Research on static recrystallization behaviour of pure molybdenum rods during forging

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Abstract

In this work, thermal compression experiment of pure molybdenum rods with sintered density of 9.7–9.8 g cm−3 were performed on the Gleeble-1500D thermal simulator. The double-pass vacuum high-temperature compression test was carried out in a deformation temperature of 1200 °C–1350 °C, a strain rate of 3 s−1 and an interval time of 10–500 s. The stress-strain curve was obtained and analysed. The static softening rate was calculated by the 2% compensation method of yield stress, and the curve of that was fitted. The results show that the softening rate is proportional to the interval time and the deformation temperature. The static recrystallization activation energy and critical temperature of pure molybdenum rod is 583.79 kJ mol−1 and 1365 °C, respectively. Besides, the static recrystallization kinetics model and grain growth model of pure molybdenum rod was established and microstructure evolution of molybdenum was analysed during the deformation process.

1. Introduction

Metal Molybdenum (Mo) has high melting point and strength, low thermal expansion coefficient and excellent electrical conductivity, thermal conductivity and corrosion resistance. It is widely used in the steel and non-ferrous metal, aerospace, electronics, chemical, and nuclear industry [1–5]. With the development of industrial technology, the size of electronic displays and industrial equipment has gradually increased, so the sizes of molybdenum targets used to prepare display coatings and molybdenum electrodes in industrial furnaces have also become larger. At present, pure molybdenum targets and electrodes are usually prepared by powder metallurgy. After powder metallurgy sintering of large-size molybdenum rod billets, it needs to undergo multiple passes of heating and forging to make the structure and performance of molybdenum rod meet the requirements of use. However, during the staying and heating process between the multi-pass forging, the deformed microstructure of molybdenum will recover and statically recrystallize, and its grain size and stress state will change greatly, which will have a greater impact on the subsequent deformation behaviour of molybdenum rod Research shows that [6–9] if the forging process of molybdenum rod is improperly controlled, incomplete static recrystallization during the multi-pass forging process will cause abnormal growth of local grains, and then the mixed grains will appear, leading to cracks in the local large grains under the subsequent forging stress.

At present, some studies have been conducted on the deformation behaviour of molybdenum. Hanfang X [10] researched the dynamic recrystallization behaviour of molybdenum. Primig S [11] investigated the textural evolution of molybdenum during the dynamic recovery and static recrystallization. Worthington D L [12] investigated the abnormal grain growth during dynamic recrystallization of pure molybdenum. Chaudhuri A [13] researched the stress-strain response, microstructure and texture evolution of hot deformed pure molybdenum. However, none of their research involves the static recrystallization mechanism and process of pure molybdenum during the forging process. In this paper, the forging process of pure molybdenum was simulated using the Gleeble-1500D thermal simulator, to study the static recrystallization behaviour of...
molybdenum rods, which can provide theoretical guidance for the determining forging process of large-size pure molybdenum rod.

2. Experimental

The material used in this work was a small sintered molybdenum rod blank with the purity of over 99.95% and a density of 9.7–9.8 g cm\(^{-3}\). The composition of molybdenum rod is shown in table 1.

The molybdenum rod was cut into cylindrical compressive samples with 8 mm in diameter and 12 mm in height by Wire Electrical Discharge Machining. The double-pass vacuum high-temperature compression tests were conducted on Gleeble-1500D thermal simulator at temperatures of 1200 °C, 1250 °C, 1300 °C, and 1350 °C and strain rate of 3 s\(^{-1}\). Because this thermal simulation test aims to investigate the static recrystallization behaviour of pure molybdenum, it is necessary to ensure that the strain is less than the critical strain of dynamic recrystallization. According our previous work [14], the strain of each pass was 20% (engineering strain) in present study. The interval time of each pass (also called holding time) was 10 s, 50 s, 100 s, and 500 s, respectively. Prior to the compression, the specimens were heated to the test temperature at a heating rate of 20 °C s\(^{-1}\). The thermal simulation process scheme is shown in figure 1.

During the interval time between hot working or the cooling process after hot working, the microstructure of metal will continuously change, eliminating part of work hardening microstructure, so that the interior of the material reaches a certain stable state. The process of this microstructure evolution is called static recovery and static recrystallization [15–17]. The degree of static recrystallization can be evaluated by the static softening rate.
Figure 3. True stress-true strain curves of different interval time at (a) 1200 °C, (b) 1250 °C, (c) 1300 °C and (d) 1350 °C.

