Brazing Molybdenum and Graphite with a Titanium-Based Powder Filler Metal

Examined were the different filler metal powder application amounts per brazed area as well as the texture of the graphite side of the brazed joint

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ABSTRACT

A new method of brazing Mo-C joints for mechanical performance up to 1650°C was found. A Ti-40 Zr-8.5 Nb-1.5 Be powder filler metal was created for this brazing application, and its melting range and phase composition were found. The effects of different filler metal powder application amounts per brazed area and the texture of the graphite side of the brazed joint were studied. EDS microanalysis of the brazed joint was carried out and the connections were analyzed for shear strength and porosity. EDS analysis revealed Ti, Zr, and Nb carbides were present in the brazed joint. When the graphite surface was smooth, the most high-quality joints were obtained with a powder application of 0.5 g/cm^2. It was found that texturing the graphite surface with concentric notches increased the shear strength of the joints by 2.5×. The strongest brazed connection, in which the graphite surface was notched, was subjected to a remelting test. The braze was maintained when heated to a temperature of 1650°C, though the composition of the brazed joint changed, exhibiting a higher concentration of carbides near the tips of the notches.

KEYWORDS

• Brazing • Joining • Molybdenum • Graphite • Microstructure

Introduction

Production of x-ray tubes for computed tomography (CT) and angiography devices requires methods of anode component joining that can ensure reliable, long-term equipment operation. The anode of an x-ray tube consists of a molybdenum disk with a tungsten layer deposited on it by vapor deposition and a heat sink made from high-density graphite MPG-6. Because the anode operates at high temperatures and tangential loads induced by rapid rotation (9000 rev/min) to achieve high x-ray fluence rates, this Mo-C joint must be very high performance.

A known method of joining the molybdenum alloy TZM and high-density graphite is by contact-reactive brazing with zirconium as an interlayer filler metal (Ref. 1). Brazing is carried out at temperatures above the eutectic temperature of Mo-Zr (1550°C), and thermal stresses can occur during postbrazing cooling, affecting the reliability of the brazed joint. Therefore, using filler metals with lower melting points than zirconium is preferred for brazing molybdenum.

Filler metal alloys based on silver activated by titanium or zirconium are used for brazing carbon (Refs. 2–4) as well as filler alloys based on titanium or zirconium with nickel and a small amount of added copper (Refs. 5, 6). Previous research has demonstrated success in brazing molybdenum by using titanium (Ref. 7).

In this work, molybdenum and graphite MPG-6 were brazed with a Ti-40 Zr-8.5 Nb-1.5 Be filler metal powder containing a particle size less than 50 microns, ground down from a stock of rapidly quenched ribbons of the alloy. Many studies (Refs. 8, 9) have shown that the usage of rapidly quenched filler metals yields several advantages for achieving high-quality joints, such as high diffusion and capillary activity.

Experimental Setup and Procedure

Ingots of the filler metal composed with iodide titanium and zirconium, niobium NB1, and alloy Ti-6% Be were melted in an argon-arc furnace MEPHI-9 (USSR, 1980). The filler metal ribbon was produced by melt spinning in the Crystal-702 facility (USSR, 1975). An optical pyrometer Promin (USSR, 1980) was used to monitor the start and end temperatures of the alloy melting.

Then the filler metal ribbon was heat treated in a vacuum oven Xerion XRETORT600 (Germany, 2014). The resulting embrittled filler metal ribbon was ground in a planetary mill Pul-

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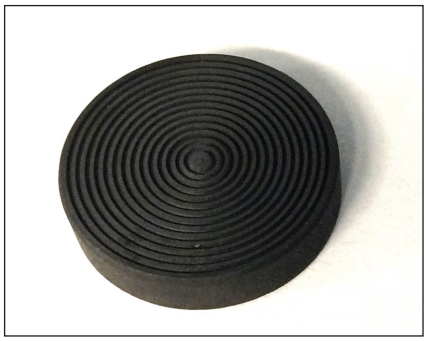


Fig. 1 — A graphite MPG-6 sample with the circular notch pattern.

