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PREPARATION OF TITANUM-ZIRCONIUM-VANADIUM FILMS BY QUANTITATIVE DEPOSITION

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Abstract

TiZrV has been used in vacuum technology and electric vacuum devices due to its high pumping speed and low activation temperature in recent years. At the same time, many preparation methods have been developed. Different from the current coating method of magnetron sputtering, this paper discusses the preparation of thin film coating from the viewpoint of vacuum sintering, which is flexible in design and more suitable for operation. Based on the analysis of the surface morphology of the sintered film, the feasibility and operability of the experimental method were explored from the surface compactness of the getter.

INTRODUCTION

With the development of science and technology, vacuum has played an increasingly important role in production and scientific research. Getter materials have been widely used in vacuum technology, thanks to their high pumping rate and large sorption capacity, as well as long service life and low economic characteristics.

To maintain and establish a vacuum environment by soaking up or bonding to residual gas in the chamber, getters use materials that readily form stable compounds with gas molecules. According to the way of surface cleaning, getter materials are mainly divided into two categories: flashed and non-evaporable getter (NEG). Meanwhile, flashed getters form films to adsorb gas molecules through evaporating, and the evaporated ions will affect the normal operation of vacuum electronic device. Compared with the flashed getter, NEG has the following advantages: firstly, it has a larger sportion capacity, which can reduce the interaction between residual gases in the vacuum chamber; secondly, the lower activation temperature keeps from thermal damage to electronic vacuum devices; thirdly, the fewer secondary electron yield (SEY) can also avoid secondary electron multiplication; in addition, NEG also has the characteristics of high pumping rate, powder free, small space occupancy, controllable precision and easy preparation and so on.

NEG materials are mainly composed of metallic or non-metallic elements such as Ti, Zr, V, Hf, Ta and C, from which columnar or thin-film getter can be obtained according to different preparation. By diffusion of the oxide layer into the bulk, NEG can adsorb H_2, N_2, O_2, H_2O and carbon oxides in the chamber except noble gases and methane [1, 2]. That the pumping rate decreases with the increase of sportion capacity, with a passivation layer formed on the surface, results in the ultimate saturation of sportion capacity [3]. Therefore, for the sake of restoring the performance, it needs to be heated and activated to remove the passivation layer, oxide film and adsorbed active gas molecules on the surface. Conventional NEG materials require an activation temperature of higher than 350 °C, while it is lower than 400 °C for stainless steel vacuum chamber and 200 °C for the aluminum alloy vacuum chamber of the Large Hadron Collider (LHC).The European Organization for Nuclear Research (CERN) discovers that after 24 h "in situ" heating at 180 °C, the thin film of TiZrV can be fully activated [4, 5].

At present, various preparation of NEG films have been developed, such as coating, screen printing and vapor deposition. This paper will describe a quantitative deposition method to prepare TiZrV film in detail. Sintering in a vacuum is an effective way to process the specially shaped devices, which greatly reduces the experimental purpose. As a matter of fact, sintering refers to the process of combining powder materials into compact materials in a vacuum atmosphere because of the high temperature, accompaning with generating strength to make it densify and recrystallize. In additon, coating is carried out under vacuum, aiming to make the getter materials completely dehydrogenated, as well as to make the powder completely sintered together and facilitate full activation. In general, vacuum sintering has several advantages: clean parts, flexible production, fewer product defects, easy maintenance of equipment and very low dust release [6]. In parallel, vacuum sintering affects material properties in terms of grain size, pore size and microstructure distribution of getters. In this case, three different sintering conditions will be considered, thus, a comparative analysis of three different results will be conducted.

EXPERIMENTAL CONTENT

Experimental Procedures

According to the method and purpose, the experimental process was mainly divided into three steps: cleaning the substrate, preparing the sample and sintering the film.