Figure 4. True stress-true strain curves of different temperature at (a) 10 s, (b) 50 s, (c) 100 s and (d) 500 s.
The double-pass compression test is a common method to study static softening behaviour. In addition, the calculation methods of static recrystallization softening rate mainly include 0.2% compensation method of yield stress, 2% compensation method, 5% compensation method of total stress, interpolation method, average stress method, and area method [18–20]. In this study, the 2% compensation method was used to calculate the static recrystallization softening rate $R$.

The formula of softening rate $R$ is as follows:

$$
R = \frac{(\sigma_m - \sigma_f)}{(\sigma_0 - \sigma_f)}
$$

Where $\sigma_m$ denotes the unloading stress of the first pass, and $\sigma_0$ and $\sigma_f$ are the yield stress (the flow stress at 2% strain) of the first pass and the second pass, respectively. The diagram of softening rate calculation is shown in figure 2. The softening rate $R$ is the result of the combined effect of static recovery and static recrystallization.

3. Results and discussion

3.1. Analysis of true stress-strain curve

The true stress-strain curves of pure molybdenum at same temperature and at different interval time are shown in figure 3, and that at different temperatures and same interval time are shown in figure 4.

As can be seen from figure 3, at 1200 °C, there is no close relationship between the flow stress and the interval time of double-pass thermal compression. The results show that prolonging the holding time does not promote recovery and recrystallization. In addition, static recovery and recrystallization do not occur at this strain, indicating that the initial temperature of static recrystallization is higher than 1200 °C. At 1250 °C, the stress of the second pass begins to decrease, which means that the recovery and recrystallization have occurred. Also, with the prolongation of the holding time, the softening degree becomes more obvious. At 1300 °C and 1350 °C, static recrystallization occurred obviously. As the holding time is prolonged, the flow stress of the second pass gradually becomes lower, indicating that the degree of static recovery and recrystallization is increasing. The reason is that the static recovery of metal occurs first in the interval time after thermal deformation, and then the deformation storage energy is slowly released until recrystallization begins to occur [21]. Besides, recrystallization is a process of nucleation and growth, which takes a certain time to complete, so prolonging the interval time is conducive to the occurrence of recrystallization.

For figure 4, at the same interval time, the flow stress gradual decrease as the temperature increases, meaning that the percentages of static recrystallization gradually increase. The reason is that with the increase of temperature, vibration and diffusion of metal atoms accelerate, meaning that the kinetic energy increases and the deformation resistance decreases. At the same strain and interval time, as the temperature increases, the more energy will be provided for static recrystallization, and static recrystallization will become easier [22].

3.2. Static softening rates curve

The static softening rate reflects the degree of static recovery and recrystallization. The main factors affecting the static recrystallization are deformation temperature, strain, strain rate, and interval time. Under the same strain...
and strain rate, the relationship curves between the static softening rate of pure molybdenum deformation temperature and interval time are shown in Figure 5.

Figure 5 is the static softening rates curve of pure molybdenum, the softening degree of pure molybdenum is positively correlated with the deformation temperature and interval time between the two passes, and the static softening rate increases significantly with the increase of temperature. During the interval of thermal deformation, the metal first experiences static recovery, releases 30% of the deformation storage energy, and then undergoes static recrystallization. When the deformation temperature is 1200 °C, the static softening rate is small, and static recrystallization does not occur. When the holding time reaches 500 s, only static recovery occurs. The reason is that the temperature is low at this time, and the strain has not yet reached the critical strain of static recrystallization. When the deformation temperature is between 1250 °C and 1350 °C, incomplete recrystallization occurs, and the recovery and recrystallization rate is the fastest when the holding time is within 50 s–100 s. The softening rate of holding 100 s at 1250 °C is similar to that of holding 50 s at 1350 °C, which indicates that the methods to improve the static softening degree of materials include increasing the deformation temperature and prolonging the holding time. When the deformation temperature reaches 1350 °C and the holding time is over 500 s, the softening rate of pure molybdenum is 0.93 (close to 1), indicating that the complete recrystallization almost occurs. In industrial production, when the strain of each pass is 0.2, it is necessary to ensure that the deformation temperature exceeds 1350 °C and the holding time between forging passes exceeds 500 s to avoid the occurrence of incomplete static recrystallization which produces a mixed grain structure.