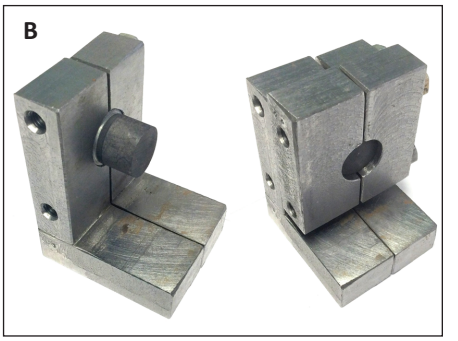


Fig. 2 — A — The samples before and after machining treatment; B — assembly for the mechanical shear tests.

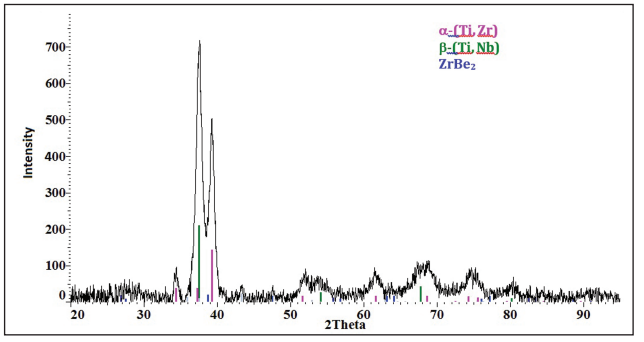
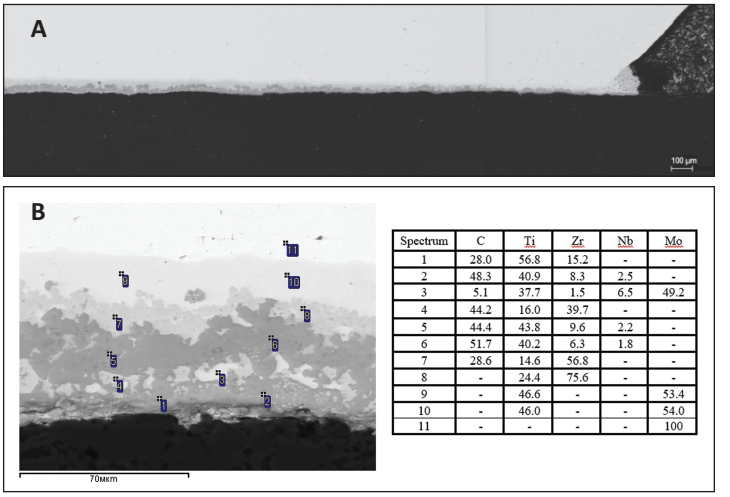


Fig. 3 — The x-ray diffraction spectrum of the Ti-40 Zr-8.5 Nb-1.5 Be filler metal.



Spectrum	C	Ti	Zr	Nb	Mo
1	28.0	56.8	15.2	-	-
2	48.3	40.9	8.3	2.5	-
3	5.1	37.7	1.5	6.5	49.2
4	44.2	16.0	39.7	-	-
5	44.4	43.8	9.6	2.2	-
6	51.7	40.2	6.3	1.8	-
7	28.6	14.6	56.8	-	-
8	-	24.4	75.6	-	-
9	-	46.6	-	-	53.4
10	-	46.0	-	-	54.0
11	-	-	-	-	100

Fig. 4 — The wedge-type, molybdenum (top side)-graphite MPG-6 (bottom side) joints (at-%) obtained by brazing with filler metal Ti-40 Zr-8.5 Nb-1.5 Be: A — Microstructure; B — microprobe EDS analysis.

verisette 5 (Germany, 1982), and the particles with a size less than 50 microns were isolated to be used as the brazing powder. An x-ray diffractometer, D8 DISCOVER (Bruker, Germany), using CuKα radiation was used to analyze the structural-phase composition of the filler metal powder Ti-40 Zr-8.5 Nb-1.5 Be. Identification of the phase composition was achieved using the Bruker AXS DIFFRAC.EVA version 3.0 software and international database ICDD PDF-2.

