

# APPLICATION OF TEM TO STUDY THE CHANGES IN SUB-SURFACE DEFECTS IN TUNGSTEN SAMPLES AS A FUNCTION OF ANNEALING TEMPERATURE

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## Abstract

Transmission Electron Microscope (TEM) is a powerful instrument that can be used for identifying and studying sub-surface defects in materials. ‘STEM (scanning transmission electron microscope) bright field’ mode of TEM, utilizing the diffraction contrast, was used for identifying the dislocations in Tungsten (W) samples. Annealing of cold rolled W foil samples was carried out at 773 K, 1173 K, 1373 K, 1838 K, and 2038 K in a vacuum furnace, for two hours each, under reducing atmosphere. The effect of annealing temperature on dislocation density and micro-structural changes in cold rolled W foils have been investigated well below and above the recrystallization threshold temperature (~1600 K) of bulk tungsten. Electron transparent specimens required for TEM study have been carefully prepared. Dislocations have been identified and the changes in nature of these dislocations with annealing temperature were studied using a FEI make 300 kV TEM (Model: Tecnai G2 F30). TEM images and their analysis has shown that the average dislocation density has reduced and the length of individual dislocations increased, with increased annealing temperature. Calculations indicated that the average dislocation density was reduced by two orders of magnitude in the samples annealed at 2038 K, when compared with that of cold rolled samples. Further, in the samples annealed at temperatures above recrystallization threshold temperature, TEM images have clearly shown the disappearance of elongated grains in place of which stress free new grains were formed.

*Key words: dislocation density, recrystallization temperature, diffraction contrast, ion-mill*

## 1. INTRODUCTION

In a nuclear fusion reactor, hot and dense D-T plasma is confined using a combination of magnetic fields in a toroidal shaped vacuum vessel. Interaction of this plasma with the wall materials of vacuum vessel is one of the very important areas of interest as plasma-wall interactions will decide the operational life-time of the reactor in terms of plasma as well as material stability. The choice of the wall-material hence becomes one of the critical factors. High atomic number materials such as Tungsten (W) and its alloys are currently considered as candidate materials due to their favourable properties such as high melting point, low sputtering yield, and low H-isotope affinity [1] etc. These plasma facing components (PFC) are expected to be subjected to extreme operating conditions in terms of high heat, neutron and other particle flux etc. The alpha particle and neutrons produced in a fusion reactor can create radiation damage and subsequent change in the material properties, which may adversely affect the favourable properties such as high material stability and low fuel retention for which tungsten was originally considered. The cascade produced by the energetic neutrons in tungsten can create vacancy clusters, dislocations, voids etc. all throughout the material [2]. Presence of these Meso-scale defects such as vacancies and dislocations can lead to H-isotope trapping near these imperfect regions which will not only reduce the mechanical strength of the material, but also can increase their activity [3]. In this context, it is important to understand the conditions in which the dislocations can be annihilated. Annealing heat treatment is one such process. Annealing of tungsten samples and their characterization can lead to the development of some basic information on kinetics and dynamics of dislocation movement and annihilation, which can be used for correlating or calibrating the practical conditions. All these defects are like bulk features of the materials and can be identified, analyzed, and quantified using only equipment like TEM.

Transmission Electron Microscope (TEM) is one of the advanced materials characterization equipment which uses a monochromatic beam of highly energetic electrons for analyzing the bulk features of electron transparent

samples. Three major areas of applications of TEM are (i) High resolution imaging (ii) Crystallography (iii) Chemical/elemental analysis. Scanning Transmission Electron Microscopy (STEM) combines the principles of both TEM and scanning electron microscope (SEM) and adds analytical capability to TEM. Bright field imaging in STEM mode, with the utilization of diffraction contrast, has been proven to be a powerful and very useful technique for studying crystal defects in materials [4]. In the bright field (bf) imaging, the direct transmitted beam – from the sample – is used for the image formation by excluding the scattered beam. In crystalline samples, when the diffraction conditions for the incoming electron beam change spatially, it can lead to the generation of good contrast in bright field images. This contrast is known as diffraction contrast which is useful in identifying grain boundaries and dislocations etc.

