures via TEM. After heat treatment at 900 °C, there were flat grain boundaries in the microstructure of the pure molybdenum sheets (Figure 9), with differences in the number of dislocations within adjacent grains. By combining this figure with Figure 8b, it is possible to observe a large number of entangled dislocations within the grains shown in Figure 9a,b. In Figure 9c, the entangled dislocations inside the grains gradually disappeared after isochronous heat treatment at 1000 °C, leaving only the dislocation outcrops.

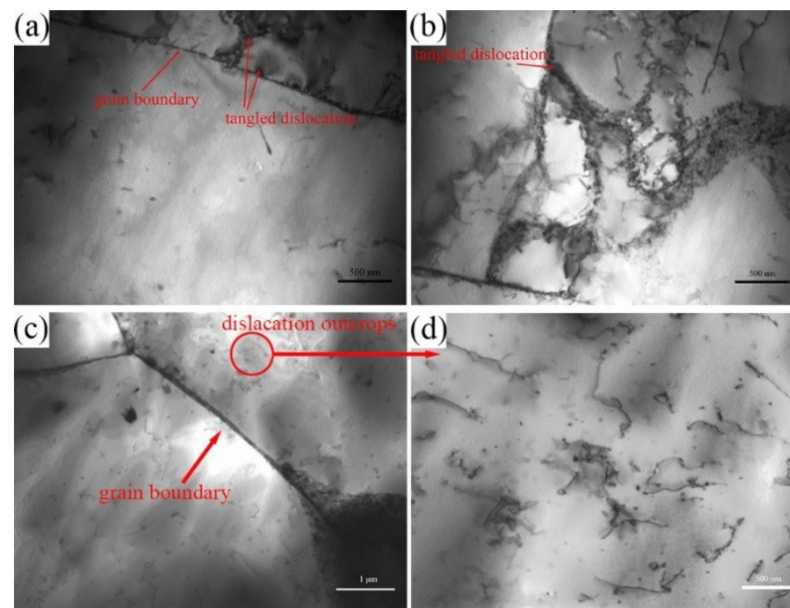


Figure 9. TEM images showing the heat treatment of pure Mo annealed for 1 h at various temperature. (a) 900 °C; (b) 900 °C; (c) 1100 °C; (d) 1100 °C.

However, the recrystallization process of the actual pure molybdenum sheet is very complicated, many factors affect the recrystallization, and various reasons for recrystallization nucleation cannot be peeled out by a microscopic analysis. It can also be seen in Figures 8 and 9 that the distribution of the recrystallized grains at this stage was not uniform. Therefore, the directional nucleation caused by the deformation and storage energy due to the texture orientation is also another way of recrystallization nucleation in the pure molybdenum sheet.

In order to better visualize the overall changes of the LAGB and HAGB, the angular grain boundaries in Figure 8 were counted, as shown in Figure 9. After annealing at 1100 °C, the HAGB proportion reached 82.23%. The gradual disappearance of the LAGB and the uniform distribution of the HAGB indicated that the recrystallization process in the sheet was gradually completed.

Figure 10 is a statistical picture of the distribution of recrystallized grains, deformed grains, and subgrains after isochronous heat treatment of the 95%-deformed pure molybdenum sheet at 800–1300 °C. In red are the rolled grain, in yellow the sub-grain, and in blue the recrystallized grain. Figure 11a shows the grain distribution of different states after heat treatment at 800 °C for 1 h. At this time, the structure was still in the rolled state, and recrystallized small grains appeared. Aggregated agglomerates were distributed in the small rolled grains, and the grain boundary density was high. Combined with Figure 8, the recrystallization nucleation mechanism in the 95%-deformed pure molybdenum sheet was subcrystalline nucleation. In the recovery stage of subcrystalline nucleation, the dislocation movement on the adjacent subcrystalline boundary gradually transferred to other surrounding subgrain boundaries, resulting in the disappearance and merge of adjacent subgrain boundaries. Due to the increase in size and dislocation density of the merged subcrystals, the phase difference between adjacent sub-grain boundaries increased, gradually turning them into HAGB, which have greater mobility than the LAGB. Dislocations during migration formed distorted recrystallized nuclei.

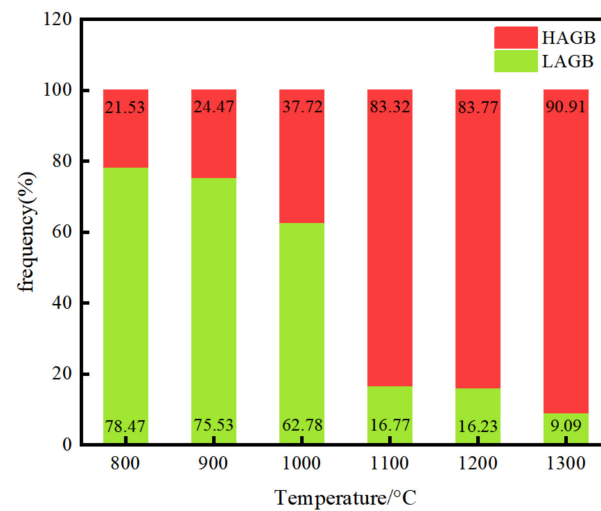


Figure 10. Misorientation angle distribution histogram of 95%-deformed samples annealed for 1 h at various temperature.