Considering that the sintering temperature exceeds 1000 °C, it was larger than the melting point of the constantan alloy. Therefore, a nickel-chromium alloy with a higher melting point was selected as the substrate material. For the sake of increasing the roughness of the substrate to increase the adhesion between the film and the substrate, the nickel-chromium alloy substrates were scraped prior to the starting of coating. Then, in order to remove the poorly soluble grease on the surface of the substrates, which can

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avoid contamination of the vacuum environment by venting surface impurities, the substrates were immersed in the diluted HF solution for a period of time. After that, the acid-soaked substrates were cleaned by the combined action of deionized water and ultrasonic wave. Next, drying the washed substrate with N_2 was the last step.

At the same time, considering the vacuum sintering process, the thickness of TiZrV film was selected to be 30 µm. Via the calculation, the quantitative Ti powder, Zr powder and V powder were uniformly mixed in a ratio of 1:1:1, with enough alcohol added as a molding agent, so that it could be stirred evenly and deposited on the substrate. Also, it should let it stand to allow the alcohol to evaporate and make it dry.

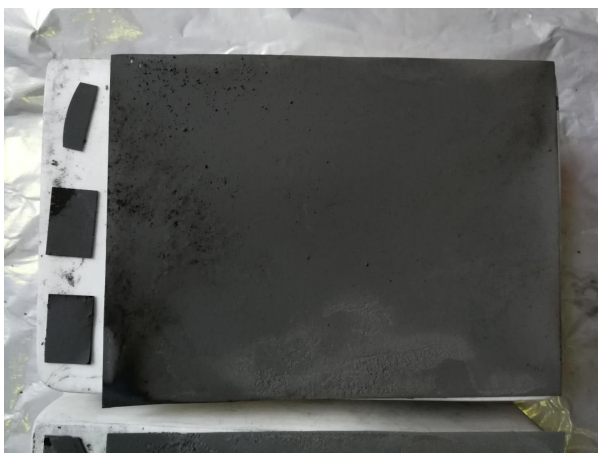
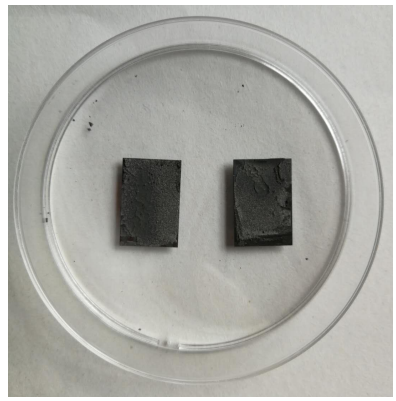


Figure 1: Completely dried sample after deposition.

Figure 2: Experimental sintering device.

Until when the sample film was completely dried, as shown in Fig. 1, it was placed into a vacuum tube furnace (cf. Fig. 2), and the inside of the tube was pumped to 10^{-3} Pa by starting oil-free molecular pump unit. After that the vacuum circumstance was stabilized and the heating program was started. The sample was sintered from room temperature to the highest temperature and kept warm. In order to investigate the effect of the sintering process on the compactness of the sample, a experimental scheme was proposed: changing



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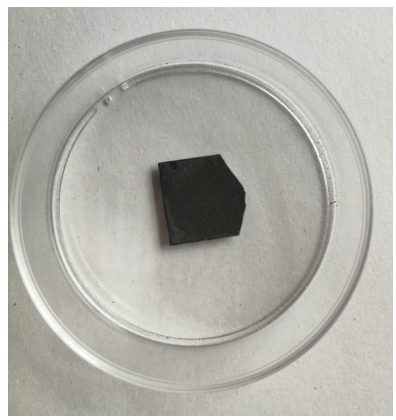

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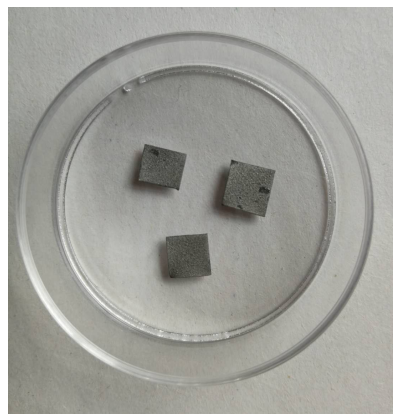

(c)

Figure 3: Film samples at different sintering temperatures: (a) 950 °C, (b) 1000 °C, (c) 1025 °C.

the highest temperature,which were 950 °C, 1000 °C, and 1025 °C respectively. The sintering temperature of the alloy was determined according to the melting point of the different kinds of powders in the alloy. In the end, the program was closed and the sample was naturally cooled with the furnace.