In the present work, STEM bf imaging technique was used for the identification and analysis of dislocations in W samples. In addition to identifying the dislocations, efforts were also made to find the effect of annealing temperature on the dislocation density and also on micro-structural changes in the samples. The STEM bf imaging was also applied for the study of irradiation effects of various ions on defect characteristics in annealed tungsten samples discussed in detail by Prashant et al [5].

## 2. EXPERIMENTAL

### 2.1 Annealing of Tungsten foils

A Tungsten (99.96% pure) foil of 100 $\mu$  thickness, from M/s Princeton scientific corp. USA, was taken up for the present study. Test material was selected in the form of a foil as it is easy for preparing samples for subjecting them to various characterization methods. The ‘as received’ foil was in a cold-rolled condition i.e. in plastically deformed condition. In order to understand the affect of annealing temperature on the grain structure and dislocation density, foil samples were subjected to annealing heat treatment at various temperatures viz. 773 K, 1173 K, 1373 K, 1838 K, and 2038 K. These temperature values were selected with the objective of studying the annealing effect both below and above the re-crystallization threshold temperature (around 1600 K) of bulk tungsten. The annealing of the W foil samples was carried out in a horizontal type vacuum furnace in which a base pressure of around  $5 \times 10^{-6}$  mbar can be achieved. The furnace is connected with a combination of rotary and turbo molecular pumps to obtain the necessary low pressures. Resistive heaters with Molybdenum heating elements were in place in the vacuum furnace for obtaining the necessary temperature. The maximum temperature that could be obtained in this furnace is 1373 K. The furnace has an effective hot-zone of 350mm (W) x 150mm (H) x 500mm (D), in which a temperature uniformity of  $\pm 5^\circ$  C can be achieved. The samples were placed at the centre of this hot-zone to ensure the uniformity of temperature across the sample. A heating rate of  $10^\circ$  C/min. was maintained. After completing the annealing process for two hours, the samples were subjected to furnace cooling by just switching off the furnace and letting the samples reach room temperature naturally. For annealing at higher temperatures i.e. at 1838 K, and 2038 K, a different vacuum furnace with high temperature capability was used. Reducing atmosphere with ‘Argon and 4% Hydrogen gas mixture’ was maintained in this furnace, during annealing, to prevent surface oxidation of tungsten samples at these high temperatures.

### 2.2 TEM sample preparation

In a TEM, a highly energetic and monochromatic beam of electrons is transmitted through an ultra thin sample. The interaction of these electrons with the electron transparent specimens generates a variety of signals, collection and processing of which gives rise to an image, spectrum, or a diffraction pattern. Typical dimensional requirements of a self supporting sample, for TEM studies, are as follows: 3 mm diameter and thickness of around 100 to 150 nm. Preparation of such small, thin samples and their handling is a very difficult task and involves a lot of skill and practise. Steps involved in the preparation of TEM samples from the 8mm x 8mm W foils are briefly described below. It is very critical to ensure that the sample preparation process itself should not alter the existing features or introduce new features in the test sample.

#### 2.2.1 TEM disc preparation

To start with, a 3 mm disc was punched out from the initial smooth foil of 8mm x 8mm size, using a Gatan make disc punch (model 659). The disc punch ensures to deliver a disc sample with sharp edges without allowing any type of cutting forces extending into the central region of the disc. At this stage the sample size was 3 mm diameter and 100  $\mu$ m thickness.

### 2.2.2 Mechanical Thinning of the discs

The 3 mm diameter disc, obtained from the step explained in 2.2.1, was wax-bonded at the centre of a steel stub. Using 'disc grinder and lapping kit' of Gatan make (model no. 623), thickness of the above disc was reduced by 30  $\mu\text{m}$  through mechanical lapping. Only the fine emery paper with 5  $\mu\text{m}$  grit of silicon carbide was used for this disc grinding process. The disc grinder can uniformly thin down the discs with 5  $\mu\text{m}$  accuracy and excellent control. After completing this step, the sample size was 3 mm diameter and 70  $\mu\text{m}$  thickness.