Two versions of the graphite disk samples for brazing were made: One offered no surface treatment and another was profiled with a pattern of concentric circles, as can be seen in Fig. 1.

This profiling was done with a lathe and resulted in a triangular radial cross section of the surface with a 0.5-mm pitch and 0.2-mm height. Such patterning increases the contact surface area of the filler metal with the graphite, which was hypothesized would increase the strength performance of the brazed Mo-C connection.

The graphite samples were heat treated in a vacuum of ~10^{-5} Torr for 2 h at 1200°C to degas prior to the brazing process. Brazing was done in a vacuum oven, Xerion XVAC1600 (Germany, 2014), at 1350°C for 30 min with a heating rate of 20°C/min. The samples were then cooled to 900°C at a rate of 20°C/min. At this point, the heaters shut off, and the chamber was allowed to cool to ambient temperature. The Mo-C with filler metal interlayer samples were arranged and secured in an assembly that provided a constant pressure of ~100 g/cm^2.

Microstructure studies were carried out with a Carl Zeiss EVO 50 (Germany, 2007) electron microscope, and the EDS microanalysis was done using INCA X-Act. All images obtained were backscattered electron images. Cylindrical molybdenum-graphite MPG-6 sample joints with diameters of 18 mm and overall heights of 5 mm were prepared for microstructural studies. Wedge-shaped molybdenum-graphite sample joints with angles of 1 deg were made to study joint clearance-dependent effects on the joint microstructure, such as capillary spreading of the melted filler metal, to cover the entire joint area. Shear strengths of the joints were measured with a Quazar-50 (Italy, 2013) containing a cross-head speed of 0.3 mm/min. Samples were 16 mm in diameter and 20 mm in height — Fig. 2A. Assembly for the shear strength test can also be seen — Fig. 2B.

Results and Discussion

Investigation of the Temperature Characteristics and Phase Composition of the Ti-40 Zr-8.5 Nb-1.5 Be Filler Metal

During production of the rapidly quenched filler metal Ti-40 Zr-8.5 Nb-1.5 Be ribbon, the alloy began to melt at a temperature of 1100°C and completely melted (liquidus) at 1280°C.

The diffraction spectrometry measurements of the powder form of the filler metal revealed these two major phases: α-phase with a hexagonal lattice structure and β-phase with a BCC lattice structure. The α-phase is a substitutional solid solution of Zr-Ti and has intermediate values of the lattice parameter between α-Ti and α-Zr. The β-phase is a solid solution of Nb in β-Ti. Also, the traces of the $ZrBe_2$ phase were found — Fig. 3.

After amorphization into ribbon form, annealing, and grinding into powder, beryllium forms a compound with zirconium: ZrBe2. This demonstrates that the alloy is a hypoeutectic, and melting of the filler metal begins with the eutectic reaction $ZrBe_2$ + (Ti, Zr), (Ti, Nb) → L.

The Microstructure of Brazed Joints Mo-Graphite MPG-6

Study of the brazed Mo-C joints revealed that quality depends on the amount of filler metal powder per unit bonded area.

Figure 4 shows the microstructure of the wedge-type, molybdenum-MPG-6 graphite connection. To determine the phase composition of the brazed joint, another EDS microanalysis was carried out at the joint section.

