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Proportion quantitative analysis and etching of {110} planes on tungsten single crystal coating surface

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ABSTRACT

Tungsten single crystal and poly crystal were treated by electrolytic etching in a 3% by weight solution of NaOH in distilled water. The method for determining the proportion of {110} planes and characteristic morphology on the coating surface after electrolytic etching were investigated using EBSD and auto-focusing microscope. Then the optimization of process parameters for electrolytic etching is achieved. In order to compare the effect of process parameters, three process parameters were selected for the tungsten single crystal electrolytic etching. Through analyzing the change of {110} planes' proportion, we found that when the coatings are etched with 1.4 amp/cm^2 and 3 min, {110} planes can be exposed in the greatest degree that can reach 61.4% on tubular surfaces. The proposed approach greatly improves the proportion of {110} planes relative to the original surface.

1. Introduction

The thermionic energy converter (TEC) can convert heat to electric power directly without an intermediate stage of heat-to-mechanical energy conversion. And thermionic fuel element (TFE) is the basic element of TEC. The creation of highly efficient TFEs with long life and stable output parameters need a number of new materials, especially new high-temperature emitter materials which are of the strictest requirements. The requirements are determined by the functional purpose and operating conditions of a given TFE unit. The TFE primary requirements consist of high vacuum work function, to optimize the TFE electrical parameters; low emissivity, specifically under low current density, to reduce heat losses onto the collector and heighten TFE efficiency; low saturated vapor pressure and resistance to chemical transport reactions, to reduce material transfer to the anode; low electrical resistance and others. Thus the single crystal materials are preferred and single crystal molybdenum emitters with single crystal tungsten coating are already used [1].

The single crystal tungsten has anisotropy of electron work function. And the {110} planes have highest vacuum work function, which is believed to be the best tungsten plane for a thermionic converter emitter surface [2]. Then the thermoelectric conversion efficiency of the TECs can be greatly improved. The single crystal tungsten coating can be prepared by high-vacuum chemical vapor transport deposition, but there is less proportion of the {110} planes in its original surface [3]. So a retreatment of the single crystal tungsten coating is needed. There is strong selective corrosion of different planes of single crystal tungsten in the same electrolytic solution. A strong preferential attack on the weak atomic planes can leave the high surface density {110} planes as flats [4], thereby increasing the coating surface's proportion of {110} planes.

As early as in late 1950s, Hughes had found that etching of tungsten wires with immersion in a room temperature solution of 70% HNO_3:30% HF for 2 min leaves {110} and {112} planes [5]. Later, Webster pointed out that low-voltage electrolytic etching of tungsten in NaOH develops {110} planes, and the tungsten coating which was of a preferred orientation with the (100) planes would expose {110} planes with the sample as the anode and 2 V applied across the cell [6]. Besides, the conditions for anisotropic plasma etching of tungsten by using SF_6/Ar Gas Mixtures were also studied by Reyes-Betanzo [7]. For about half a century, the anisotropic etching technology of the tungsten material has obtained substantial development. However, the quantitative statistics method for the proportion of the different planes on the single crystal tungsten coating surfaces was rarely reported. Thus the process

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parameters optimization of anisotropic etching was limited to some extent.

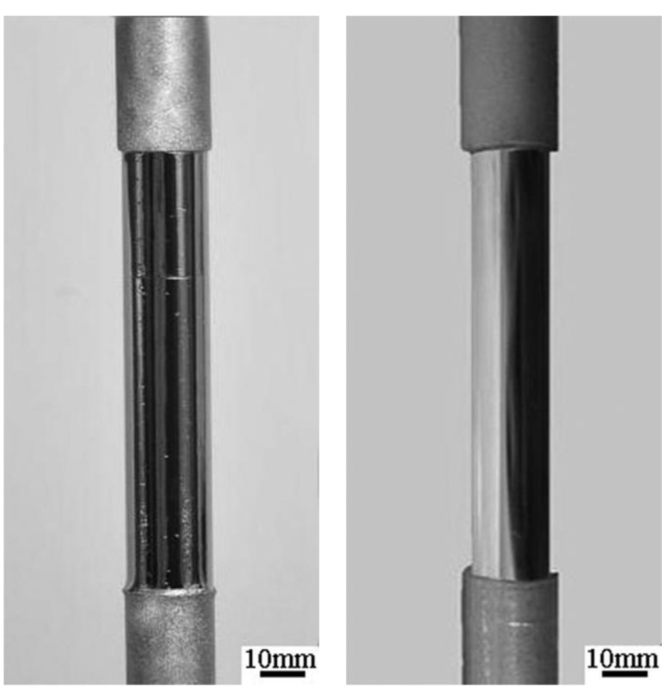
In the present paper, we provided a method of determining the {110} planes proportion. This method is mainly based on the direct observation to the coating surface morphology. The representative morphology of differences planes were determined by using auto-focusing microscope and EBSD. Then, the proportion of {110} planes was obtained by the comparative statistics of the surface morphology between the coating surface and the representative planes. The main advantage of this method is that it can be easily used to identify crystal plane index of the coating surface making up the surface morphology, which puts the base for optimizing process parameters of electrolytic etching. It has been proved that the method is effective and can be as a means of nondestructive test in tungsten single crystal coating.

