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A study of hydrogen blistering mechanism for Molybdenum by Tritium radio-luminography

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ABSTRACT

In order to study blistering mechanisms of Molybdenum (Mo), hydrogen distributions at and around blisters formed on Mo surfaces are examined by Tritium (T) radio-luminography or autoradiography (TARG). TARG shows that large amount of hydrogen (T) is accumulated at and near grain boundaries and some blisters are covered with Ag precipitates representing T under the blister skins. Two independent types of blistering mechanisms seem to occur on Mo surface simultaneously. One is typical blistering due to bubble coalescence accompanying plastic deformation of the blister skins and only very thin blister skins allow T detection by TARG. Another is exfoliation or cracking of a grain caused by mechanical fracturing of the grain boundaries and/or defect clusters due to brittle nature of Mo, remaining tritium on the fractured surface.

1. Introduction

Interaction of energetic hydrogen with material surface is one of the most important issues of plasma surface interactions. Blistering phenomena have been widely observed in various materials and extensive works have been done [1–6]. Different from inert gas ions injection like helium (He), neon (Ne) and argon (Ar), which hardly diffuse and accumulate to make bubbles in bulk and blisters on surface, hydrogen (H) easily diffuses in materials and some times makes strong chemical interactions with target atoms. Hence mechanism of hydrogen blistering could be somewhat different from blistering by the inert gas ions. This motivated us to apply a tritium tracer technique, tritium autoradiography (TARG), to observe hydrogen (tritium (T)) distributions at and around blisters. TARG has been utilized to show hydrogen accumulation in steels [7–9] detecting β-electrons emitted from T by a photographic emulsion film deposited on samples surface. This is the same technique to make a photograph which uses visible light.

In the previous work [10], we have succeeded to show hydrogen distribution at blistered surface of Al with clear indication of hydrogen (T) accumulation in blisters. In this study, we have applied TARG to understand hydrogen blistering of Molybdenum (Mo), for which two different types of blistering mechanisms have been proposed, i.e. one is hydrogen bubble coalescence to make surface blisters and the other is grain exfoliation due to hydrogen accumulation at grain boundaries and/or clustered defects due to brittle nature of Mo.

2. Experimental

Samples used here were hot-rolled polycrystalline Mo sheets (DBTT (ductile–brittle transition temperature) is around 400 K). The size of the sheets was $5 \times 10\ mm^2$ with the thickness of 1 mm. The surface of the specimens was mechanically polished with abrasive papers and mirror finish using 0.3 μm Al_2O_3 powder. Tritium (T) was loaded by an AC glow discharge method with H_2 gas pressure of 60 Pa containing T with 5.0×10^{-6} in T/H ratio. Applied AC voltage was 3 kV between two electrodes on which the specimens were fixed to be exposed to the discharge for long time to get blisters and their exfoliation on the surface. The incident energy of the ions was not measured but is likely below 100 eV. The irradiated specimen surfaces were observed by an optical microscope and a scanning electron microscope (SEM).

TARG was done as follows. Two layers, a collodion film with 20 nm and a layer of nuclear photographic emulsion of AgBr grains (Amersham EM-1), were deposited and dried on the hydrogen loaded (tritiated) specimen surface with dipping method in a photo dark room. The former was placed between the specimen surface and the nuclear emulsion in order to avoid any chemical reactions of AgBr with the specimen metal. The photographic film thus produced was exposed to tritium β-electrons escaping form the specimen surface at liquid nitrogen temperature for about 20 days in a shield box to avoid T migration and release during the exposure. After the exposure, the photographic film was developed and fixed to get Ag precipitates with about 0.3 μm in diameter. The profile of Ag precipitates, which correspond to T profile on and in near surface layers, was observed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

