Study of Ti-Zr-Nb-Be filler metal interaction with silicon carbide based ceramics during brazing process

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Abstract. This work is devoted to an analysis of the composition of a silicon carbide based ceramic brazed seam as a result of its interaction with rapidly quenched titanium-zirconium-niobium-beryllium filler metal. Structural-phase studies based on EDX and EBSD analysis, mechanical shear tests, and microhardness measurements of brazed joints were carried out. It was shown that titanium, zirconium, and niobium silicides as well as particles of titanium carbosilicides and silicon carbides in the silicon matrix are formed in the brazed seam, probably because of the presence of free silicon in the base material, which leads to increasing joint microhardness and unstable shear strength results.

1. Introduction

Ultrafast solidification technology makes it possible to obtain flexible ribbons and powders from hard-deformed ingots that have a range of advantages over their crystalline counterparts: they have a uniform phase state throughout the volume, narrow melting and solidification intervals, and high adhesive and capillary activity. Rapidly quenched filler metals have proven themselves well for dissimilar material brazing [1] and for creating ceramic–ceramic and ceramic–metal joints that can withstand mechanical stresses without noticeable deterioration of their properties [2–4].

Silicon carbide has great technological importance in modern industries and applications in different areas due to its high chemical resistance and thermal stability. It shows promise for use as the basis of a composite material in generation IV thermal neutron reactors. The shells of fuel elements made of ceramic based on silicon carbide have a lower value of thermal neutron capture cross-section than classical zirconium alloys and also show increased radiation resistance when irradiated [5]. The application of silicon carbide based ceramic in pressurized-water reactors (PWRs) as fuel element cladding will provide a radical increase in the radiation safety of modern nuclear power plants in line with the concept of accident-tolerant nuclear fuel that is resistant to accidents with loss of coolant (LOCA) [6]. However, after some manufacturing methods, silicon carbide may contain additives that will greatly effect the fuel element shell operation and the brazing process itself. One such additive is free silicon, which often remains after silicon carbide reaction bonding processes [7,8]. In this regard, study of the brazing process in the presence of free silicon in silicon carbide is an urgent task.

Brazing of silicon carbide can be carried out with filler metals based on gold or silver with titanium additives [9,10]. Unfortunately, due to the high cost of gold and silver, it is promising to use filler metals based on titanium, for example, in Ref. [11], where silicon carbide was brazed using active...
solder Ti-24 at.% Ni with zirconium additives to reduce residual thermal stresses. Good results for the mechanical shear strength of brazed joints of Cf/6SiC composite were obtained in Ref. [12], where filler metal of the Ti-Zr-Be system was used. It was shown that a brazed seam consists of possible phases of carbides, silicides, and carbozirconides of titanium and zirconium, which has a high melting point. The presence of high-temperature melting point phases in the brazed seam has great importance because the LOCA accident temperature can rise up to 1200 °C [13]. The authors of Ref. [14] note that the most promising results for high-temperature applications of silicon carbide joints can be achieved with filler metals based on titanium.

The aim of this work is to study the interaction of Ti-40Zr-8.5Nb-1.5Be filler metal with silicon carbide ceramics containing free silicon during brazing, to analyse the structural-phase state of brazed joints, and to evaluate the mechanical characteristics.

2. Materials and Experimental Methods
Ingots of Ti-40Zr-8.5Nb-1.5Be (w.p.%) filler metal were produced by the argon-arc melting method in an MIFI-9 furnace from pure components: titanium and zirconium, NB1 alloy, and Ti-6Be ligature. The obtained ingots were used for filler metal ribbon production on Crystal-702 installation in a helium atmosphere. The fabricated filler metal tape had a thickness of 50 ± 10 μm and full melting temperature of 1280 °C.

As the main material in the work, samples from ceramics based on silicon carbide, in which the volume fraction of free silicon was 18.5% and the free porosity rate was 2%, were used. Silicon carbide ceramic samples for microstructural studies and mechanical tests were brazed in an ShVE-1.25/25 vacuum furnace with the use of Ti-40Zr-8.5Nb-1.5Be filler metal at a temperature of 1420 °C for holding times of 1, 5, and 20 min. in a vacuum at ~ 8 · 10⁻⁵ torr. Such a high brazing temperature was chosen in order to obtain the most stable and refractory phase composition in the brazed joints. After brazing, the joints were cooled at a rate of 5 °C/min. to a temperature of 600 °C and then cooled with a speed of furnace cooling.