### 3.3. Activation energy of static recrystallization

The activation energy of static recrystallization of metal is an inherent property of the material itself. It is the same as the activation energy of dynamic recrystallization. It has nothing to do with deformation temperature, strain rate, strain and other deformation conditions, but only with the density and chemical composition of the material itself. Generally, the activation energy of static recrystallization is calculated according to the time corresponding to 50% recrystallization degree in the curve of static recrystallization softening rate. The time \( t_{0.5} \) corresponding to 50% recrystallization degree is determined by the equation \( (2) \) [23–27].

\[
t_{0.5} = A d_0^p e^{\frac{Q_{\text{ex}}}{R T}} \exp(Q_{\text{ex}}/RT)
\]

Where \( A, s, p, q \), and \( Q \) are material constants, \( d_0 \) is the original grain size, \( Q_{\text{ex}} \) is the activation energy of static recrystallization, \( R \) is the gas constant (8.314 J mol\(^{-1}\)·K), and \( T \) is the Kelvin temperature. Taking the logarithm of both sides of equation \( (2) \), then gives,

\[
\ln t_{0.5} = \ln A + s \ln d_0 + p \ln \varepsilon + q \ln \dot{\varepsilon} + \frac{Q_{\text{ex}}}{RT}
\]

In which \( \ln t_{0.5} \) and \( \frac{Q_{\text{ex}}}{RT} \) are linearly related, that is, \( \frac{Q_{\text{ex}}}{R} \) is the slope of the relationship curve between \( \ln t_{0.5} \) and \( \frac{1000}{T} \). Based on the static softening rate curve of pure molybdenum, the relationship between \( \ln t_{0.5} \) and \( \frac{1000}{T} \) is obtained as shown in Figure 6.
According to figure 6, the slope $n = 70.21793$, that is, $\frac{Q_{\text{rec}}}{R} = 70.21793 \text{ K}$, so the activation energy $Q_{\text{rec}}$ of static recrystallization of pure molybdenum is 583.79 kJ mol$^{-1}$.

3.4. Static recrystallization critical temperature

The static recrystallization critical temperature (SRCT) of metallic materials is the lowest temperature at which the grains will be completely recrystallized [28–30]. However, SRCT is related to deformation conditions such as strain rate and strain. In this paper, the SRCT of pure molybdenum is researched in a 40% (20% per pass) strain, a strain rate of 3 s$^{-1}$ and an interval time of 500 s. The softening rate $R$ under this condition is linearly fitted [31, 32], and the result is shown in figure 7.

So, the linear fitting equation of the SRCT of pure molybdenum obtained from the slope and intercept can be expressed as:

$$X_S = 0.00394T - 4.38$$  \hspace{1cm} (4)

Setting $X_S = 1$, it can be concluded that the SRCT of pure molybdenum is 1365 °C.

3.5. Kinetic equation of static recrystallization

Extensive research has been conducted on the static recrystallization behaviour of metals. Therein, the Avrami equation [33–36] is widely applied to describe the static recrystallization volume fraction, as shown in equation (5):

![Figure 7. SRCT fitting figure.](image1)

![Figure 8. The linear relationship between K and ln t.](image2)
Figure 9. The metallographic images at same interval time and different temperature.

Figure 10. The metallographic images at same temperature and different interval time.
Among them, \( C = -0.693 \), \( X_S \) is the volume fraction of static recrystallization, and \( t_{0.5} \) is the time when the static recrystallization rate reaches 50%. Taking the logarithm of both sides of equation (5), then gives:

\[
\ln \ln \left( \frac{1}{1 - X_s} \right) = \ln C + n \ln t - n \ln t_{0.5}
\]

(6)

Setting \( \ln \ln \left( \frac{1}{1 - X_s} \right) = K \), from equation (6), we can see that, \( K \) and \( \ln t \) are linearly related, and the slope of that is the value of \( n \). Therefore, the material constant \( n \) can be obtained by calculating the value of \( K \) at different time and making the linear fitting diagram of \( K \) and \( \ln t \). The linear relationship between \( K \) and \( \ln t \) is shown in figure 8.

According to figure 8, the \( n \) value of pure molybdenum at different temperatures ranges from 0.286 to 0.660, and the average value is 0.473. Therefore, and then the kinetic model of static recrystallization of pure molybdenum is as follows:

\[
X_S = 1 - \exp \left\{ -C \left( \frac{t}{t_{0.5}} \right)^n \right\}
\]

(7)

### 3.6. Hot deformed microstructure

During the double-pass thermal compression process, the deformation temperature and interval time on the microstructure evolution of molybdenum are analysed and observed. Figure 9 is the metallographic images of molybdenum at same interval time and different temperature, while that at same temperature and different interval time are shown in figure 10.