According to this microanalysis, carbon is found in sections 1, 2, 4, 5, 6, and 7 as labeled in Fig. 4. This indicates the presence of carbides Ti, Zr, and Nb. Spectrum 8 reveals a solid-solution phase of titanium and zirconium. Spectrums 9 and 10 reveal solid solutions of titanium in molybdenum. In Spectrum 3, a phase with high molybdenum content and low carbon content was detected. This phase is assumed to derive from a grain of molybdenum that, prior to brazing, was near the filler metal junction, and during brazing was isolated from the base metal by convective entrainment of the filler metal. As a result, it formed a composite brazed joint, including a

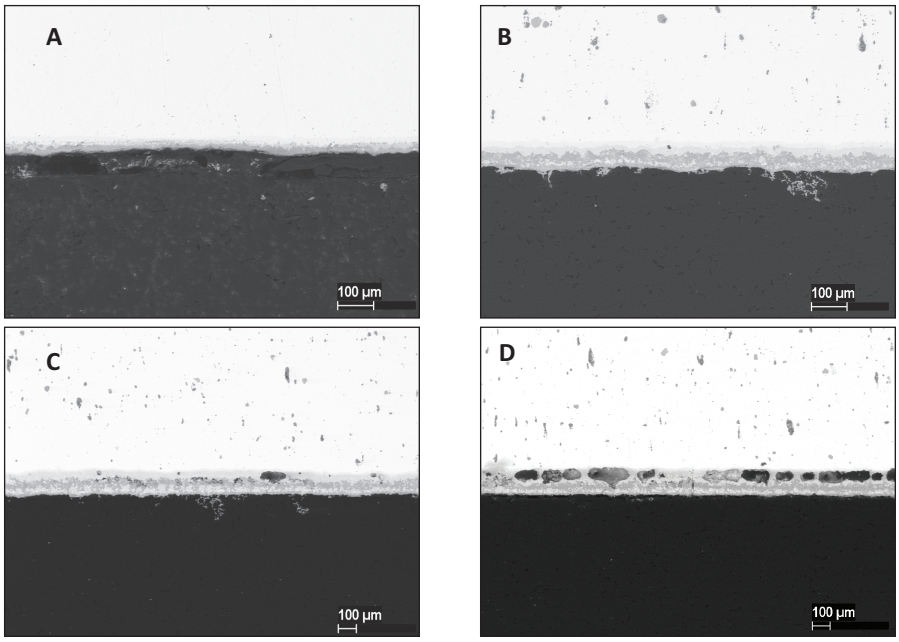


Fig. 5 — The microstructure of the brazed molybdenum (top side)-graphite MPG-6 (bottom side) joints without surface pretreatment at various application amounts of filler metal powder Ti-40 Zr-8.5 Nb-1.5 Be: A — 0.04 g/cm²; B — 0.05 g/cm²; C – 0.075 g/cm²; D – 0.1 g/cm². (The top side is graphite or molybdenum.)