Microstructure images of the silicon carbide ceramic brazed joints were obtained in the backscattered electron mode using a Carl Zeiss EVO 50 scanning electron microscope. Elemental analysis was performed by INCA X-Act EDX analyzer. The crystal lattice identification of the phases formed in the brazed seam was performed by an EBSD NORDLYS detector. The relative fraction of porosity in the brazed joint was estimated by ImageJ image processing software. The image obtained at a magnification of 100× was graphically processed and the relative fraction of pores was calculated by relation of the pore area to the area of the brazed seam. The Gibbs energy of the reactions during brazing was calculated in the HSC6 software package per 1 mol of interacting silicon/carbon/silicon carbide at a brazing temperature of 1420 °C.

The shear strength test of silicon carbide brazed joints obtained with Ti-40Zr-8.5Nb-1.5Be filler metal was carried out on a Quazar 50 testing machine with a traverse speed of 1 mm/min. The Vickers microhardness of the joint was measured on an HVS1000 machine with a load of 300 grams and a holding time of 30 sec.

3. Research results and discussion

3.1. Study of the structural-phase state of silicon carbide ceramic brazed joint obtained with Ti–40Zr–8.5Nb–1.5Be filler metal
The brazed joints of silicon carbide ceramics obtained with Ti-40Zr-8.5Nb-1.5Be filler metal are shown in Figure 1.

It is noted that in the brazed joint and main material of silicon carbide ceramic, pores were formed. The size and quantity of pores depend on the exposure time at the brazing temperature. The relative fraction of pores in the brazed joint is shown in Table 1. The brazed joint thickness was 50 μm for holding times of 1 and 5 min. and 80 μm for a holding time of 20 min.
Figure 1. Microstructure of silicon carbide ceramic brazed joints obtained with rapidly quenched filler metal Ti-40Zr-8.5Nb-1.5Be at a temperature of 1420 °C and brazing times of (a) 20 min, (b) 5 min, and (c) 1 min.

Table 1. Relative fraction of pores in silicon carbide ceramic brazed joints.

| Brazing mode               | Percentage porosity |
|----------------------------|---------------------|
| 1420 °C – 1 min.           | 18.0                |
| 1420 °C – 5 min.           | 10.6                |
| 1420 °C – 20 min.          | 9.7                 |

In Figure 2, a fragment of brazed seam is shown with the results of EDX and EBSD analysis, while Figure 3 shows an X-ray map of the whole joint.

Figure 2. EDX (a.p.% ) and EBSD microanalysis of silicon carbide ceramic brazed joints obtained with Ti-40Zr-8.5Nb-1.5Be filler metal and a brazing mode of 1420 °C for 20 min.
Figures 2 and 3 show that the brazed seam consists of a silicon matrix (diamond-type lattice) and inclusions of mainly silicides of titanium, zirconium, and niobium as well as silicon carbide particles smaller than 1 μm in size. The presence of some amount of carbon-rich phase-carbosilicides (possibly Ti₅SiC₂ or Ti₅SiC) in the interface of the brazed seam and the base material was also found.

According to the EBSD analysis, titanium-zirconium-niobium silicides crystallize in the hexagonal lattice corresponding to the NbSi₃ compound and have sizes from 1 to 30 μm. Titanium, zirconium, and niobium silicides (ZrSi₂, TiSi₂, NbSi₂) as well as titanium carbosilicides and pure silicon have high melting points (more than 1200 °C), which are suitable for high temperature applications. The formation of silicides with a silicon content of 66% and chemical formula of (Ti,Zr,Nb)Si₂ is probably caused by a large excess of silicon in the base material, since it was calculated that the formation of a silicide with a higher content of titanium or zirconium is more thermodynamically beneficial (1)–(4):

\[
\begin{align*}
\text{Ti} + 2\text{Si} & \rightarrow \text{TiSi}_2 & \Delta G = -79.3 \text{ kJ/mol (T = 1420 °C)} \\
5\text{Ti} + 3\text{Si} & \rightarrow 5\text{TiSi}_2 & \Delta G = -195.3 \text{ kJ/mol (T = 1420 °C)} \\
\text{Zr} + 2\text{Si} & \rightarrow \text{ZrSi}_2 & \Delta G = -70.3 \text{ kJ/mol (T = 1420 °C)} \\
5\text{Zr} + 3\text{Si} & \rightarrow 5\text{ZrSi}_2 & \Delta G = -187.5 \text{ kJ/mol (T = 1420 °C)}
\end{align*}
\]

The probable mechanism of (Ti,Zr,Nb)Si₂ formation consists in the following silicide formation reaction with formulas (5), (6) starting with reactions (2), (4):

\[
\begin{align*}
\text{Ti}_5\text{Si}_3 + 2\text{Si} & \rightarrow 5\text{TiSi} & \Delta G = -26.1 \text{ kJ/mol (T = 1420 °C)} \\
\text{TiSi}_2 + \text{Si} & \rightarrow 5\text{ZrSi}_2 & \Delta G = -31.0 \text{ kJ/mol (T = 1420 °C)}
\end{align*}
\]

