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PRESSURE BONDING MOLYBDENUM ALLOY (TZM) TO REACTION-BONDED SILICON NITRIDE

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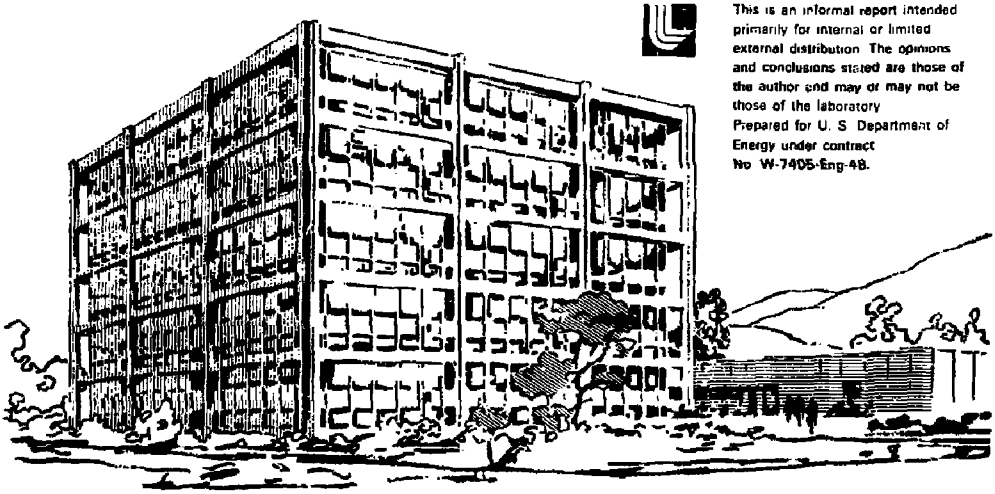

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ABSTRACT

Topping cycles could boost the energy efficiencies of a variety of systems by using what is now waste heat. One such topping cycle uses a ceramic helical expander and would require that a reaction-bonded silicon nitride (RBSN) rotor be bonded to a shaft of TZM (Mo-0.5 wt% Ti-0.08 wt% Zr). Coupon studies show that TZM can be bonded to RBSN at 1300°C and 69 MPa if there is an interlayer of $MoSi_2$. A layer of finely ground (10 μm) $MoSi_2$ facilitates bond formation and provides a thicker bond interface. The hardness and grain structure of the TZM and RBSN were not affected by the temperature and pressure required to bond the coupons.

INTRODUCTION

The high-temperature topping cycle concept has the potential to increase energy efficiency by as much as 50% for existing power stations. Fossil fuel systems, electrical conversion processes, and nuclear reactors are between 34 and 40% efficient; topping cycles are expected to increase efficiencies to 50 to 60%.[1] The topping cycle increases efficiency by using what is now waste heat. Energy demands in the United States are continuously on the rise. The available energy could be increased ~ 50% by modifying existing facilities with topping cycles.

The 50 to 60% potential requires ceramic components that will withstand high temperatures. Our specific topping-cycle design involves reaction-bonded silicon nitride (RBSN) helical rotors and housing components (Fig. 1). Silicon nitride was chosen after tests of ten commercial ceramic candidates.[2] Thermal shock resistance, oxidation resistance, thermal creep resistance, environmental testing, and fabrication properties dictated the selection of RBSN.[3]

The helical rotor design was found to be superior to conventional turbine designs for ceramic components.[4] The shaft through the rotor (Fig.1) demanded refractory stiffness, axial strength, and a good thermal expansion match to the RBSN. Molybdenum-0.5 wt% Ti-0.08 wt% Zr (TZM) was

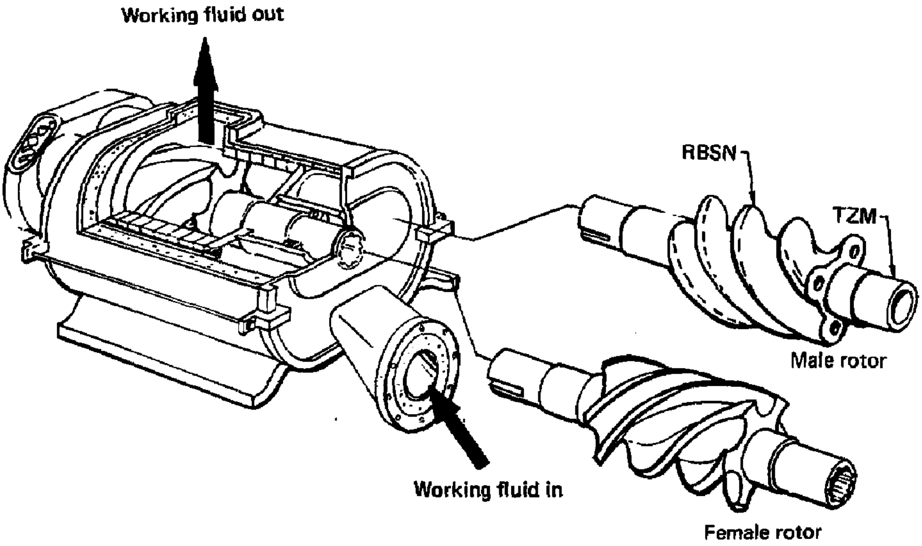

Fig. 1. A ceramic helical-rotor expander.