### 2.2.3 Dimple Grinding

As discussed earlier, the required final thickness of the TEM sample is around 100-150 nm. As the final thinning technique that is available with us is based on ion milling, the sample needs to be pre-thinned from 70  $\mu\text{m}$  down to 10-20  $\mu\text{m}$ . This pre-thinning step would greatly reduce the final ion milling time. Gatan make dimple grinder (model 656) was used for this pre-thinning process. Mechanism of dimpling process reduces the thickness of TEM disc sample only in the centre and leaves a thick supportive rim for specimen handling i.e. creates a dimple shape in the middle of the sample. A phosphor bronze grinding wheel and abrasive diamond paste (3 $\mu\text{m}$  size) were used for the necessary removal of material from the disc sample. A counter weight of 20 gm was applied on the sample, and the rotation speed of dimple wheel was set at 3 rpm during dimpling process. Depth of the dimple can be controlled very precisely with this dimple grinder. This dimpling process was continued till the sample thickness was reduced to below 20  $\mu\text{m}$  in the central region of the disc sample. This dimple-ground sample was then subjected to fine polishing to get rid of any fine scratches formed during the previous processes. For this polishing process, the phosphor bronze grinding wheel was replaced with a felt polishing wheel and fine alumina suspension was used as an abrasive.

Therefore after the dimpling process was completed, the sample was still of 3 mm diameter but with a rim of 70  $\mu\text{m}$  thickness and having a dimpled area at the middle with a minimum thickness of 20  $\mu\text{m}$ .

### 2.2.4 Ion Milling

The minimum thickness of the W disc sample, obtained after dimple grinding was just below 20 $\mu\text{m}$  and was still very high for the TEM analysis. Further reduction in thickness was carried out in an ion mill, in which thinning down was effected through sputtering off the sample material by bombarding it with energetic Argon ions. Precision ion polishing system (PIPS-II) of Gatan make (model 695) was used for ion-milling the W samples. The dimpled W sample was held in a clamp type duo-post for ion-milling. PIPS-II is equipped with two ion-guns which are positioned opposite to each other.

The acceleration voltage for the ion beam was set at 5 kV and the beam incidence angle was fixed at 5° with reference to the horizontal surface of the sample. The duo-post rotation was set at 3 rpm. The ion-milling was carried out for a few hours, with auto-terminator on, till a small perforation was made in the sample. A small area around this perforation is only the area that is electron transparent and suitable for TEM analysis.

## 2.3 TEM Study

All the samples that were carefully prepared, were then subjected to TEM study. Both single-tilt and double-tilt holders were used for inserting the samples in to TEM and for further analysis. A 300 kV FEI make (Model: Tecnai G2 F30) TEM, available at Institute for Plasma Research, Gandhinagar, India; was used for the study. Beam with 300 kV accelerative voltage was for the studies. The STEM bright field images were captured for the dislocation identification. In the bright field imaging, only the elastically scattered electrons and un-interacted electrons – during interaction with the sample material – are collected by the detector and used for the image formation. When the sample is having features that can strongly diffract the incoming beam with a relatively higher forward scattering angle, good contrast can be generated in the image; and dislocations and grain boundaries are examples of such features.

## 3. RESULTS AND DISCUSSION

The STEM bright field micrograph of as received cold-rolled tungsten sample is shown in figure 1a. As expected the grains are elongated, due to the directional plastic deformation that they were subjected to during cold rolling process. Width of these elongated grains is of the order of 1  $\mu\text{m}$  or less, while the length is observed

to be around 10  $\mu\text{m}$ . Dense network of dislocations is also clearly visible along with the elongated shape of grains. A magnified view of the same sample is shown in figure 1b.