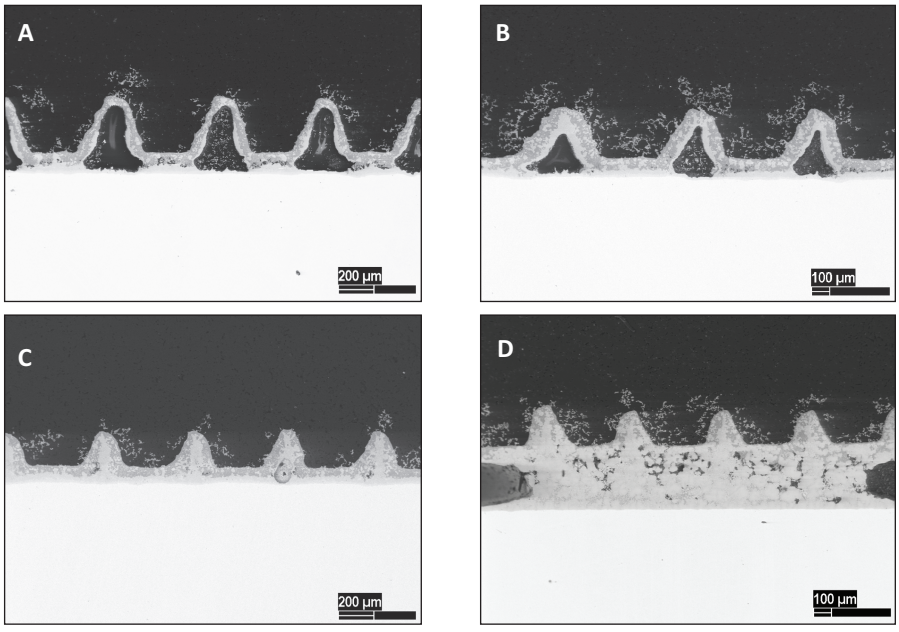


Fig. 6 — Scanning electron microscope images of brazed molybdenum (bottom side), MPG-6 graphite, with notching (top side) joints at various application amounts of the filler metal powder Ti-40 Zr-8.5 Nb-1.5 Be: A — 0.075 g/cm²; B — 0.1 g/cm²; C — 0.125 g/cm²; D — 0.15 g/cm².

Table 1 — Shear Strengths of the Brazed Molybdenum-MPG-6 Graphite Joints

	Graphite with Smooth Surface				Graphite with Notched Surface					
Failure Stress [MPa]	2.4	1.8	2.1	1.4	5.2	6.1	7.5	5.3	7.5	7.4
Average [MPa]	1.9 ± 0.4				6.5 ± 1.1					

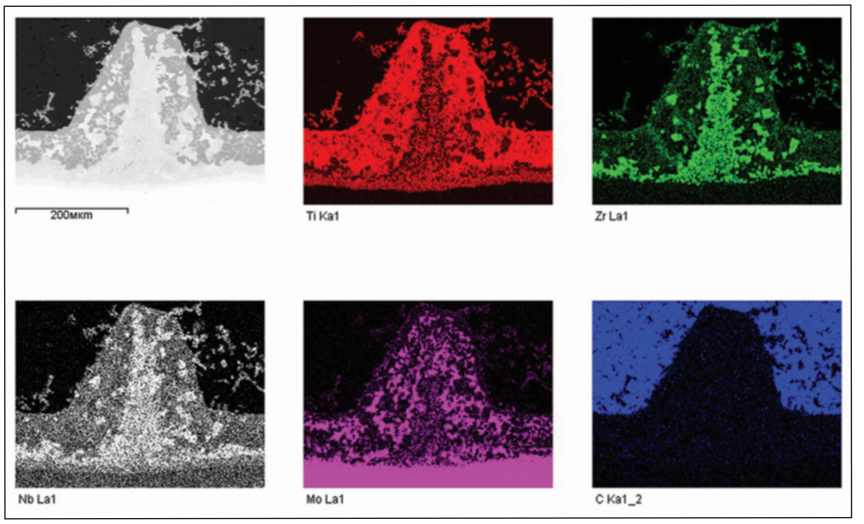


Fig. 7 — X-ray mapping of the brazed molybdenum-MPG-6 graphite (with notching) joint, at the Ti-40 Zr-8.5 Nb-1.5 Be filler metal powder application of 0.125 g/cm².

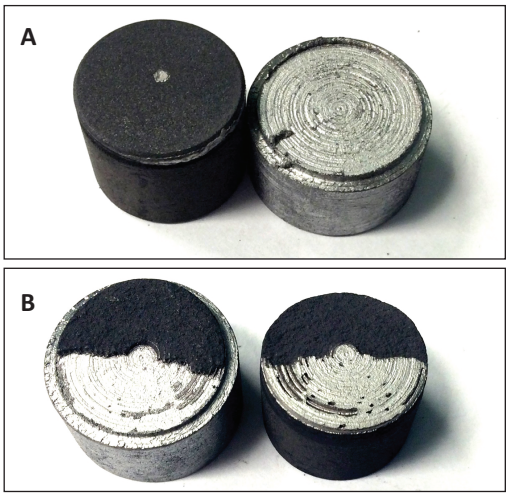


Fig. 8 — Molybdenum-MPG-6 graphite joint samples after fracture: A — Smooth surfaced graphite; B — notched surface graphite.

