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INTERFACE REACTION BETWEEN Y_2O_3 DOPED $BaZrO_3$ AND TiNi MELT

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Abstract

Using the solid reaction method, the Y_2O_3 4mol%-doped $BaZrO_3$ powder was prepared by $BaCO_3$, ZrO_2 and Y_2O_3 as raw materials, the effect of sintering temperature on the property and microstructure of Y_2O_3-doped $BaZrO_3$ pellets was investigated, the crucible made of this Y_2O_3-doped $BaZrO_3$ was utilized to melting the TiNi alloy by the vacuum induction method. The phase constitution of doped powder and the interface reaction between the crucible and the melt were studied by XRD and SEM. The results showed that this Y_2O_3-doped $BaZrO_3$ consists of two phase ($BaZrO_3$ and Ba_2YZrO_6), the pellets sintered at 1750℃ for 6h reached the maximum relative density of 98.0%. Besides, there was no obvious interaction layer and element diffusion between the crucible and the melt, which may imply that the Y_2O_3-doped $BaZrO_3$ refractory is a promising candidate for melting titanium alloys.

Introduction

Titanium alloys were widely applied in various industrial fields, such as weaponry, aviation, aerospace, chemical, medical .etc, because of their excellent performance, such as low density, high specific strength, non-magnetic and high temperature mechanical properties[1,2]. However, as titanium and titanium alloys can react chemically with almost all of the refractory in the molten state, they should be melted with the inert protective gas atmosphere, resulting in the increasing of difficulty and cost with melting titanium and titanium alloys. With the development of technology, preparation of titanium was also in constant development and improvement stage.

Currently, water-cooled copper crucible melting process was widely used in titanium alloy melting. But it had high energy consumption and increased the production costs. At the same time, this process made titanium organization serious segregation and affected the performance of titanium alloy because of the non-uniform thermal field. The researchers found that vacuum induction melting technology can reduce the cost of production, and vacuum induction furnace had a strong electromagnetic stirring, keeping the alloy melt a high degree of superheat, which was conducive to the elimination of segregation to obtain uniform composition of titanium[3]. With the proviso, there must be a material that had no interfacial reaction with titanium melt[4]. Crucible materials used for melting titanium alloys were mainly of graphite, oxides[5], BN[6] and so on currently. In addition, according to the research of Zhang Zhao[7], the stability of refractory still needed to be improved.

The structure of $BaZrO_3$ is cubic perovskite, the melting temperature and lattice constant are 2700℃ and 0.4193nm, respectively. It was an ideal crucible material for the preparation of high-quality single-crystal YBCO superconducting because of its low thermal conductivity, excellent mechanical properties and structural stability[8]. The Y_2O_3 belongs to the cubic crystal system, and it was a good transparent ceramic material and infrared material due to its excellent heat resistance, corrosion resistance and high temperature stability [9,10]. In present, Y_2O_3 as doping agent, such as Y_2O_3-doped ZrO_2, was also widely used, which is remarkable to the researchers due to its high chemical thermal stability, high strength, etc [11]. Meanwhile, the Y_2O_3-doped $BaZrO_3$ was also widely utilized as proton conductor in the electrolyte material with solid fuel cell [12-14]. However, using the Y_2O_3-doped $BaZrO_3$ for melting titanium alloys, as the refractory, was reported rarely.

In this paper, the powder of Y_2O_3-doped $BaZrO_3$ was prepared by solid phase synthesis, and then its constituent was analyzed by X Ray Diffraction (XRD). The crucible made of this Y_2O_3-doped $BaZrO_3$ was utilized for melting the TiNi alloy by the vacuum induction method. The interface reaction between the crucible and the melt were studied by scanning electron microscope (SEM) and point scanning technology (EDS).

Experimental

Preparation of Powder

The powder was prepared by industrial-grade $BaCO_3$ (purity> 99.0%), ZrO_2 (purity> 99.2%) and Y_2O_3 (purity> 99.0%) with a molar ratio of n ($BaCO_3$): n (ZrO_2): n (Y_2O_3) = 1: 1: 0.04, and the TiO_2 (0.5%) was added into the powder as a sintering aid. Then the powder was sintered at 1400℃ for 12 hours.