Also the presence of an excess of free silicon in the brazed ceramic affects the phase composition of the brazed joint, as it was expected that during the interaction of filler metal with the silicon carbide, the formation of carbides will occur according to the possible formulas (7-8):

\[
\begin{align*}
\text{Ti} + \text{SiC} & \rightarrow \text{TiC} + \text{Si} & \Delta G = -105.6 \text{ kJ/mol (T = 1420 °C)} \\
\text{Zr} + \text{SiC} & \rightarrow \text{ZrC} + \text{Si} & \Delta G = -121.7 \text{ kJ/mol (T = 1420 °C)}
\end{align*}
\]

However, as shown in Ref. [12], titanium and zirconium carbides can be formed during silicon carbide brazing, but the base material should consist not of free silicon but of carbon, which makes possible the implementation of the reaction according to formulas (9) and (10):

\[
\begin{align*}
\text{Ti} + \text{C} & \rightarrow \text{TiC} & \Delta G = -163.4 \text{ kJ/mol (T = 1420 °C)} \\
\text{Zr} + \text{C} & \rightarrow \text{ZrC} & \Delta G = -179.5 \text{ kJ/mol (T = 1420 °C)}
\end{align*}
\]
Thus the obtained phase composition of the brazed seam can be primarily described by the interaction of filler metal with free silicon and the formation of mainly silicides, while the formation of carbides is less thermodynamically beneficial and is blocked by the lower Gibbs energy (11).

\[
\text{Ti} + 2\text{SiC} \rightarrow \text{TiSi}_2 + 2\text{C} \quad \Delta G = -21.5 \text{ kJ/mol (T = 1420 °C)} \quad (11)
\]

The small silicon carbide particles in the brazed seam are related to the good solubility of carbon in liquid silicon (the brazing temperature is higher than the melting point of silicon) and the complete absence of solubility in solid, which leads to the formation of silicon carbide particles during crystallization, while the porosity is probably associated with large areas of silicides-brittle inclusions in the brazed joint and their subsequent chipping from the silicon matrix of the brazed joint and the base material during sample preparation for the research.

3.2. Study of the silicon carbide ceramic joint mechanical characteristics obtained with Ti–40Zr–8.5Nb–1.5Be filler metal

The microhardness and shear strength results of silicon carbide ceramic brazed joint obtained with rapidly quenched Ti-40Zr-8.5Nb-1.5Be filler metal are shown in Table 2.

**Table 2.** Average microhardness and shear strength of silicon carbide ceramic brazed joints.

| Brazing mode     | Average microhardness of the brazed joint, GPa | Average value of brazed joint shear strength, MPa |
|------------------|-----------------------------------------------|-----------------------------------------------|
| 1420 °C – 1 min. | 12.2 ± 0.4                                    | 22.5 ± 9.3                                    |
| 1420 °C – 5 min. | 11.3 ± 0.4                                    | 37.8 ± 19.2                                   |
| 1420 °C – 20 min.| 12.5 ± 0.6                                    | 24.5 ± 9.9                                    |

The average microhardness of brazed joints ranged from 11.3 GPa (with a brazing holding time of 5 min.) to 12.5 GPa (with a holding time of 20 min.) due to the presence of hard particles of titanium, niobium silicides, titanium carbosilicides, and silicon carbides in the silicon matrix of the brazed joint.

According to the shear strength results (Table 2), the silicon carbide ceramic brazed joints have a shear strength of 22.5 (with a holding time of 1 min.) to 37.8 MPa (with a holding time of 5 min.). Large scatter in the shear strength results is connected with the high average microhardness as well as the presence of fragile silicon and silicide phases in the brazed seam.

**Conclusions**

An analysis of the interaction of Ti-40Zr-8.5Nb-1.5Be filler metal with silicon carbide ceramic consisting of free silicon during the brazing process was carried out. The study of the structural-phase state of brazed joints obtained at a temperature of 1420 °C and holding times of 1, 5, and 20 min. is presented. It is shown that the brazed joint consists of pure silicon with inclusions of titanium, zirconium, and niobium silicides as well as titanium carbosilicides and silicon carbides, due to the presence of free silicon in the base material. No formation of fusible inclusions was found in the compounds, but the resulting brazed joint has high microhardness due to the presence of fragile silicide inclusions in the silicon matrix, which leads to a large scatter in the shear strength results. Increasing the exposure time to 20 min. leads to a decrease in the porosity level with an increase in the thickness of the brazed joint from 50 to 80 μm.

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