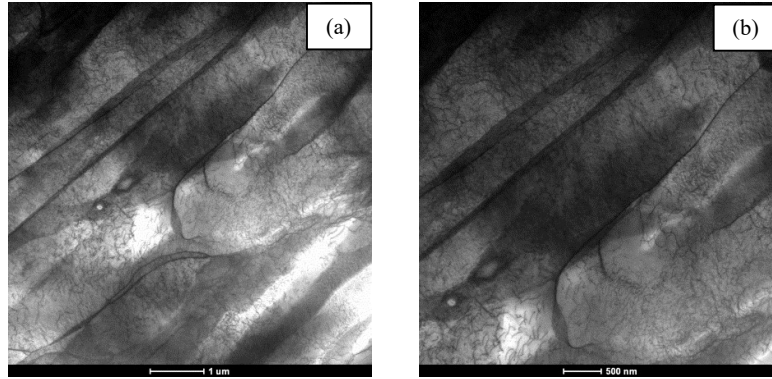


FIG. 1. STEM bf images of as received W samples in cold rolled condition

BF micrographs of other W samples that were annealed at 773 K, 1173 K, and 1373 K; i.e. all below the recrystallization temperature of W ( $\sim 1600$  K), are shown in figure 2a, 2b, 2c respectively. From the images it is visible that the grains are still elongated, as the annealing temperature maintained was below the recrystallization temperature. In all the samples the dislocations are clearly visible and the closer analysis has revealed that the average dislocation density has reduced with annealing temperature.

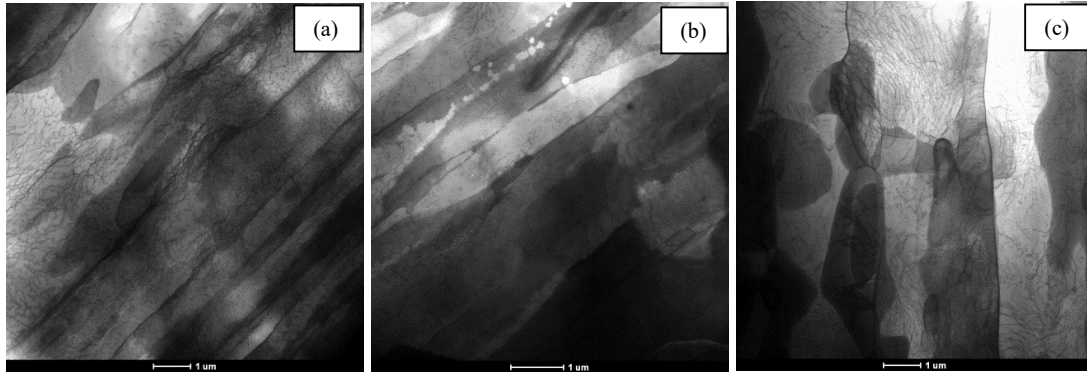


FIG. 2. STEM bf micrographs of W samples annealed at (a) 773 K, (b) 1173 K, and (c) 1373 K

Similarly the resulting bf micrographs obtained from W samples annealed at 1838 K and 2038 K are shown in figure 3. These temperatures are clearly above the recrystallization temperature, above which nucleation and growth of the new crystals would occur. The driving force for the nucleation of new grains from the deformed grains is the stored strain energy in the crystals present due to the plastic deformation during cold rolling. By the first stage of recrystallization is complete, known as primary recrystallization, the newly nucleated crystals consume all the strain energy present in the material [6]. Accordingly, in the present study also, the dense dislocation networks present in the cold rolled samples were found to disappear as shown in figure 3. With further increase in annealing temperature, the metal can still lower its energy by decreasing the total surface area of the grains, which is manifested in the form of grain growth. The same is confirmed in the STEM bf micrographs shown in figure 3, in which it is clear that in place of elongated grains new grains are formed and the size of these grains looks to be greater than 10  $\mu\text{m}$ , as only one grain boundary could be seen in the micrographs. It is further observed that the grain boundaries are growing thicker at these high temperatures. This may be because of the fact that with the growth of freshly nucleated crystals some of the dislocations might be pushed along the new boundary wall and get accumulated near them leading to the formation of high angle grain boundaries. Further study is needed to confirm the same. The length of the dislocations also seems to be increasing with the annealing temperature.

