Issue VII, November 2024
e-ISSN 2707-9481
ISBN 978-601-80473-3-6
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https://doi.org/10.31643/2024.21

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Wetting and interaction of titanium melt with barium zirconate

Abstract: The paper presents the results of a study of the reaction interaction and the contact angle of wetting during contact of titanium melt with the surface of a barium zirconate substrate. It is shown that the titanium melts at 1720°C wets the barium zirconate substrate. The wetting process is considered, accompanied by gas evolution, penetration of the titanium melt through capillaries between $BaZrO_3$ particles and partial dissolution of the substrate. Upon completion of the spreading process, the contact angle of wetting of the $BaZrO_3$ substrate by the titanium melt is 18°. The high wettability of $BaZrO_3$ ceramics and its dissolution in the titanium melt does not allow its use as components of lining and molding materials for melting and casting of titanium alloys in cases where high requirements are imposed on the castings for chemical composition and, accordingly, mechanical properties.

Keywords: titanium, wetting, barium zirconate, interaction, alloys.

Introduction

Recent studies have made significant contributions to the understanding of material interactions and technological advancements in metallurgy. Panichkin et al. (2019) explored the interaction of titanium melt with refractory oxides of various metals, shedding light on the complex behaviors during alloy production, which can influence the properties of the final material. Similarly, Kenzhaliyev (2019) presented innovative technologies for improving the extraction of non-ferrous, precious, and rare earth metals, emphasizing the need for efficiency in metallurgical processes. In a more specialized area, Chukmanova et al. (2023) examined the use of ceramic molds based on yttrium oxide for casting titanium alloys, an approach that promises to enhance the precision and quality of castings in advanced material applications. Additionally, Panichkin and Kshibekova (2023) assessed how flux composition affects the removal of non-metallic inclusions in high-chromium cast iron, providing valuable insights into refining techniques aimed at improving the quality of iron alloys. These studies collectively highlight the ongoing developments in the fields of metallurgy and materials science.

Due to high specific strength and corrosion resistance, titanium and titanium alloys are widely used in various fields of technology. However, the volumes of production of titanium products are small due to high production costs associated not only with the increased cost of raw materials but also with the high cost of all stages of processing. The production of titanium alloy castings is in demand in chemical engineering, orthopedics and prosthetics in dentistry. Improving the quality of castings and reducing production costs play an important role in ensuring the competitiveness of products. Vacuum induction furnaces are the most accessible of the furnaces that provide the ability to melt titanium in a vacuum. Their use can significantly increase the scale of obtaining titanium castings. However, the high reactivity of Ti-based alloys makes it impossible to use traditional refractory and molding materials for lining induction furnaces and for obtaining casting molds (Panichkin et al., 2016). The development of refractory materials characterized by minimal interaction with titanium melts is necessary for the further development of foundry production in the titanium industry.

For many decades, studies have been conducted to find materials that are inert or relatively inert to titanium melts (Panichkin et al., 2016; Fashu et al., 2020; Kenzhaliyev et al., 2024; Li et al., 2010; Klotz et al., 2019; Zhang et al., 2006; Chen 2018; Zhu et al., 2002; Li et al., 2018). These studies examined the interaction of titanium melts with many simple and complex oxides, nitrides, carbides, and graphite. It was found that titanium melt interacts least actively with the oxides Y_2O_3, $CaZrO_3$, and $BaZrO_3$. This made it possible to propose using these compounds for lining induction furnaces and manufacturing crucibles for melting titanium alloys. However, ceramics made of Y_2O_3, despite the best resistance to titanium melts, are expensive and can only be used in low-tonnage production. Refractories and molding materials made of $CaZrO_3$, $BaZrO_3$ (Kenzhaliyev et al., 2024; Li et al., 2010; Klotz et al., 2019; Zhang et al., 2006; Chen et al., 2018; Zhang et al., 2018) are more economically attractive. However, as studies have shown (Mamayeva et al., 2022; Zhang et al., 2013), $CaZrO_3$, when in contact with titanium melt, still interacts and causes contamination of the titanium melt with zirconium and oxygen. This calls into question the prospects for using ceramics, lining and molding mixtures based on this compound in the titanium industry. The work describes the absence of a boundary reaction layer between a crucible made with $BaZrO_3$ alloyed with Y_2O_3 and a TiNi alloy (Zhang et al., 2013). The authors propose this material as a crucible coating or as part of $BaZrO_3/Al_2O_3$. Although the work by Chen et al. (2018) considers the interactions between $BaZrO_3$ crucibles and titanium melts, where it is shown that the dissolution of $BaZrO_3$ refractory in titanium melts led to crucible erosion and melt contamination, the degree of which increased with increasing Ti content in the melts.