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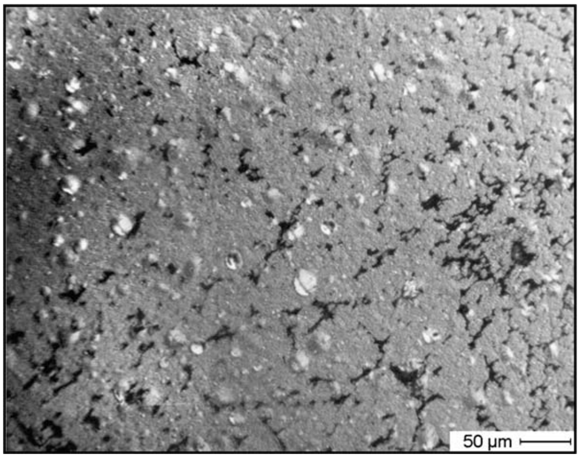

Fig. 1. Optical microscope image of hydrogen loaded Mo.

3. Results

Fig. 1 is an optical microscope image of the Mo specimen surface after hydrogen loaded. Dark or roughened area in Fig. 1 corresponds to grain boundaries and/or trace of grains exfoliations. Apart from the roughened surface, blisters with various shapes with diameters ranging from 10 to 50 μm were distributed rather homogeneously in the image. One can also see some blisters fractured and some appeared across the grain boundary.

In magnified SEM images, one can distinguish three different surface appearances partly owing to inhomogeneous hydrogen loading in macro scale, for which TARG images are shown in Fig. 2(a–c) together with EDX spectra (d) taken at a cross point in (c). The EDX spectra shows Mo, Ag, and C are dominant species. Most of white areas in these images contained Ag, indicating precipitation of Ag or existence of T. Carbon is mostly originated from the collodion film. In Fig. 2(a), most of Ag precipitates were localized on or along grain boundaries and no clear blisters appeared. Fig. 2(b) depicts clear blister formation but only some part of the blister was covered by Ag precipitates. Fig. 2(c) is a mixed area. One can note some blisters appeared across the grain boundary. Different from Fig. 2(a), Ag precipitated very inhomogeneously on grain boundaries and much wider than the boundaries.

