On the Recrystallization Behavior of Technically Pure Molybdenum


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Abstract

In the last decades the amount of interstitial impurities in the raw material used for powder metallurgical production of Molybdenum has been reduced significantly. Concurrently, the quality of the production process has been adapted to the latest technological standards and, consequently, the properties of technically pure Molybdenum have changed accordingly. For processing pure Molybdenum and the resulting mechanical properties, the recrystallization behavior, which strongly depends on the concentration of the prevailing impurities, e.g. Carbon, Nitrogen and Oxygen, is decisive. Unfortunately, the only reliable recrystallization diagram of Molybdenum was published in the mid sixties of the last century, which does not accurately describe the recrystallization behavior of the current quality of technically pure Molybdenum. Consequently, in the present investigation a diagram which reflects the static recrystallization behavior of Molybdenum containing a low amount of interstitial impurities was established. The recrystallization behavior has been monitored on differently deformed and subsequently heat-treated samples by means of hardness testing, light-optical microscopy and scanning electron microscopy employing electron channeling contrast imaging (ECCI). Especially ECCI investigations offer the possibility to analyze the change of microstructure with regard to recovery and recrystallization effects, e.g. the evolution of subgrains. The quantity of the impurities was determined by applying standard chemical analysis methods. Being a bcc metal, Molybdenum exhibits a high stacking fault energy. Thus, the recrystallization behavior is strongly dominated by concurrent recovery processes, which deviate from that of fcc metals showing a comparably low stacking fault energy. Finally, the revised recrystallization diagram for technically pure powder metallurgically processed Molybdenum is presented.

Keywords

Recrystallization diagram, technically pure Molybdenum, interstitial impurities, ECCI, in-situ recrystallization

Introduction

Pure Molybdenum possesses a unique combination of physical properties including excellent high-temperature strength, high corrosion resistance except oxidation resistance, high thermal conductivity, a high elastic modulus and a low thermal-expansion coefficient. Because of these outstanding properties, technically pure Molybdenum is used in a wide range of applications, including lighting-technology, high-
performance electronics, high-temperature furnace construction and sputter targets for coating-technology. However, one main disadvantage of Molybdenum, especially for the use as structural materials, is its poor low-temperature ductility. Highly deformed Molybdenum is ductile at room-temperature, but recrystallization leads to room-temperature embrittlement, which is not an intrinsic property of Molybdenum itself, but is caused by the presence of interstitial impurities such as Carbon, Nitrogen and in particular Oxygen [1, 2]. Because of its high melting point (2620°C), Molybdenum is nowadays mostly produced by powder metallurgical (PM) procedures. During the last decades, the amount of these interstitial impurities in the raw material has been reduced significantly. At the same time, the properties of technically pure Molybdenum have changed by adapting the PM production process to the latest technological standards, i.e. by improving reduction processes, cold-isostatic pressing as well as sintering. The recrystallization behavior of Molybdenum, which is strongly influenced by the process parameters of the thermo-mechanical treatment and the purity of the material, is decisive for the resulting mechanical properties, for example ductility, hardness, strength and toughness. Therefore, a recrystallization diagram is essential for the prediction of the recrystallized grain size and to gain knowledge about how the recrystallization temperature depends on the degree of deformation. Unfortunately, the only reliable recrystallization diagram of Molybdenum was recorded in the mid-sixties of the last century by Pink [3]. Pink’s recrystallization diagram does not accurately describe the recrystallization behavior of the current quality of technically pure Molybdenum. In addition, there is only very little information about the history of the material used for the study conducted by Pink. Consequently, a diagram which reflects the static recrystallization behavior of current technically pure Molybdenum was established. Furthermore, the use of state-of-the-art investigation methods as electron channeling contrast imaging (ECCI) allows a doubtless distinction between recrystallized and deformed grains [4]. Being a bcc metal, Molybdenum exhibits a high stacking fault energy. That is the reason, why the recrystallization behavior is strongly dominated by the concurrent recovery processes, which deviate from that of fcc metals, showing a comparably low stacking fault energy. Especially ECCI investigations offer the possibility to analyze the change of microstructure with regard to recovery and recrystallization effects, e.g. to study the evolution of subgrains. That is the reason, why at the present time the recrystallization behavior can be investigated at a much higher level of accuracy. In our work, the recrystallization behavior of PM manufactured Molybdenum has been investigated on differently deformed and subsequently heat-treated sheet samples by means of hardness-testing, light-optical microscopy (LOM) and scanning electron microscopy (SEM) including ECCI. The findings of the present study are discussed in comparison with Pink’s recrystallization diagram.