To assess the prospects for using $BaZrO_3$ in titanium alloy casting, it is necessary to continue research on the interaction of this compound with titanium alloys. In particular, it is necessary to study the processes of reactive diffusion and wetting of the $BaZrO_3$ surface with titanium melt.

The works devoted to the general theory of wetting are extensive (Passerone et al., 2016; Zhu et al., 2002; Eustathopoulos 1998; Li et al., 2018; Barbosa et al., 2006; Lin et al., 1999). Wetting of ceramics by metal is determined by two types of interactions occurring at the interface, leading to non-reactive wetting and reactive wetting ((Mamayeva et al., 2022; Zhang et al., 2013; Kenzhaliyev, 2019)). Non-reactive wetting occurs in liquid/solid systems in which mass transfer across the interface is very limited and has little effect on the interfacial energy. Wetting involving chemical change and/or diffusion of chemicals across the interface is reactive wetting, which often occurs in metal/ceramics systems at high temperatures. However, only a small number of studies on interfacial phenomena and wettability of ceramics by titanium melts are reported in the literature.

The paper examines the processes of interaction of liquid titanium with zirconates and titanates of some alkaline earth metals (Kenzhaliyev et al., 2024). Characteristic reactions between ceramics and titanium melt during short-term contact are presented. The results of a study of the interaction of titanium melt with BaZrO3 and $SrZrO_3$ zirconates, as well as $SrTiO_3$ titanate under vacuum and inert atmosphere are presented. However, no studies were presented on determining the contact angle of titanium melt on these substrates, so there is a need to consider the wettability process with the measurement of the contact angle.

In this regard, the aim of this work is to consider the processes developing during contact of titanium melts with barium zirconate by the method of determining the contact angle of wetting and studying the transition zone.

Research Method

The synthesis of $BaZrO_3$ zirconate was carried out by the solid-phase method. The batch of barium oxide BaO and zirconium oxide ZrO_2 was subjected to joint-intensive milling and mixing in a mill. Then, tablets of ∅40 mm and 5 mm in height were obtained from the obtained mixed powders on a hydraulic press at a pressure of 40 MPa. These tablets were subjected to heat treatment at 1550-1670°C for 5 hours in a normal atmosphere in an RHTV 120-600/C 40 "Nabertherm" tubular furnace. The phase composition of the obtained ceramic tablets was studied on a D8 Advance X-ray diffractometer (BRUKER), the results are presented in Table 1.

Table 1. Phase composition of synthesized barium zirconate

Pattern #	Compound Name	Formula	S-Q
PDF 01-070-3667	Barium Zirconium Oxide	$Ba(ZrO_3)$	100%

To determine the parameters of wetting of ceramic substrates with titanium melt, an experimental setup was created in the metal science laboratory of JSC "IMOB" in Almaty (Figure 1). This setup ensures the heating of a ceramic substrate with a titanium alloy cylinder installed on its surface to a specified temperature, with a video recording of the process of spreading titanium melt over the surface of the ceramic sample in horizontal projection. The heating process occurs under high vacuum conditions, which is ensured by a two-stage vacuum pumping system. During the heating process, the melt temperature is recorded using a stationary infrared spectral ratio pyrometer Thermoscope-800-2S-VT1.

A cylinder of titanium alloy grade VT1-0 (Grade2) ∅ 10 mm and 5 mm high was installed in the centre of the BaZrO3 substrate. They were placed on a molybdenum tray in the furnace of the installation to determine the contact angle of wetting. After pumping out the installation chamber to a residual pressure of 3-5*10-3 Pa, the furnace was heated. At the moment of the beginning of titanium melting, the video recording was turned on, while the melt temperature was continuously recorded. After reaching the specified temperature, isothermal holding was carried out. Upon completion of the holding, the furnace heating was stopped and the sample was cooled under conditions of continuous pumping to 50-100°C.