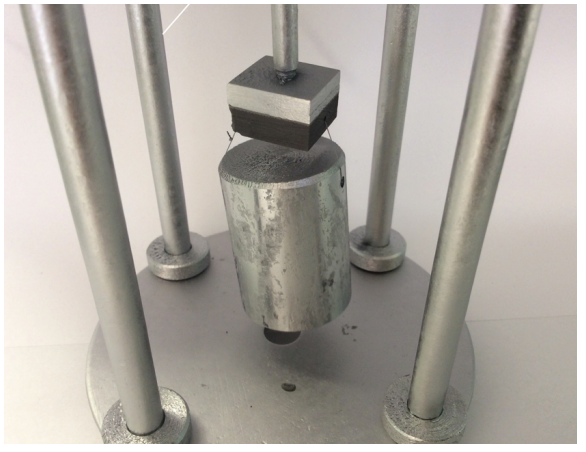


Fig. 9 — Equipment for separating the brazed joints under the load at high temperature.

mixture of the carbides titanium, zirconium, and niobium with the individual molybdenum-titanium grains.

It was found that an increase in the thickness of the filler metal increases the thickness of the carbide layer while the thickness of the Ti-Mo solid solution remains constant, in the range of 20–30 micrometers.

Figure 5 shows the microstructure of the brazed molybdenum-graphite MPG-6 joints without surface treatment with various application amounts of the filler metal powder per surface area.

The powder dose of 0.04 g/cm² allowed a tangential crack along the border of the brazed joint on the graphite side and large areas without a brazed connection. At 0.075 g/cm² and 0.1 g/m² doses of powder, the thicknesses of the brazed joints increased, but the quality of the joints decreased as porosity increased — Fig. 5C, D. The optimal application of filler metal powder was 0.5 g/cm², which created a high-quality brazed joint with a 50–60-micron-thick carbide layer and 20-micron-thick layer of a solid solution of molybdenum-titanium.

To improve the shear strength of the brazed joints, the surfaces of the graphite samples were profiled with concentric triangular notches 200 microns tall — Fig. 6.

The optimal filler metal powder application amount was 0.125 g/cm², which resulted in a high-quality, nonporous joint. Brazing with powder application amounts of 0.075 and 0.1 g/cm² resulted in porosity near the tips of the notches. The application amount of 0.15 g/cm² resulted in an uneven distribution of the filler metal throughout the thickness of the brazed joint.

According to the microanalysis mapping results, the brazed joint on the graphite side consists mostly of titanium carbides, and the middle of the joint is dominated by zirconium and niobium carbides — Fig. 7. Additionally, there are many fine molybdenum-titanium grains dispersed among these carbides.

Mechanical Testing of the Brazed Molybdenum-MPG-6 Graphite Joints

Tensile strength measurements were performed on four samples of molybdenum–graphite (smooth-surfaced) joints with a filler metal application of 0.05 g/cm² and six samples of molybdenum–graphite (notched) with a filler metal application of 0.125 g/cm². The results are shown in Table 1.

Preparing the graphite surface with the 200-micron notches increased the bond strength by more than 2.5×. Failure of the samples brazed with smooth-surfaced graphite occurred at the joint between the graphite and carbides as shown in Fig. 8A. The samples from the notched-graphite group failed in the form of cracking in graphite near the brazed joint as shown in Fig. 8B.

Assessment of the Stability of the Brazed Molybdenum-MPG-6 Graphite Joint to Debrazing and Microstructure Changing

The equipment shown in Fig. 9 was designed and constructed to test the ability of the brazed molybdenum-graphite joint to be separated under the load at 1500°C for an exposure time of 5 min. The brazed area of the joint was ~2.8 cm².