2. Experimental

2.1. Experimental materials

The tungsten single crystal coatings were deposited on molybdenum single crystal substrates with <111> axis orientation using high-vacuum chloride vapor transport deposition in our laboratory [3]. Fig. 1(a) is the original surface of the tubular single crystal coating, which has distinct polyfaces with alternating rough {110} and flat {112} surfaces. To eliminate the surface impurity of the coating, the mechanical polishing, the electro polishing (in a 3% by weight solution of NaOH in distilled water, 10 v), and the chemical cleaning (alcohol solution, 15 min) are all required before etching experiments. The coating surface was changed into a smooth surface after preprocessing as shown in Fig. 1(b).

The tungsten poly crystal material was prepared by hydrogen reduction of tungsten hexafluoride at 540 °C and atmospheric pressure [8]. The preprocessing of the poly crystal surface was the same as the tungsten single crystal. Fig. 2 is the EBSD results of crystal orientation of tungsten poly crystal, the analysis showed



(a) (b)

Fig. 1. Sample preparation. (a) Original surface. (b) After pretreatment.

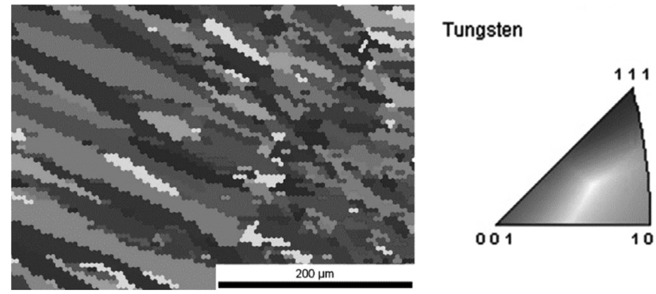


Fig. 2. EBSD images of crystal orientation of tungsten poly crystal.

this surface had (100) preferred orientation, meanwhile, various crystal orientations coexistence on its surface. And it has been found experimentally that characteristic structures of different crystal planes can be obtained on tungsten poly crystal surface by electrolytic etching with 0.5 amp/cm^2 and 1 min.

2.2. Electrolytic etching and statistical for proportion of {110} planes

Three process parameters for the tungsten single crystal electrolytic etching were selected to compare the influences on the process parameters. By setting the voltage, the electric current density was respectively 0.6, 1.0 and 1.4 amp/cm^2, the etching time is 3 min.

Statistical for proportion of {110} planes on tungsten single crystal surface consist of 1) establish the corresponding relation between the crystal planes and the characteristic morphology, and obtained the whole characteristic morphology of the tubular emitter surface; 2) determine the angle zone of {110} planes area on the entire surface by comparative statistics; 3) finally the total of angles zone of {110} planes divide by 360° to get the proportion.

The relation between the crystal planes and the morphology were obtained by using EBSD. The morphology of the tubular surface were obtained by auto-focusing microscope after etching under three different process parameters. The microscope exist the automatic regulation system of focus, which can be easily shown the entire surface.

3. Results and discussion

3.1. Tungsten poly crystal morphology analysis

The morphology of tungsten poly crystal surfaces after etching in the NaOH solution are presented in Fig. 3.

It has been established by EBSD experiments of known the crystal orientations of the marking positions, and the results are shown in Table 1. The {110} planes (Fig. 3(a)) shows short risers steps microstructure, and the size of those steps is not uniform; the {112} planes (Fig. 3(b)) also display step microstructure and the ratio of the projected lengths of the sides of the ribs is 1: 1; the {123} planes (Fig. 3(c)) are similitude with {112}, but the ratio of the projected lengths is changed into 1: 2.5; the {111} planes (Fig. 3(d)) possess the three sided pyramids microstructure, very often the pyramids are stacked together; and for {100} planes, there are many etch pits on its surface [9], and the shape of etch pits exhibits as inverted pyramids with bottom surfaces parallel to the {100} planes as shown in Fig. 3(e). The experimental results are the same as the theoretical features proposed by Thompson [5].