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Review Article

A Review on the Preparation Techniques of Titanium Alloy and the Selection of Refractories

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Abstract

Attributed to the high processing temperatures and high chemical activity of titanium and titanium alloys, it has become serious obstacles for the current industrial production of high-quality titanium and titanium alloys. Based on the cost and quality of production, this review evaluates the current main techniques for the preparation of titanium and titanium alloys, and finds that the conventional induction melting still has irreplaceable value. Subsequently, a variety of refractories that can be used for melting titanium and titanium alloys were sorted out, and a quite promising refractory, $BaZrO_3$ composite, was introduced

Abbreviations:

EBM: Electron Beam Melting; CCM/SM: Cold Crucible Melting or Skull Melting; VAR: Vacuum Arc Remelting; PAM: Plasma Arc Melting; ISM: Induction Skull Melting; EDS: Energy-Dispersive Spectroscop

Introduction:

Due to its advantages of light weight, good toughness, excellent high temperature performance, biocompatibility and corrosion resistance, titanium alloys are widely used in aerospace and automotive industries, biomedical components and surgical instrument manufacturing, chemical and petrochemical engineering, marine applications and other fields [1-5]. Although the potential is great, the production of titanium and titanium alloys is usually low due to high costs since the very high processing temperature (pure Ti, melting point (m.p.)=1668 °C; Ti6Al4V alloys, m.p.=1640 °C; TiAl(γ)alloys, 42~50 at.% Al, m.p.=1485~1575 °C; TiNi alloys, m.p.=1240~1310 °C). Unfortunately, at such high temperatures, molten titanium becomes extremely active, and it is chemically corrosive to almost anything it comes into contact with [6]. How to obtain titanium and titanium alloys with low cost, high purity, uniform microstructure and excellent performance is a real problem to be solved at present.

Methods for Preparing Titanium and Titanium Alloy:

To obtain titanium alloy products, casting is indispensable, of course, powder metallurgy can also be selected, but the powder metallurgy routes has some disadvantages such as ingot chemical and microstructural heterogeneity, components geometry are limited, porosity leads to serious oxygen contamination, and high cost [7]. Thus, casting seems to be the first way to obtain high quality titanium alloy products at low cost. However, due to the active chemical nature of molten titanium, it is easily contaminated, such as oxygen and nitrogen in the air, and the crucible material used for melting. Therefore, the preparation process of titanium alloy must be carried out in a vacuum or inert protective atmosphere, which will undoubtedly increase the cost of production, and more importantly, how to select a suitable crucible refractory. Although with the rapid development of metallurgical technology, some new concepts of melting titanium alloys have been developed, such as levitation melting (LM) [8] and Cold Crucible Melting or Skull Melting (CCM/SM) [9], the core idea of which is to avoid direct contact between the molten metal and the crucible. LM technique uses electromagnetic force or gas pressure to suspend the molten metal, while CCM/SM technique forms a solid skull with the same composition as the parent alloy on the surface of the water-cooled copper crucible. According to different heating principles, CCM/SM technique has spawned various techniques such as Vacuum Arc Remelting (VAR) [10], Induction Skull Melting (ISM) [11], Electron Beam Melting (EBM) [12], and Plasma Arc Melting (PAM) [13]. However, LM technique is obviously not suitable for large-scale production. VAR technique needs to press the pre-electrode before melting, which not only increases the cost but also requires high cleanliness of raw materials. In addition, the inclusion and segregation of VAR castings are serious, which requires multiple remelting and long subsequent heat treatment. ISM technique, due to a part of the heat has taken away by the water-cooled copper crucible, which results in low energy efficiency and is not easy to form superheat molten metal, as well as heterogeneous composition and microstructure of castings. EBM and PAM technique also have the problem of low superheat, only superheat near the heat source, resulting in poor fluidity of the molten metal. What's more, EBM technique will lead to the volatilization of element with high evaporation pressures, such as Al, Sn, Cr, etc., so that the fluctuation of ingot composition is difficult to control. In general, contactless melting technique has its advantages, but its disadvantages are also obvious. Perhaps in the future, various heat sources can be integrated, combined with the advantages of all parties, through numerical modeling and analysis, to further understand the distribution of temperature field in the melting process, so as to optimize the entire process.