**Experimental**

The starting material used for deformation and subsequent annealing treatment was a recrystallized Molybdenum sheet with a thickness of 20 mm exhibiting an average grain size of about 100 µm parallel to the rolling direction and about 70 µm in the transverse direction. The chemical composition of the sheet-material is listed in table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R1</th>
<th>R2</th>
<th></th>
<th>Sample</th>
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<tr>
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<td>20</td>
<td>S*</td>
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<td>P***</td>
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<tr>
<td>H**</td>
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<td>&lt;1</td>
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<td>7</td>
<td>Ca***</td>
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<tr>
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<td>136</td>
<td>Cr***</td>
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<td>9</td>
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<tr>
<td>Na***</td>
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<td>&lt;5</td>
<td>Mo bal.</td>
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</table>
The sheet was produced by cold-isostatic pressing of Molybdenum powder followed by a conventional sintering process. The rectangular sinter plate was hot-rolled to a thickness of 20 mm. The final passes were carried out with regard to a sufficient degree of deformation to ensure complete recrystallization upon annealing. After hot-rolling, strips were taken from the as-rolled sheet. Then, recrystallization annealing for one hour at 1300°C in hydrogen atmosphere was carried out in order to achieve an uniform, fully recrystallized microstructure as described in the beginning of this section. Subsequently, these strips were hot-rolled with technical deformations of 5%, 10%, 15%, 20%, 25%, 30%, 44% and 68%. After cooling to room temperature, samples for subsequent annealing tests were taken from the centers of the sheets in order to achieve homogenously deformed material. Afterwards the samples were heat-treated in hydrogen atmosphere within a temperature range of 900°C – 2500°C for one hour. The heating time was 20 minutes, and the sheet samples were cooled in the furnace by turning off the power. Metallographic specimens of the cross-section in longitudinal direction were prepared using standard metallographic methods (grinding and polishing) [4], and the grain size was determined by means of LOM and the use of the linear intercept method parallel to the rolling direction. Combining all results, a recrystallization diagram was plotted, i.e. grain size as function of annealing temperature and degree of deformation. Several metallographic specimens, especially in the state of initial recrystallization, were additionally examined by means of SEM (Zeiss Evo 50, acceleration voltage 15 kV) employing ECCI in order to gain more detailed information about the microstructure as well as the volume fraction of the recrystallized grains. For the SEM investigations, specimens had to be electropolished (electrolyte Struers A3) in order to remove the uppermost deformed layer from the specimen surface [5]. Additionally, hardness tests (HV10) were performed on all specimens.

**Results and Discussion**

A LOM overview of the microstructure taken on the longitudinal section of all differently deformed and subsequently heat-treated samples is summarized in fig. 1. The solid line and the broken line confine the area of recrystallization determined by means of LOM. All samples in between these two lines are recrystallized partially.