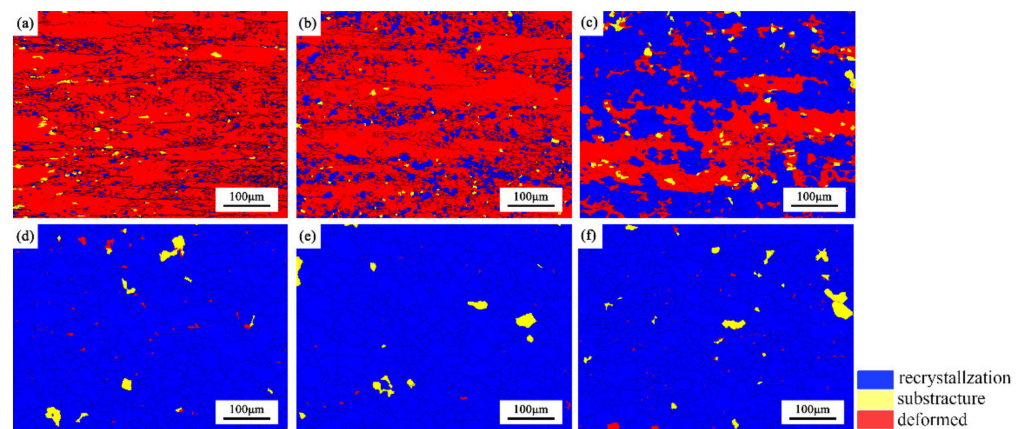


Figure 11. Grain distribution in different states after isochronous 1 h heat treatment at 800–1300 °C of the 95%-deformed pure molybdenum sheet. (a) 800 °C; (b) 900 °C; (c) 1000 °C; (d) 1100 °C; (e) 1200 °C; (f) 1300 °C.

When the heat treatment temperature was increased to 900 °C, the number of nucleated recrystallized grains shown in Figure 11b and of small previously recrystallized grains gradually increased, and the recrystallized grains were distributed substantially parallel to the rolling direction in the entire structure. Both the recrystallized nuclei and the recrystallized nuclei grown into grains in this stage consumed the energy stored in the rolled grains. As the heat treatment temperature was further increased, the recrystallized grains in Figure 11d–f replaced the rolled grains and became the main grains in the structure.

Statistical analysis of the recrystallization volume fraction at each grain ratio in Figure 11 (Figure 12) showed that after heat treatment at 1100 °C, the recrystallization volume fraction of the 95%-deformed pure molybdenum sheet was as high as 97.96%, indicating an almost complete recrystallization. Compared with the heat treatment at 1000 °C, the recrystallization volume fraction increased by 33.05%.

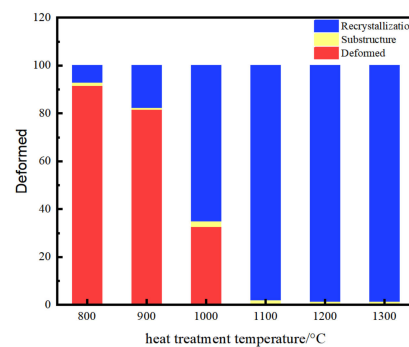


Figure 12. Statistical histogram of the different grains in the 95%-deformed pure molybdenum sheet after isochronous heat treatment at 800–1300 °C.

Recrystallization is a thermally activated process. From a deformed unsteady state, through the typical nucleation and grain growth process of recrystallization, the distortion energy is released to a steady state. Discussing the recrystallization behavior and the kinetics of recrystallized grain growth is helpful to analyze the recrystallization mechanism of the annealing process, which can reveal its thermodynamic features, important for studying the growth of grains and the migration of grain boundaries. Therefore, by analyzing the recrystallization volume fraction to understand the evolution of these parameters, it is possible to obtain the nucleation and growth mode of the recrystallization process.

Assuming that nucleation is uniform, nuclei are spherical, and nucleation rate $\dot{N}$ and grain growth rate $\dot{G}$ do not change with time, the recrystallization volume fraction X can be expressed by the JMAK equation [22] after t time at a constant temperature:

$$X = 1 - \exp\left(\frac{-f\dot{N}\dot{G}t^4}{4}\right) \quad (2)$$

After simplifying Equation (2)

$$X = 1 - \exp(-Bt^n) \quad (3)$$

Here, $B = -f\dot{N}\dot{G}t^4/4$, and Formula (3) is often called the JMAK equation; n is the Avrami index. It is assumed that nucleated grains grow in three dimensions. According to Formula (3), we obtain that $n = 4$.

For Equation (3), considering the logarithm twice on both sides, we obtain:

$$\ln[-\ln(1 - X)] = \ln K + n \ln t \quad (4)$$

The analysis of heat-treated metallographs of pure molybdenum sheets was performed using the grid method to determine their recrystallization volume fraction. The statistical results are shown in Table 4. Combined with the data in the Table 4, according to Formula (2), the $\ln[-\ln(1 - X)] - \ln t$ curve in the recrystallization process could be obtained, shown by the straight line in Figure 13.