selected for initial bonding studies since it showed strengths of 480 MPa at the maximum operating temperature (1000°C) and a thermal expansion compatible with silicon nitride. The bonding area between the shaft and the rotor must withstand temperatures of 1000°C and stresses up to 240 MPa (Ref. 5).

We have been able to find practical conditions for forming a bond between TZM and RBSN that meets the performance requirements.

LITERATURE SURVEY

Two basic theories explain the adherence of ceramics to metals. According to King, Tripp, and Duckworth,[6] adherence can be attributed to either chemical bonds or to mechanical keying of the ceramic to a roughened base metal. Actually a combination of these two seems to create the strongest bond. According to Pask and Fulrath,[7] good adherence requires the development and maintenance of a strong chemical bond at the interface. Theoretical strengths of elements or compounds with chemical bonds have been calculated to be more than 7 GPa. The maximum strength of a mechanical bond is generally only about 34 MPa.

There are several requirements for good bonding between a ceramic and a metal. One requirement is that chemical bonds form between the base metal and some of the metallic ions in the ceramic.[6] Another requirement is that the ceramic, at the interface, be saturated with an oxide of the metal and this oxide not be reduced by the metal.[8] If a heavy oxide scale develops on the metal during the early stages of firing, it must be removed before bonding is attempted.[6] The metal surface can also be roughened to promote mechanical adherence.[9] Surface roughness, although not essential for excellent adherence, may improve the apparent adherence when the chemical bond between the ceramic and the metal is relatively weak.[8]

Bonding between metal and ceramic can be promoted by liquid-phase sintering aids. For good bonding, a liquid phase (that wets the bonding surfaces) must be developed at the interface. When a piece of metal is placed in a furnace and heated in an air atmosphere, an oxide layer forms on the exposed surfaces of the metal. The thickness of the layer generally increases as the temperature rises. Once the liquid phase seals off the metal surface from the air, the oxidation of the metal is temporarily stopped. The liquid phase must wet the oxide layer on the metal to achieve a strong bond. Preliminary studies can be made to establish the degree of wetting between a liquid phase and an oxide layer. From such studies, the surface energies of the components in the controlled environment can be calculated.[10] Gases absorbed on the surface affect these interfacial energies, primarily the surface energy of the metal and the interfacial energy between metal and ceramic. Optimum bonds are achieved by controlling the environment and surface compositions during this wetting process.

It is important to point out that every combination of metal and ceramic has required some empirically determined differences in treatment to develop adherence. It may be possible that many of the previously mentioned requirements may not apply in a particular instance. However, an oxide film plays an important role in most versions of the chemical theory. The oxide film is attached to both the metal and the ceramic, and forms a transition zone between the two materials.[6] According to Borom,[11] in certain cases no ceramic-metal bond is produced when an initial oxide layer is absent. Another requirement common to many bonds is the necessity for a good match of thermal coefficients of expansion between the ceramic and metal.[6,8,11] Another way of viewing chemical bonding is that there must be a balance of bond energies across the transition zone at the interface between metal and ceramic. This balance of bond energies is achieved when thermodynamic equilibrium exists at the interface or transition zone. Any two phases that are compatible or in thermodynamic equilibrium can form a chemical bond or a balance of bond energies at their interface.[12]

To gain the additional benefit of mechanical bonding there must be a rough ceramic-metal interface. The differences in methods to achieve this type of bond arise mainly in the manner in which roughness is produced. One particular approach is based on the precipitation of a metallic phase from the metal. Electrolytic roughening of the base metal is another approach.[6] In either case, wetting is required (which requires oxygen at the interface) and the result is an interlocking ceramic-metal structure.

Other evidence indicates that the roughness of the interface does not completely account for adherence. Poor adherence has been observed on very rough interfaces and fairly good adherence has been obtained without surface roughening.[6]

In conclusion, the literature includes several articles dealing with reactions between molybdenum and silica,[13] high-pressure bonding between several metals and ceramics,[14] a look at molybdenum disilicide and its reactions with metals,[15] and several other informative articles.[16,17,18] No information on the direct or indirect bonding of RBSN to a refractory metal like TZM has been previously published.