![Fig. 1: LOM overview of all differently deformed and subsequently heat-treated Molybdenum sheets. All images were taken on longitudinal cross-sections. The annealing time for all heat-treatments was 1 hour. The start and end of recrystallization as determined by means of LOM are marked by the solid and broken lines, respectively. The start of recrystallization as determined by means of ECCI is marked by the dash and dot line. RD indicates the rolling direction and ND is the direction normal to the surface of the sheet sample.](image)

Samples above and to the left of the solid line are still in their as-rolled state, whereas those beneath the broken line are entirely recrystallized. However, it is difficult to precisely determine the start of recrystallization just by means of LOM, because deformed and recrystallized grains can only be distinguished by their shapes but not by their substructure. For this reason, samples in vicinity of the
recrystallization start line (solid line) were additionally investigated in the SEM by means of ECCI. By applying this method, the subgrain cell-structure of the deformed grains can be revealed, since this method is sensitive to local variations in orientation. Grains in deformed or recovered state appear speckled, whereas recrystallized grains appear of uniform contrast. A series of ECCI-images taken on longitudinal cross-sections for different annealing temperatures but the same degree of deformation (10%) are shown in fig. 2. In the image of sample A, which has been annealed at 1100°C for 1 hour, no recrystallized grains are visible. In sample B (1200°C, 1 h), some recrystallized grains are already discernible (marked with arrows) and in sample C (1300°C, 1 h) recrystallization has progressed further. This behavior differs from the results established by means of LOM, where after 1200°C and deformation of 10% no recrystallized grains could be detected. The same is also true for sample series annealed after different degrees of deformation. Due to the results obtained by ECCI, the onset of recrystallization as determined by LOM has to be corrected. This adjustment is indicated by the dash and dot line in fig. 1.

Fig. 2: ECCI images of sheet samples after 10% degree of deformation at subsequent annealing of 1100°C (A), 1200°C (B) and 1300°C (C) for 1 hour

(A) "as-rolled" state (10% deformed and 1100°C annealed – no visible recrystallization)
(B) some grains are recrystallized (arrows)
(C) increased volume fraction of recrystallized grains

In addition to microstructural characterization, room temperature hardness tests as a function of annealing temperature for each sample series exhibiting the same degree of deformation were performed. The obtained results are displayed in fig. 3. At 1500°C all samples are already softened by recrystallization except the 5% deformed sample. These results match with the broken line (end of recrystallization determined by means of LOM) in fig. 1. However, it is difficult to identify exactly if the start of recrystallization, which comes along with a decrease in hardness, matches with the start of recrystallization determined by means of LOM or ECCI. For example, at a degree of deformation of 10%, the hardness curve shows a drop between 1100°C and 1200°C which fits with the dash and dot line in fig. 1 (ECCI results). At 5% deformation the decrease in hardness is rather located in between 1300°C and 1400°C, which matches with the broken line in fig. 1 (LOM results).
Fig. 3: Dependence of hardness on annealing temperature for different degrees of rolling deformation (see inset). The filled square (arrow) represents the hardness of the fully recrystallized starting material (see text).

The size of the recrystallized grains was determined from the LOM images shown in fig. 1. Based on the obtained results, a recrystallization diagram for technically pure Molybdenum was established, which is shown in fig. 4.

Fig. 4: Recrystallization diagram of technically pure Molybdenum sheet material. The purity (table 1) corresponds to current standards of PM processing. The deformation was achieved by rolling of sheet samples. The annealing time was 1 hour and the heating time was 20 minutes, respectively. The sheet samples were cooled in the furnace. The distribution of the grain size is visualized by a grey-scale constrain (see inset).
As expected for primary recrystallization, the recrystallized grains show a large size for small deformation ratios and high annealing temperatures. At higher degrees of deformation, the grain size decreases even for high annealing temperatures. The reason for that might be on the one hand a larger density of nucleation sites caused by higher deformation and on the other hand the presence of a few grains, which obviously show a strong resistance against recrystallization (fig. 5). These grains exhibit a stable substructure, which can still be found at high annealing temperatures. These “recrystallization-resistant” grains seem to slow down the growth of adjacent recrystallized grains.

Fig. 5: Molybdenum sheet sample which was deformed by rolling (44%) and subsequently annealed for 1 hour at 1200°C. The arrows indicate grains which are resistant to recrystallization (see text). The straight lines are scratches from the sample preparation.