Table 4. Recrystallization volume fraction of the pure molybdenum sheet with 95% deformation under 900 °C isothermal heat treatment.

Time/h	Recrystallization Volume Fraction of Pure Molybdenum Sheet/%
0.5	14.2
1	17.5
2	21.5

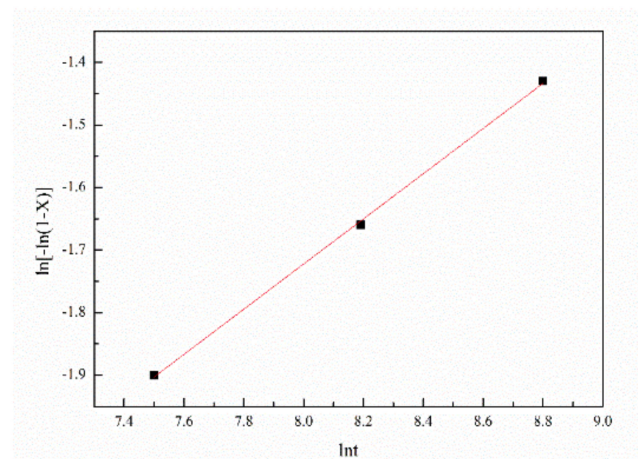


Figure 13. Fitting diagram of the JMAK equation at 900 °C for the 95%-deformed pure molybdenum sheet.

The fitted results in Figure 13 correspond to a primary function, indicating that the recrystallization mechanism did not change during recrystallization. In the JMAK equation, it is assumed that nucleation occurs randomly and uniformly in the matrix, the nucleation rate is constant, and the ideal value of the Avrami index is 4. The fitting Avrami index of the pure molybdenum sheet with 95% deformation in the process of recrystallization at 900 °C was 3.6, i.e., less than the ideal value of 4. This was mainly due to the unevenness of the tissue leading to an uneven distribution of the stored strain energy in the sheet. Some large grains did not have a subgrain structure with small grain boundaries inside; therefore, the recrystallization nucleation did not show a uniform random distribution.

3.4. Variation of the Microhardness

This section discusses the effect of the heat treatment temperature on the mechanical properties of pure molybdenum sheets. The microhardness variation curves of pure molybdenum sheets with different deformations (70%, 80%, 90%, 95%) after heat treatment at 800–1300 °C for 1 h are shown in Figure 14. The curve showing the microhardness changes after isochronous heat treatment of the pure molybdenum sheets at 800–1300 °C with four degrees of deformation clearly indicates three stages: a slow decrease at 800–950 °C, a rapid decrease at 950–1050 °C, and smooth fluctuations of the hardness values after 1050 °C. After heat treatment at 1250 °C, the microhardness of the pure molybdenum plates with four deformation degrees (70%, 80%, 90%, 95%) was 191.7 ± 3.9 HV, 202.4 ± 7.5 HV, 208.5 ± 3.8 HV, 210.0 ± 5 HV.

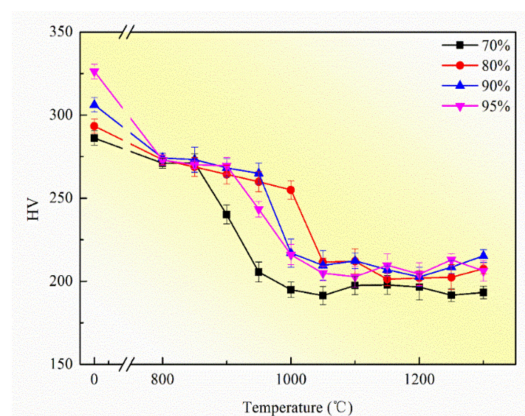


Figure 14. Microhardness curves for four kinds of pure molybdenum sheets after 1 h of isothermal heat treatment at 800–1300 °C.

4. Conclusions

The effects of deformation and heat treatment on the microstructure and microhardness of pure molybdenum sheets were studied. The main findings of this study are as follows:

(1) For the heat treatment process of large pure molybdenum sheet with plastic deformation, increasing the heat treatment temperature was more effective than extending the annealing time to increase the rate of recrystallization of the deformed structure of the pure molybdenum sheet. An effective heat treatment process for the recrystallization of pure molybdenum sheets with 95% large plastic deformation appeared to be annealing in the range of 1000–1100 °C with a holding time of 1 to 2 h.

(2) In the process of heat treatment of the 95%-deformed pure molybdenum sheet, Goss texture always existed in the sheet, and its strength decreased with the increase of the temperature. The Copper texture changed from the orientation of {001}<001> to the cubic texture type eventually, and the higher the heat treatment temperature, the better the formation of the cubic texture.

(3) The inhomogeneous organization of pure molybdenum sheets with large plastic deformation led to an inhomogeneous distribution of strain energy storage in the sheet, and the nucleation growth extent was close to that of three-dimensional nucleation.

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