Analysis of Experimental Results

It should be noted that the degree of vacuum in the tube is lower than that before sintering, so it can be predetermined

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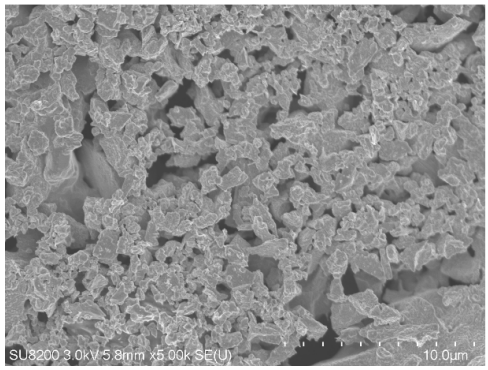

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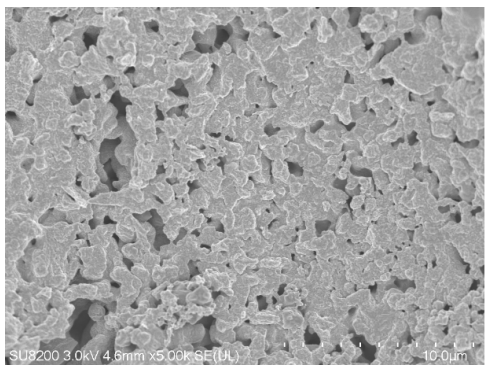

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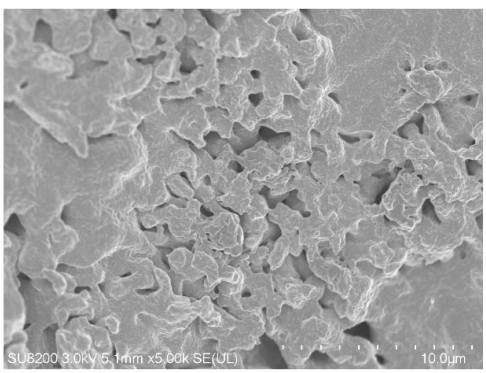

(c)

Figure 4: SEM images of film samples at different sintering temperatures: (a) 950 °C, (b) 1000 °C, (c) 1025 °C.

that the getter film having a certain gettering property has been sintered. Figure 3 shows the samples obtained under different sintering temperatures. The surface of the sample prepared at 950 °C has a film peeling off, which proves that the mixed powder is not completely sintered at this temperature. However,the surface of the sample for 1000 °C and 1025 °C are scratched, and no powder is dropped. So it can be simply judged that the sample for 1000 °C and 1025 °C has good mechanical properties.

At present, the surface topography scan analysis of these samples are shown in Fig. 4. As it can be concluded from the figure that the powder can be completely sintered at two temperatures of 1000 °C and 1025 °C, and large holes were filled to make the surface of the sample dense, while at 950 °C, the surface pores of the sample were too large to cause poor adhesion. According to the analysis of surface pore size, at 1000 °C, the sample has the better compactness, resulting in better mechanical properties and larger sorption capacity.

CONCLUSION

The quantitative deposition method for preparing TiZrV film described in this paper has certain feasibility. The prepared film has good compactness and certain pumping performance. During the sintering process, the solid particles were interkaged with each other. When the crystal grains growed, the pores and grain boundaries were gradually reduced, with the total volume shrinking and the density increasing, finally becoming a dense polycrystalline sintered body. From the surface morphology analysis, the surface compaction of the film sintered at 1000 °C is higher than at 950 °C and 1025 °C, so 1000 °C can be used as the highest sintering temperature condition for further film performance investigation.

ACKNOWLEDGEMENTS

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