Since the preparation method without direct contact with the crucible has low energy efficiency, high cost and heterogeneous composition and microstructure of the ingot (generally requires subsequent processing and modification, which further increases the cost), so it goes back to the previous point of view-choose the appropriate crucible refractories are particularly importantThe development of inert and durable refractories for melting titanium alloys is definitely valuable work. Refractories that need to be used and in close contact with the melt are mainly Vacuum Induction Melting (VIM) [14,15]. Compared with other melting methods, because the thermal conductivity of refractory materials is generally lower, VIM technique allows the metal liquid to superheat, and the composition and microstructure of the casting are more homogenization due to electromagnetic stirring. More valuable, VIM technique is inexpensive and suitable for large-scale industrial production. The most critical part of VIM is how to choose refractories that are inert, durable and inexpensive, so as to apply to industrial production.

Selection of Refractories:

In the past two decades, in order to find suitable refractory materials for melting titanium and titanium alloys, various high-temperature ceramic materials such as oxides, carbides, nitrides, silicides, sulfides, and borides have been evaluated, but the results have been not satisfying [16]. For example, BN and AlN ceramic crucible melting titanium alloy will cause interface reaction [17,18], while using graphite crucible will cause carbon contamination of the titanium alloy [19]. Among the most used ceramic oxides, generally only Al_2O_3, ZrO_2, CaO, and Y_2O_3 meet the relevant thermodynamic considerations (Figure 1). But Al_2O_3 and ZrO_2 will form an inevitable reaction layer with the titanium alloy melt at the interface [20,21]. Due to thermodynamically stable and inexpensive, CaO is a very promising refractory for melting titanium alloys, but CaO crucibles have poor water resistance and high oxygen content in melted titanium alloys. Studies have shown that the contamination of Y_2O_3 crucibles for titanium alloys is far less than other refractories, but expensive and poor thermal shock resistance are fatal flaws. It can be seen that a single refractory material will always have one or other defects, and it is difficult to meet all needs. Faced with this situation, how should we choose? In order to solve this problem, two ideas of coating [21,22] and doping [23-26] came into being. For example, the corrosion resistance of Y_2O_3 crucible is good, but the cost is high and the thermal shock resistance is poor, while the performance of Al_2O_3 crucible is just the opposite. Therefore, Y_2O_3 can be coated on the inner wall of the Al_2O_3 crucible. The formed Y_2O_3/Al_2O_3 crucible perfectly combines the advantages of the two materials and avoids the disadvantages of both sides. There are also many examples of doping, such as CaO doped ZrO_2, BaO doped ZrO_2 ($CaCO_3$ or $BaCO_3$ and ZrO_2 are solid-phase sintered at a molar ratio of 1:1 to form $CaZrO_3$ or $BaZrO_3$) [26-29]. $CaZrO_3$ and $BaZrO_3$ are perovskite refractories and meet the thermodynamic conditions for melting titanium and titanium alloys (Figure 1). Since $BaZrO_3$ has higher thermodynamic stability than $CaZrO_3$, and literature shows that BaZrO3 crucible has less contamination to titanium alloy than Y_2O_3 crucible (Figure 2), so we will focus on $BaZrO_3$ refractories.

According to the previously mentioned ideas, a single refractory material is difficult to meet all needs [30]. Even if the performance of the BaZrO3 crucible is already very good, we can also dope with other refractories in order to pursue a more perfect effect. For example, $BaZrO_3$ crucible doped with CaO [24] or Y_2O_3 [25,31], in order to determine the best doping ratio, can be guided by the ternary phase diagram. (Figure 3) shows the isothermal section of BaO-ZrO_2-$YO_{1.5}$ and BaO-CaO-ZrO_2 at 1750 °C and 1820 °C, respectively. In order to avoid mismatch of physicochemical properties of different phases, the composition of materials should be controlled in the single-phase region or two-phase region with similar properties [32]. Therefore, refractory materials located in the BZ and BCZ phase reigns are the most likely candidates for melting titanium alloys. (Figure 4) shows the SEM images of surface microstructure of $BaZrO_3$ crucible with different doping. (Table 1) lists the energy-dispersive spectroscopy (EDS) results that were taken in regions indicated in (Figure 4). It can be seen from the (Figure 4(a)) that the densification of the $BaZrO_3$ crucible is excellent. Although the densification will be slightly reduced after doping with CaO or Y_2O_3, the exciting thing is that the grain size is significantly reduced (Figures 4(b) & (C)), mainly because CaO or Y_2O_3 will become the nucleus point (Table 1), the formation of new phases also has the effect of hindering the movement of the grain boundary, which will undoubtedly increase the strength of the material. (Figures 4(d) & 4(e)) is the doping of different molar amounts of $CaZrO_3$, which can form a microstructure inlaid with small and large grains. This special microstructure will improve the bundling and densification of crucible, which is conducive to improving the thermal shock resistance and Corrosion resistance of the crucible, and the crucible will be more durable. Of course, excessive addition of $CaZrO_3$ will also have a counter-productive effect (Figure 4(d) & Table 1).