Preparation of pellets

The powder was pressed into pellets, and then sintered at 1550℃, 1650℃ and 1750℃ for 6h respectively.

Preparation of crucible

The crucible mold compacted with the powder was placed inside cold isostatic press at 140MPa for 3min, and the green body of crucible was prepared. Then the green body was pre-sintered at 900℃ for 3h to remove the organic compounds and to achieve bisques with much higher mechanical strength. Finally, the sintering process was carried out at 1750℃ for 6h.

Melting experiment

The TiNi alloy (50g) was placed into the homemade crucible and was melted in a WZG-2 type vacuum induction melting furnace. Before the melting process, the alloy bar was polished, cleaned and dried, and then it was melted in the homemade crucible with a certain proportion under a dry argon atmosphere at 0.06Mpa. Before the heating cycle, vacuum degree within the furnance was evacuated up to less than 10^{-2} pa, and then the furnance was backfilled with argon 3 times in order to reduce the oxygen content to a minimum level. When the alloy bar was completely melted, the melted-alloy was held at the superheating temperature of 1400℃ for 60s to get chemical homogenization. Sample was prepared after cold set, cutting, rough grinding, fine grinding and polishing. The scanning electron microscopy (SEM) was used for evaluating the surface topography and microstructure of the sample, and the energy dispersive spectroscopy (EDS) was used for analyzing the chemical composition of the sample.

Characterization

The powder, after solid phase synthesis reaction, was analyzed by D/Max - 2200-type X-ray diffraction. The density of pellets after sintering was measured by the AccupycII1340 density tester. The morphology of ceramic surface and interfacial reaction layer was observed by JSM-6700F scanning electron microscope with the energy spectrum analysis.

Result and discussion

Phase analysis of powder

The XRD spectra of the synthesized powder (1400℃，12h). As shown in Figure 1.

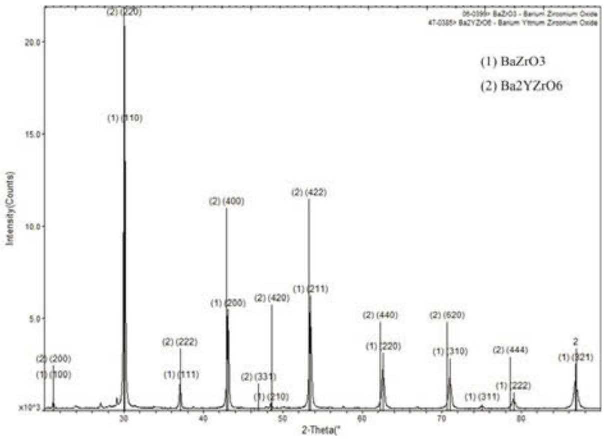

Fig. 1 XRD patterns of Y_2O_3-BaO-ZrO_2 composite powder synthesized at 1400℃

Figure 1 showed the phase composition of the synthesized powder, mainly Ba_2YZrO_6 and $BaZrO_3$ phases, and no diffraction peak of Y_2O_3 existed, which indicated that the Y_2O_3 doped had been reacted with $BaZrO_3$, and Ba_2YZrO_6 was synthesized.

Pellets analysis

It was pointed out that the relative density of the ceramic had a great influence on the quality of the melt [15]. In this experiment, pellets were divided into three groups (sample a, sample b and sample c) and were sintered at 1550℃，1650℃，1750℃ for 6h respectively. Then their densities were measured. As shown in table 1. The relative density of the sample 3 was up to 98%, and this sintering process can be used in the preparation of crucible.

Table 1 Density of pellets prepared under different temperatures

Sample No.	Temperature/ ℃	Density /(g·cm^{-3})	Relative density/%
a	1550	5.950	95.5
b	1650	6.074	97.3
c	1750	6.105	98.0

Figure 2 shows the SEM photo of the pellet sintered at 1750℃ for 6h.