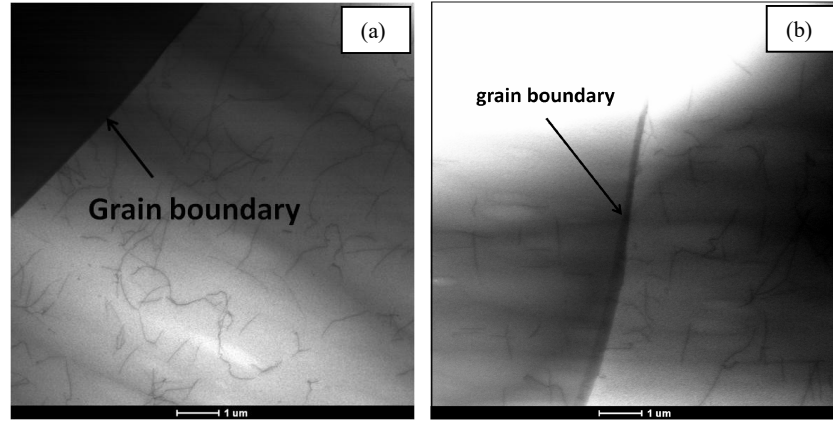


FIG. 3. STEM bf micrographs of W samples annealed at (a) 1838 K, and (b) 2038 K

The dislocation densities in all the above samples were calculated by analyzing the concerned TEM images using line-intercept method [7]. In this method, three lines of 10  $\mu\text{m}$  length were drawn randomly with different orientation, on the TEM images (using imageJ). The number of ‘intersection points (N) on this line with dislocations’ divided by ‘the length of the randomly drawn line ( $L_r$ ) multiplied with the sample thickness (t)’ gives the dislocation density  $\rho$ , and the formula is given below. Sample thickness was considered as 200 nm for all the samples.

$$\rho = \frac{N}{L_r t}$$

The calculated dislocation densities for samples annealed at different temperatures is shown in table 1.

TABLE 1. CHANGE IN DISLOCATIONS DENSITIES WITH ANNEALING TEMPERATURE

Sample	Average dislocation density (/cm <sup>2</sup> )
As received (cold rolled)	$2.3 \times 10^{10}$
Annealed at 773 K	$1.5 \times 10^{10}$
Annealed at 1173 K	$8.5 \times 10^9$
Annealed at 1373 K	$6.5 \times 10^9$
Annealed at 1838 K	$5 \times 10^8$
Annealed at 2038 K	$3.3 \times 10^8$

Dislocations in metals can arise, during solidification and cooling, because of many reasons. In most of the metals, the average dislocation density can be in the range of  $10^6$ - $10^8$  /cm<sup>2</sup>, even in normal condition [6]. The plastic deformation can tremendously increase this dislocation density and the same is observed in the present case of cold rolled tungsten samples i.e.  $2.3 \times 10^{10}$ /cm<sup>2</sup>. This value can be even higher based on the amount of plastic deformation that the metal was subjected to, which is quantified in per cent deformation. Presence of dislocations in such high numbers leads to the storage of substantial strain energy in the lattice. This makes the cold worked materials thermodynamically unstable when compared with the un-deformed materials. Therefore the deformed metal in principle will try to return to a low free energy state. However, this cannot occur spontaneously but is possible only at high temperatures where thermally activated processes like diffusion, cross-slip, climb can take place. This rate of approach to equilibrium is governed by an Arrhenius equation of the form

$$\text{Rate} = A \exp\left(\frac{-Q}{kT}\right)$$

Where A is a constant, k is the boltzman constant, T is the absolute temperature, and Q is the activation energy which depends on impurity content and strain etc. In accordance with the above rate equation, the dislocation density is found to reduce with annealing temperature in the present study. Further, it is also very clear from table 1 that the average dislocation density in the fully recrystallized samples (i.e. annealed at 2038 K) is two orders of magnitude less than that of in the as received samples in cold rolled condition. Similar observations were also made by Manhard in his thesis [8].

#### 4. CONCLUSIONS

Transmission electron microscopy was successfully applied for the identification of dislocations in tungsten samples. Electron transparent samples were prepared from W foils, using various sample preparation equipment. The complications of the sample preparation process were discussed. STEM bright field imaging was carried out for obtaining the necessary contrast to highlight the dislocations. It was attempted to study the effect of annealing temperature on the changes in nature of dislocations and their density, and also on the grain size and shape. The elongated grains with high density of dislocations, present in the as received samples were observed to change in to equi-axial type relatively stress free grains when they were annealed at temperatures greater than their recrystallization threshold temperature. Analysis of TEM micrographs clearly indicated the decrease in average dislocation density with the increase in annealing temperature. The average dislocation density in the fully recrystallized samples (annealed at 2038 K) was found to be two orders of magnitude lower than that of as received cold rolled tungsten samples. The change in the shape of grains from elongated to equi-axed grains was also confirmed with TEM micrographs. The length of dislocations was also observed to increase with annealing temperature.

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