When measuring the contact angle, still frames of a video of the melt-spreading process on the substrate were used. The contact angle measurements were performed using the Image J program. The structure of the contact zone of the melt and the ceramic substrate and the composition of the phases formed in it were studied using a Leica DM IRM optical inverted microscope and a JEOL JXA-8230 electron probe microanalyzer (Japan). These studies were performed on transverse sections.

Figure 1. External view of the installation for determining the contact angle under high vacuum conditions

Results and Discussion

Figure 2 shows the key stages of interaction between the titanium melt and the surface of the barium zirconate substrate after melting (Figure 2 a) and during holding at 1720 °C. As follows from the presented freeze frames, at the moment of melting, the titanium melt poorly wets the $BaZrO_3$ substrate, the contact angle is 105 °C. Upon reaching 1720 °C, the interaction of the melt with the substrate begins. At the initial stage, dynamic oscillation of the melt droplet is observed with a periodic increase in its size

(Figure 2 b, c). This indicates the release of a gas phase in its volume. The release of gas bubbles onto the melt surface causes partial splashing of the melt. At the same time, melt spreading also intensifies. Oscillation of the droplet causes a change in the contact angle in the range of 83-126 °C. After 20 seconds, the stage of intensive interaction and melt spreading is completed (Figure 2 d). The contact angle stabilizes at 18-20°. The dependence of the contact angle of wetting of the BaZrO3 substrate by the titanium melt at 1720°C on the contact time is shown in Figure 4.

a b c d

a - after melting; b - 1720 °C 18 s; c -1720 °C 22 s; d - 1720 °C 24-105 s

Figure 2. Still frames of the process of wetting the $BaZrO_3$ substrate with titanium melt

Figure 3. View of the sample after the experiment on the wettability of titanium melt on a $BaZrO_3$ substrate

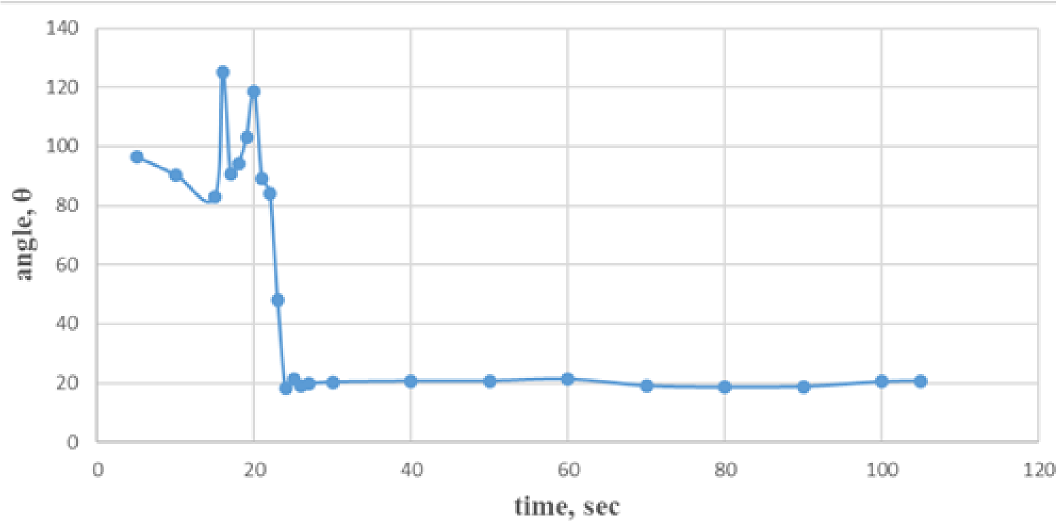
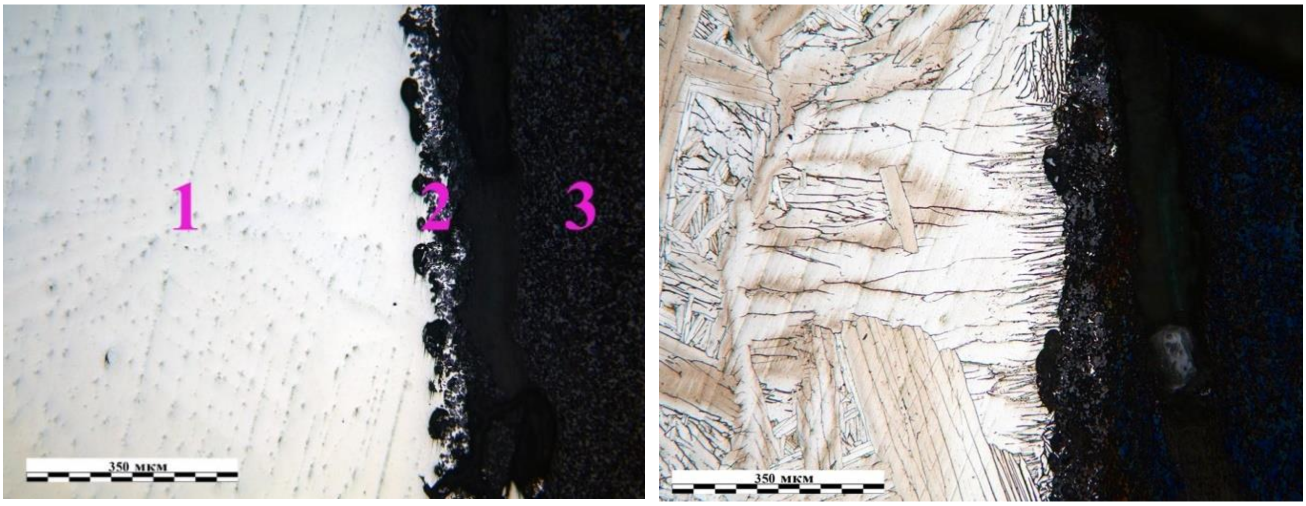