It is assumed that these “recrystallization-resistant” grains are not sufficiently deformed because of their orientation to the rolling direction, and therefore have a greater tendency for recovery instead of recrystallization. For comparison and to make the following discussion easier, fig. 6 shows the recrystallization diagram reported by Pink [3]. Note, that the annealing time in Pink’s experiments was only 30 minutes. Additionally, no information on heating and cooling rates is given. Extensive grain coarsening stops at a deformation of 30% and above in the diagram of this study (fig. 4), as well as in the diagram established by Pink [3]. The temperatures for recrystallization start and finish decrease with increasing degree of deformation in both diagrams. In Pink’s diagram exists a region of extreme large grain sizes which is caused by secondary recrystallization (abnormal grain growth) at a degree of deformation of 95% and annealing temperatures in the range of 2200 and 2400°C. However, this region is not reached in our recrystallization diagram. A reason for that is certainly the limited deformation in our experiments, which is not as high as in the case of Pink. Another reason might be the applied deformation mode. Barto and Ebert [6] demonstrated that recrystallization characteristics are strongly influenced by the deformation stress-state, e.g. pure compression produces much larger grains than simple tension. Rolling deformation takes up a middle position, as the rolling process induces mainly compression stress, but also for a minor part tension stress.
Because Pink deformed his samples by pure tension, larger grain sizes are expected in our recrystallized samples, which have been deformed by rolling. Additionally and unfortunately, there is no detailed description about the explicit procedure of the tensile tests and where the samples were taken from the tensile specimens for the subsequent heat-treatments in Pink’s paper. Another reason for the observed larger grains in our diagram (fig. 4) is the lower impurity content of the present material resulting in higher grain boundary mobility. However, by simple comparison of both three-dimensional diagrams, it is difficult to deduce, if the grain size in the new diagram is truly larger. To facilitate a comparison, the dependence of the grain size for 5% and 20% deformation is shown in fig. 7.
Indeed, fig. 7 indicates that the grain size of the investigated technically pure Molybdenum is actually larger at least up to annealing temperatures in the range of 1800°C, i.e. the rapid increase of the grain size of 5% in Pink’s diagram is not observed in the material investigated in this study. It is assumed, that the “recrystallization-resistant” grains inhibit grain growth at low deformation in our study.

Being a bcc metal, Molybdenum exhibits a high stacking fault energy. That is the reason why the recrystallization behavior is strongly dominated by concurrent recovery processes. It is believed that low impurity contents increase the stacking fault energy. In consequence, it is assumed that the formation of recrystallization nuclei in technically pure Molybdenum occurs by the growth of subgrain regions, which is frequently referred to as in-situ recrystallization. During this in-situ recrystallization, subgrains coalesce with their immediate neighbors by small rotations of their orientations. Hot-rolled Molybdenum exhibits a sharp texture [7, 8] and orientation differences between neighbouring grains are especially small. Guttman [9] studied the nucleation process in pure Molybdenum and observed in-situ recrystallization as a prominent mechanism. This nucleation mechanism was also found in our material. For example, fig. 8 illustrates a small region of coalesced subgrains -a recrystallization nucleus- surrounded by deformed subgrains.

Fig. 8: Microstructure of a Molybdenum sheet sample which was deformed for 44% and then annealed at 1100°C for one hour. The arrow indicates a small recrystallized grain which was formed by in-situ recrystallization (see text).

Summary

A recrystallization diagram, which reflects the static recrystallization behavior of PM Molybdenum sheet containing low interstitial impurities, was established. The recrystallization behavior has been monitored on differently rolled and subsequently heat-treated material by means of hardness testing, light-optical microscopy and scanning electron microscopy employing electron channeling contrast imaging. The obtained results are discussed in comparison with a recrystallization diagram established by Pink [3] in the mid-sixties of the last century. It was demonstrated, that the grain size in the current material is larger due to reduced impurity contents. At temperatures >2200°C the grain size is comparably small when compared to the data of Pink. This might be attributed to the presence of “recrystallization-resistant” grains. It is assumed that the start of recrystallization nucleation process occurs by the growth and arrangement of subgrain regions (in-situ recrystallization).
References

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