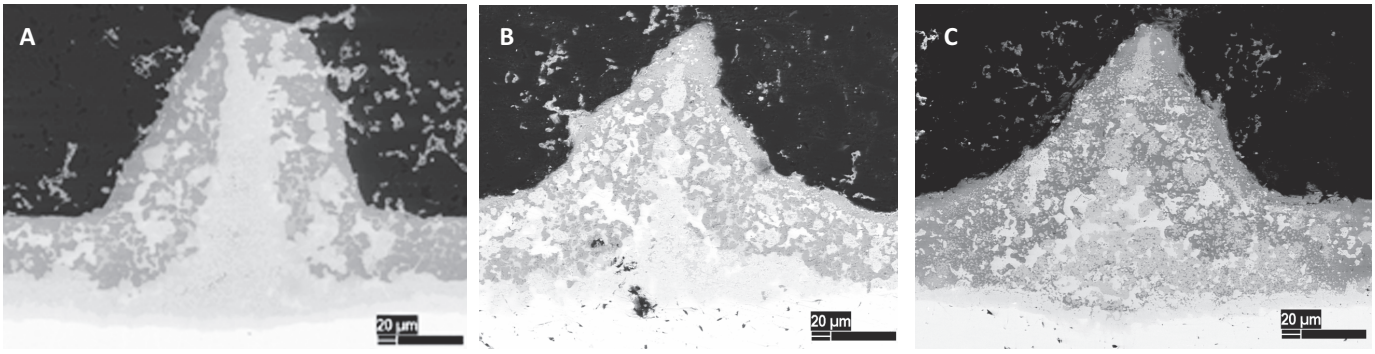


Fig. 10 — The microstructure of the brazed molybdenum (bottom side)-graphite MPG-6 (top side) joint, during the following: A — Before and B — after heat treatment at 1500°C for 5 min; C — after heat treatment at 1500°C (5 min) and then 1650°C for 5 min.

The joint was resistant to separation and withstood a static load of 100 g/cm^2. However, after heating the sample to 1500°C for 5 min, the microstructure of the brazed connection changed significantly, exhibiting a higher concentration of carbides due to the dissolution of graphite along the tops of the notches — Fig. 10A, B. Further, the sample was heated to 1650°C for 5 min, and the joint maintained integrity. Figure 10C shows the joint notch after heating to 1500°C and subsequently 1650°C, which resulted in fragmenting of the previously uniform zirconium carbide areas.

Conclusions

A Ti-40 Zr-8.5 Nb-1.5 Be filler metal was designed for brazing molybdenum to graphite MPG-6. The main phases of the filler metal are a solid solution of titanium in α-Zr and niobium in β-Ti. There is the additional presence of $ZrBe_2$-zirconium beryllide.

The filler metal begins to melt at 1100°C and completes melting at 1280°C. The brazing process involved heating to 1350°C at a rate of 20°C/min and holding for 30 min before cooling to 900°C at 20°C/min. Then the samples were cooled in a vacuum furnace at 10^{-5} Torr.

A textured graphite surface was compared to a smooth graphite surface to test for the effect on joint strength. The surface pattern consisted of concentric triangular notches with heights of 200 microns with an apex angle being approximately 120 deg. According to microstructure studies of the brazed joints, the optimal filler metal powder amount per unit brazing area was 0.05 g/cm^2 for smooth-surfaced graphite and 0.125 g/cm^2 for graphite with concentric triangular notches.

The brazed joint compositions are dominated by carbides of titanium, zirconium, and niobium with grains of solid solution Mo-Ti (Mo-38% Ti, at-%).

Shear strength tests of the brazed joints demonstrated the strength of the molybdenum-graphite joints with concentric triangular notches outperformed the smooth-surfaced graphite joints by more than 2.5×. The resulting connections are stable at 1650°C. However, it should be known that heating the samples to this temperature caused changes in phase composition, specifically an increase in carbides.

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