Figure 4. Dependence of the contact angle θ on time

Metallographic analysis showed that characteristic areas are revealed in the contact zone of titanium and $BaZrO_3$ ceramics (Figure 5 a): 1 - titanium, 2 - transition layer, 3 - ceramic zone impregnated with titanium melt. A crack formed at the boundary between the transition layer and the ceramic substrate, which is explained by the difference in the temperature coefficients of linear expansion of titanium and $BaZrO_3$. Titanium has a structure characteristic of β-titanium (Figure 5 b). A chain of pores is found in the transition layer, which indicates the formation of a gas phase during the reaction interaction. The width of this layer varies in different areas in the range of 70-120 µm. The layer is two-phase and is formed by discrete particles of a polyhedral shape in a metal matrix. The characteristic colour and shape of the particles allow us to conclude that the discrete particles are ceramic particles impregnated with the melt.



a b

Figure 5. Microstructure of the $BaZrO_3$+Grade2 contact zone before and after revealing the titanium structure (x150)

The study of the structure of the contact zone by scanning electron microscopy confirmed that in the transition layer between $BaZrO_3$ and titanium, as a result of physicochemical interaction, a ceramic layer impregnated with titanium melt is formed. EDS analysis of this section (Figure 6, points 5, 7, 8, 9 of Table 2) shows that the concentration of Zr, O, Ba, Ti in the ceramic particles corresponds to $BaZrO_3$. The analysis at point 6 shows that $BaZrO_3$ particles dissolve in the titanium melt without forming other intermediate phases. At the same time, at points 1, 2, 3 and 4, the concentration of barium, zirconium and oxygen in titanium decreases with distance from the reaction zone. Thus, at a distance of 130 µm from the reaction zone at point 1, oxygen and barium are not detected in the titanium composition. However, oxygen is detected in white layers between the branches of the dendrites of the solid solution of zirconium in titanium (point 4). This indicates that oxygen and barium in the form of a vapour-gas mixture are predominantly removed from the contact zone, which manifests itself in the form of pore formation and melt bubbling. However, some oxygen remains in the titanium and is displaced by the crystallization front during solidification.