According to figure 9, at the same interval time and different temperature, the grains change significantly. At 1200 \( ^\circ \)C, there are many original coarse grains, and the microstructure is still uneven after double-pass thermal compression. At 1250 \( ^\circ \)C and 1300 \( ^\circ \)C, the numbers of recrystallized grains increase obviously. After double-pass thermal compression, the grain distribution is relatively uniform. At 1350 \( ^\circ \)C, the grains are basically small and uniformly distributed equiaxed grains. Therefore, it can be inferred that the static recrystallization of molybdenum has obviously occurred at 1250 \( ^\circ \)C. In addition, with the increase of temperature, the softening degree increases, and the recrystallization trend becomes more obvious. The changing law of the metallographic images conforms to the changing law of the stress-strain curve and static softening.

Compared with temperature, the effect of interval time on recrystallization is relatively low, but the change of metallographic images can still be recognized. For figure 10, when the interval time is 10 s, the grains after double-pass thermal compression are still coarse and uneven, because the recrystallized grains have no enough time to grow. It can be seen that at interval time of 50 s and 100 s, since the time is still short, equiaxed grains cannot be formed. At interval time of 500 s, the grains after the double-pass thermal compression are basically uniform, which is obvious different from the grain morphology at interval time of 10 s. These indicate that static recrystallization is completed basically, which is consistent with the changing law of the stress-strain curve and static softening.
3.7. Grain growth model

At present, there are many models to calculate the grain growth of metal materials, such as Beck model, Hillert model and Sellers model. In our work, the Beck model is selected to calculate the grain growth of pure molybdenum.

The Beck model \[37\] constructs the grain size equation by heating temperature and holding time, which can be expressed as:

\[ D = K t^n \]  

(8)

Among them, \( K \) is a constant and represents the growth rate of the grains; \( n \) is the growth index of the grains. Different materials have different values of \( K \) and \( n \). Taking the logarithm of both sides of formula (8), then gives:

\[ \ln D = \ln K + n \ln t \]  

(9)

In which \( \ln D \) and \( \ln t \) are linearly related, \( n \) is the slope of it. Bring the grain size of the same temperature and different holding time into the equation. Fitting the data, the result is shown in figure 11.

According to figure 11, the slope \( n = 2.83929 \), and the intercept \( K = 0.0967 \). In addition, the \( K \):

\[ K = K_0 \exp \left( \frac{Q}{RT} \right) \]  

(10)

Substitute the \( Q \) value, the \( K_0 = 4.8537 \times 10^{10} \), and the Beck model is as follow:

\[ D = 4.8537 \times 10^{10} \exp \left( \frac{583790}{RT} \right)^{2.83929} \]  

(11)

4. Conclusion

In this paper, the static recrystallization of pure Molybdenum rod is researched. The following inferences are obtained.

(1) At 1200 °C, there is no close relationship between the flow stress and the interval time of double-pass thermal compression, indicating that the degree of static recovery and recrystallization is very low. With the increase of deformation temperature, the flow stress of the second pass compression decreases significantly. The obvious static recovery and recrystallization occur at 1350 °C.

(2) According to the static softening rate curve of pure molybdenum, the static recovery and recrystallization degree of pure molybdenum is positively correlated with deformation temperature and interval time. Molybdenum begin to undergo static recovery and recrystallization at 1250 °C and the interval time is over 50 s. The incomplete static recrystallization of pure molybdenum will occur between 1250 °C and 1350 °C. The static recrystallization take place obviously at 1350 °C, and complete static recrystallization almost occurs when the interval time exceeds 500 s.

(3) The activation energy \( Q_{\text{rec}} \) of static recrystallization of pure molybdenum is 583.79 kJ mol\(^{-1}\). The Static recrystallization critical temperature of pure molybdenum is 1365 °C. The kinetic model of static recrystallization of pure molybdenum is \( X_S = 1 - \exp \left\{ 0.693 \left( \frac{1}{T_S^{0.47}} \right) \right\} \).\( \text{ and the holding time exceeds 500 s. After that, the follow-up process can be carried out, in order to avoid incomplete static recrystallization and mixed grains.} \)

(4) In industrial production, when the strain is 40% and the strain rate is 3 s\(^{-1}\), it is necessary to ensure that the deformation temperature of pure molybdenum exceeds 1350 °C and the holding time exceeds 500 s. After that, the follow-up process can be carried out, in order to avoid incomplete static recrystallization and mixed grains.

(5) The changing law of the metallographic images conforms to the changing law of the stress-strain curve and static softening. Besides, the model of grain growth is as follows:

\[ D = 4.8537 \times 10^{10} \exp \left( \frac{583790}{RT} \right)^{2.83929} \]

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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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