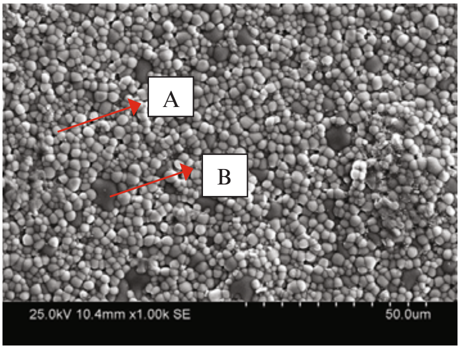

Fig. 2 SEM photograph of the pellet sintered at 1750℃ for 6h.

Figure 2 showed that the pellet was composed of two areas, point A and B. The color of grain B was darker than that of A, and the grain size of B was bigger than that of A. It also showed that the grain B was surrounded by grain A. At the same time, the composition of point A(white grain) and B(black grain) were obtained by EDS analysis, as shown in Table 2. The atom ratio of Ba:Zr:Y for grain A was about 1:1:0, the value for grain B was about 2:1:1, this fact may imply that they were $BaZrO_3$ and Ba_2YZrO_6, respectively, which was consistent with the XRD results in Figure 1.

Table 2 EDAX result of the different positions

Position	Elements		
	Ba(at%)	Zr(at%)	Y(at%)
A	47	53	0
B	48	28	24

Interface analysis between crucible and melt

Macro analysis The crucible after sintering at 1750℃ for 6h was used for melting TiNi alloy. The sample obtained from the end of melting was shown in Figure 4, and it was very easy to peel off between metal ingot and crucible, and no reaction layer existed. It was a sign of reaction between the metal and the crucible if they were madefacted each other and the roughness of the surface was the most intuitive reflect to wettability[16]. The ingot had a smooth surface by using the crucible, claiming that the wettability between crucible material and titanium alloy melt was poor, meaning that the refractory was resistant to the titanium melt.

Fig. 4 External appearance of crucible after melting

Microstructure analysis The sample after melting was cooled by a curing agent, and the reaction layer of the metal - crucible was obtained by mechanical method. The sample was analyzed by SEM and EDS, and the results were shown in figure 5. In Figure 5, the area A is a refractory material and the area B is the melt. The results from EDS line scan showed that the contents of Ba, Zr and Y in the area B decreased significantly, while the contents of Ti and Ni in the refractory materials were almost equal to zero. The gaps in area A was due to the cracks of the crucible, caused by the mechanical cutting. The boundary between area A and area B was clear, and no transition layer existed. This phenomenon was rare in other research about melting of titanium alloy[17-19].

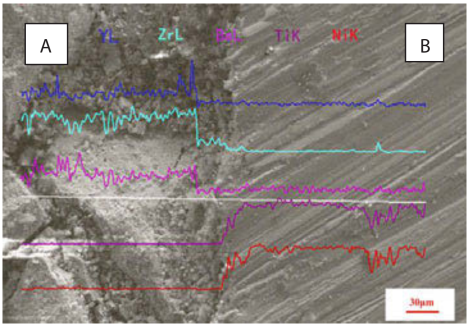

Fig. 5 SEM/EDS photograph of interfacial reaction layer

Conclusion

(1) Using Y_2O_3, $BaCO_3$ and ZrO_2 as raw materials, the powder of Y_2O_3 doped $BaZrO_3$ prepared by solid-phase synthesis at 1400℃ for 12h was composed of $BaZrO_3$ and Ba_2YZrO_6.

(2) This powder was shaped by cold isostatic pressing at 120MPa for 3min as well as sintered at 1750℃ for 6h, which density reached 98.0%

(3) The TiNi alloy was melted by the crucible prepared using mentioned-above condition, there was no obvious interaction layer and element diffusion between the crucible and the metal, so the Y_2O_3-doped $BaZrO_3$ refractory is a promising candidate for melting titanium alloys.

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