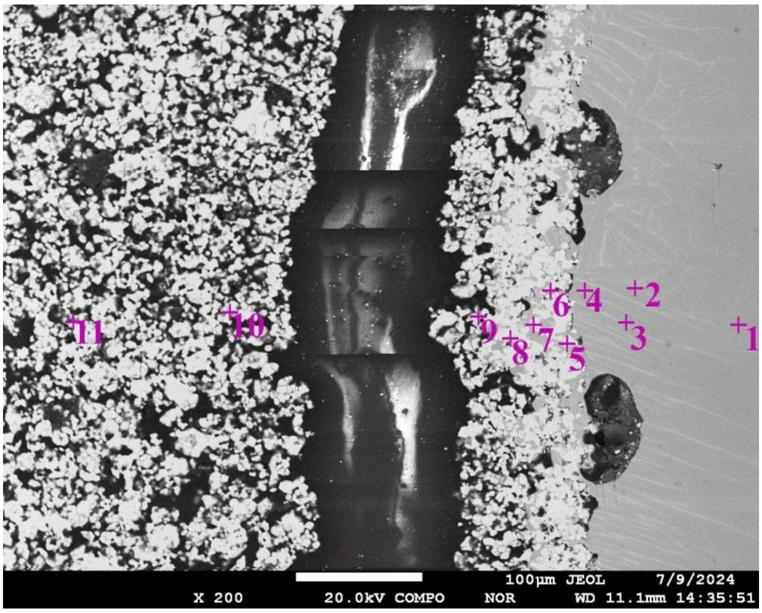


Figure 6. Structure of the transition layer formed between titanium melt and barium zirconate, EDS analysis points

Table 2. Results of microprobe analysis of the transition zone at the points indicated in Figure 6.

№	**Ti**	**Zr**	**O**	Ba
	mol%	**mol%**	**mol%**	**mol%**
1	97.98	2.02	-	-
2	91.35	8.65	-	-
3	81.80	9.48	-	7.42
4	52.94	7.08	39.58	-
5	-	20.76	60.91	17.6
6	13.95	15.87	56.95	13.23
7	1.30	19.31	61.70	17.69
8	-	18.95	64.87	16.18
9	0.97	20.13	62.37	16.53
10	-	16.47	70.80	12.73
11	-	13.20	78.87	7.93

Conclusions

Thus, the conducted studies indicate that the barium zirconate substrate at 1720 °C is well-wetted by the titanium melt. When the titanium melt contacts the $BaZrO_3$ substrate, the molten titanium penetrates through the channels between the $BaZrO_3$ particles under the action of capillary force and physical wetting. In this case, the surface of the particles dissolves. Zirconium and partially oxygen diffuse in the volume of the melt. Barium and partial oxygen evaporate at the interface, which causes the melt to bubble. Based on the results of the conducted studies, it can be said that the contact angle of wetting correlates with the reaction interaction of barium zirconate with titanium.

Thus, the established features of the interaction of titanium melt and barium zirconate, indicating the development of wetting and dissolution of the $BaZrO_3$ ceramics surface by the titanium melt, show that lining materials, crucibles and molding materials based on $BaZrO_3$ cannot be used for melting and casting titanium alloys in cases where high requirements are imposed on the castings for chemical composition and, accordingly, mechanical properties. A promising area may be the search for additives that reduce the interaction of BaZrO3 ceramics with titanium melts.

Acknowledgement. The research was carried out with the financial support of the science of the Republic of Kazakhstan within the framework of the program - BR18574018 "Creation of a theoretical base of technologies based on physicochemical studies of metal-containing systems under conditions of high-temperature and hydrochemical processes."

CRediT author statement: **A. Panichkin:** Conceptualization, Methodology, Software; **A. Uskenbaeva:** Supervision, Data curation, Writing draft preparation, Management, Conducting the research; **B**. **Kshibekova**: Conducting the research, Management; **Zh. Alibekov:** Providing resources, Conducting the research; **M. Chukmanova:** Providing resources, Conducting the research.

Cite this article: Panichkin, A.V., Uskenbaeva, A.M., Kshibekova, B., Alibekov, Zh., Chukmanova, M. (2024). Wetting and interaction of titanium melt with barium zirconate. *Challenges of Science*. Issue VII, pp. 145-151. https://doi.org/10.31643/2024.21

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