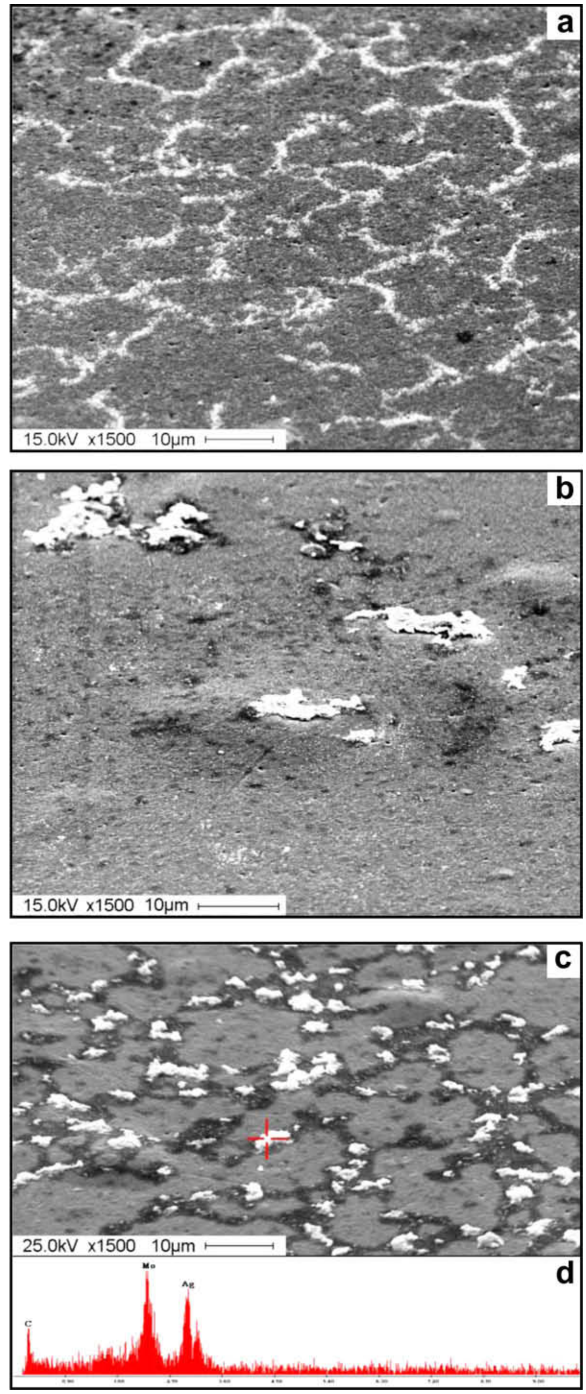

Fig. 2. SEM surface images of hydrogen loaded Mo with same magnification, (a) Ag precipitates accumulating at grain boundaries, (b) blister formed area, (c) mixed area, (d) EDX spectra taken at a cross point in (c).

4. Discussion

Since the average energy of β-electrons emitted from T, is as small as 5.7 keV, TARG can detect tritium retained near surface layers within their escaping depths. The escaping depth depends on electron stopping power of materials and can be calculated by a simulation code like the MCNP code [11]. The result for the escaping depths of 6 keV closed to average energy for Mo was calculated as shown in Fig. 3. One can see that TARG can detect tritium retained within only ~0.2 μm for Mo. Hence T accumulated at grain boundaries is clearly observed as in Fig. 2(a), while those in blisters can not be detected if the blister skin is thicker than the range. Local Ag precipitations on the blisters are very likely caused by thinning of the blister skins by permanent deformation. Localized Ag precipitates on and near the grain boundaries in Fig. 2(c) indicate hydrogen accumulation at the grain boundaries leading to the exfoliation of small grains or cracking of the grain into smaller grains near boundaries. Hydrogen (T) accumulated in the grain boundaries connected to the surface are apparent but those buried inside, deeper than the range, could not be detected.

Considering all above results, two independent types of blistering mechanisms seem to occur on Mo surface, i.e. one is blistering due to bubble coalescence accompanying plastic deformation of the blister skins (thinning of the skins). Another is exfoliation or fracture of a grain caused by mechanical cracking started at the grain boundaries and/or defect clusters. In this case, internal stress given by retained hydrogen in grains and accumulated hydrogen at grain boundaries weaken the binding force between the grains and makes crack penetration easier. Thus, surface swell up, sometimes giving totally exfoliate grains as often observed on W [12–13]. In the present discharge condition, the surface temperature, which was not measured, was likely over 350 K, and both types of surface modification appeared simultaneously. The grain exfoliation will

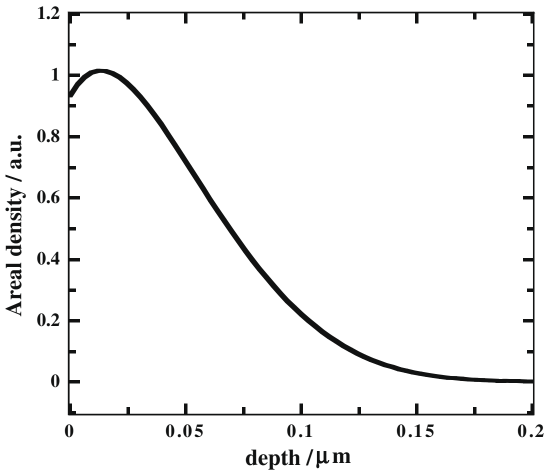

Fig. 3. Penetration depth of β-electrons with incident energy of 6 keV in Mo calculated by the MCNP-code.

disappear for hydrogen loading above DBTT of Mo, which must be confirmed in future.

5. Conclusion

In this study, we have applied TARG to examine blistering mechanism of Mo produced by AC glow hydrogen loading. The results are summarized as follows. Two independent types of blistering appeared simultaneously on Mo surface. One is blistering due to bubble coalescence accompanying plastic deformation of the blister skins, and TARG detected T only on the limited area of the blister surface where is thinned by plastic deformation to allow β-electrons to escape. The other is exfoliation or fracture of a grain caused by mechanical cracking started at the grain boundaries and/or defect clusters owing to brittle nature, which is evidenced by T accumulation on the grain boundaries and on the trace of the irregular shaped cracked area.

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