Figure 5 shows the erosion of the metal-crucible interface. Analysis the composition of the three points A, B and C by EDS and the morphology of the metal-crucible interface in (Figure 5(a) &Table 2). It can be seen that the TiNi alloy corrodes the CaO crucible more seriously. In contrast, the thickness of the interface reaction layer of $CaZrO_3$ and TiNi alloy is about 30μm (Figure 5(b)). Even better, the thickness of the interface reaction layer of $BaZrO_3$ and TiNi alloy is only about 8μm (Figure 5(c)). Best of all, there is almost no interface reaction layer between the Y2O3-doped $BaZrO_3$ crucible and TiNi alloy (Figure 5(d)). It can be seen that compared with CaO and $CaZrO_3$ crucibles, $BaZrO_3$ crucibles are more effective for preparing TiNi alloys, and the performance of Y2O3-doped $BaZrO_3$ crucible has been further improved. This may be because Y^{+3} occupies the lattice position of Zr^{+4} to form two new phases, $BaZr_{1-x}Y_xO_3$ and Ba_2YZrO_6 [25], and the new phases are widely distributed at the grain boundaries (Erosion generally starts at the grain boundaries), thus resisting the corrosion of TiNi melt. Considering the high cost of the $BaZrO_3$ crucible, it is possible to adopt the idea of coating. For example, the cost-effectiveness of the $BaZrO_3/Al_2O_3$ crucible is very attractive [33,34].

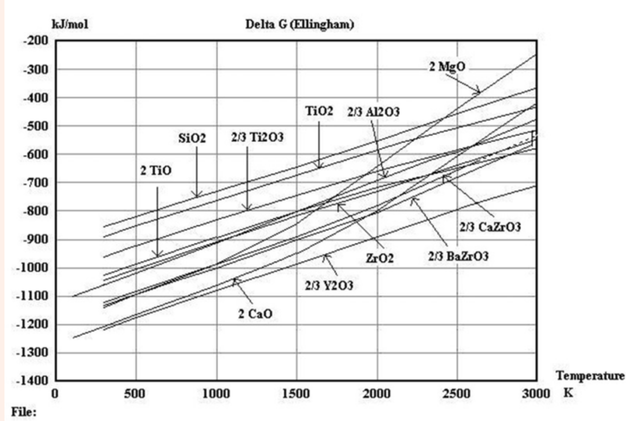

Figure 1: Variation of standard free energies of formation of some relative oxides with temperature.

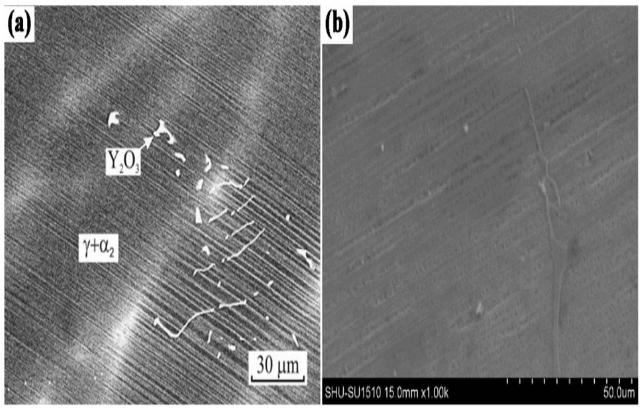

Figure 2: : Microstructure of TiAl alloys melted by (a) Y_2O_3 crucible [30] and (b) $BaZrO_3$ crucible [29].

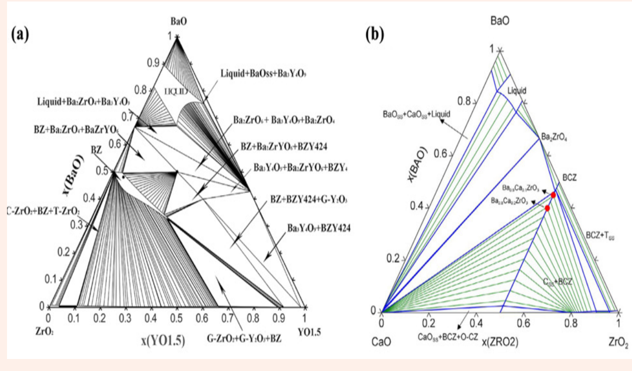

Figure 3: (a) The isothermal section of BaO-ZrO_2-$YO_{1.5}$ at 1750 °C [32]; (b) The isothermal section of BaO-CaO-ZrO_2 ternary system at 1820 °C [33].

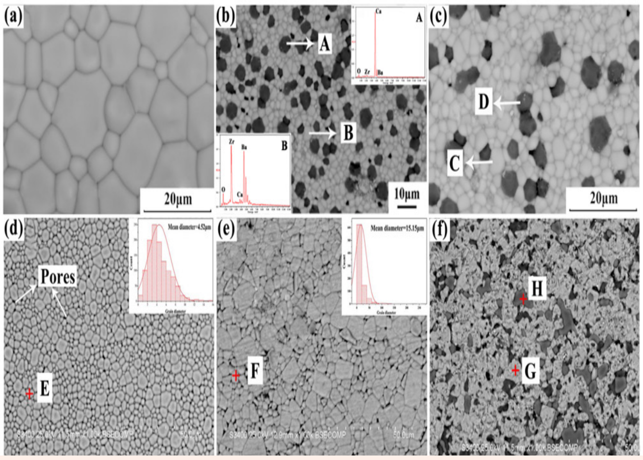

Figure 4: SEM images (backscattered electron mode) of surface microstructure of $BaZrO_3$ crucible with different doping. (a) the $BaZrO_3$ crucible [25]; (b) the CaO-doped $BaZrO_3$ crucible [24]; (c) the Y_2O_3-doped $BaZrO_3$ crucible [25]; (d), (e) and (f) are the $BaZrO_3$-$xCaZrO_3$ crucibles, mole ratio n ($BaZrO_3$): n ($CaZrO_3$)=(1− x): x (x=0.1, 0.2, and 0.3) in (d), (e) and (f), respectively [33].

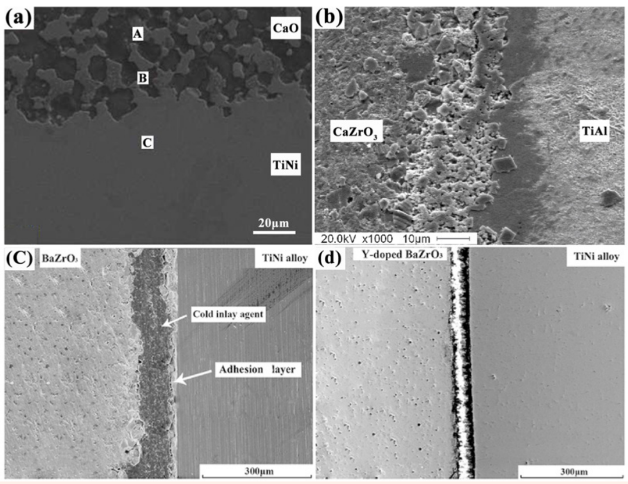

Figure 5: SEM photographs of the interaction between the crucibles with the TiNi alloys melting at 1500 °C, hold for 5 minutes. (a) CaO crucible [34]; (b) $CaZrO_3$ crucible [27]; (c) $BaZrO_3$ crucible [25]; (d) Y_2O_3-doped $BaZrO_3$

Position	Elements/at.%					Possible Phase
	Ba	Ca	Zr	Y	O	
C	31.39	/	23.27	3.56		$BaZr_{1-x}Y_xO_3$
D	39.16	/	20.35	17.56		Ba_2ZrYO_{6-d}
E	29.82	2.21	30.96	/		$Ba_{1-x}Ca_xZrO_{3-\delta}$
F	24.09	2.84	26.92	/		$Ba_{1-x}Ca_xZrO_{3-\delta}$
G	24.29	4.77	28.27	/		$Ba_{1-x}Ca_xZrO_{3-\delta}$
H	1.78	27.89	28.4	/		$CaZrO_3$

Table 2: The EDS results of points A, B and C in (Figure 5(a)) [34].

Postion	Mole Fraction, x/%			
	Ca	Zr	Ti	Ni
A	88.68	6.9	3.09	1.33
B	25.85	12.72	38.93	22.51
C	0.21	0.35	39.58	59.85

Conclusion:

Finally, to obtain high-quality titanium and titanium alloys, it is necessary to explore more novel melting processes, break the barriers of materials, physics, chemistry, mathematics and other disciplines, and integrate the knowledge of multiple disciplines. In addition, the traditional preparation process is still worthy of in-depth study, such as obtaining better refractories. To evaluate the practicality of a crucible, we must consider its corrosion resistance, durability, cost, high temperature stability, thermal shock resistance, hydration resistance and wettability to the melt. BaZrO3 is a kind of refractory material with great potential, but it still needs a long way to go to the standard of industrial mass production, such as choosing one or more better doping materials and the corresponding ratio, explore more detailed erosion mechanisms, establish corresponding thermodynamic models, and optimize related multiphase diagrams.

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