EXPERIMENTAL PROCEDURE

Specimen Preparation

An 11.11-mm (7/16 in.) diam rod of TZM was cut into right circular cylinders 6.35 mm (1/4 in.) thick. The surfaces of the metal were smoothed on a silicon carbide grinder. A solution of nitric and sulfuric acids removed organic films and excessive oxide layers from these surfaces. A low-speed diamond saw was used to cut pieces 3 × 3 × 5 mm (1/8 × 3/16 × 1/8 in.) of RBSN from a bar supplied by Associated Engineering Development (A.E.D.) of Rugby, England.

An intermediate layer of $MoSi_2$ was applied in an acetone slurry. This $MoSi_2$, which was supplied by Sylvania, was previously ground in a tungsten carbide ball mill 48 h, to a particle size of less than 10 μm. The RBSN was coated with a relatively uniform layer of the slurry and the flat face of the TZM cylinder was placed over the slurry and pressed to form a "sandwich".

Thicker $MoSi_2$ interfaces were prepared with hot-pressed $MoSi_2$ disks. A 60% dense pellet of $MoSi_2$ was hot pressed at 1700°C and 20 MPa. A graphite die (12.7-mm 1/2 in.) in the resistance-heated hot press made a 12.7-mm (1/2 in.) long pellet. Disks (0.51, 0.38, and 0.30 mm thick) were cut from the pellet with a slow-speed diamond saw. Sandwiches were made with the 0.51-mm (20 mil) disks surrounded by the slurry and packed between the RBSN and the TZM. In the first experiment, the RBSN surface was not cleaned. In the second experiment, the outer layer of RBSN was removed. In the third case, no $MoSi_2$ slurry was used around the $MoSi_2$ disk, and in the fourth trial, only the $MoSi_2$ slurry was used as the intermediate layer with cleaned surfaces.

Bonding

In several early experiments, bonding was attempted in a vacuum furnace with no pressure applied perpendicular to the interfaces. Under those conditions, there was no bond formation up to 1400°C, even after several hours. Higher temperatures were not attempted because of their adverse effect on TZM (see Discussion). Failure to bond indicated the need for pressure bonding at elevated temperatures ($\leq$ 1400°C). Parts were pressure bonded in a resistance-heated graphite-die hot press. The combination of a thermocouple and an optical pyrometer was used to monitor the temperature, and a hydraulic pump was used to apply the pressure to the graphite punches in the die. Dies of 12.7 to 25.4 mm (1/2 to 1 in.) inside diameter gave sufficient space for pressure bonding the coupons. Each heating cycle consisted of a selected temperature held for 15 min., with heating and cooling at 50°C/min. Pressure was applied during heating at around 1000°C and released during cooling at about 800°C.

Microstructure Determination

Metallographic examination of the bonding area provided a better understanding of the bonding mechanisms. A diamond saw was used to cut cross sections of the bonded coupons for metallographic examination. Cross sections of as-received TZM were also prepared for comparison with the TZM exposed to pressure bonding. Cold mounting epoxy was used to hold each cross section for grinding, polishing, and etching. Surfaces were examined with the light microscope and photomicrographs were taken of selected areas before and after etching. The etchant consisted of 81% lactic acid, 16% nitric acid, and 3% hydrofluoric acid applied for 10 min.

To determine the effects of heat treating on the hardness of the metal, a Leitz microhardness tester was used to indent several samples of TZM. Vickers diamond indentations were made on as-received TZM, as well as on TZM heated from 1300 to 1400°C. Hardness values (at 100-and 200-g loads) were determined parallel and perpendicular to the rolling direction.

RESULTS AND DISCUSSION

Bonding must be achieved at a temperature below 1300°C to avoid recrystallization and the corresponding loss of strength in TZM. Bonding below 1400°C can be accomplished by placing an interlayer of $MoSi_2$ between TZM and RBSN. By grinding the $MoSi_2$ powder and applying it to the RBSN as a slurry, penetration of the open pores was possible. The RBSN is a relatively porous (10 - 2 [illegible] material. Penetration was greater when finer $MoSi_2$ particles were used. With a thin ($\leq$ 0.1 mm) layer of $MoSi_2$, the bonded coupon fractured through the RBSN when cooled because of the difference in thermal expansion between the RBSN and the TZM. Failure through the RBSN indicated that the bond was stronger than the RBSN. When we increased the thickness of $MoSi_2$ (0.2 - 0.3 mm), the RBSN coupon remained intact.

The use of the hot-pressed $MoSi_2$ disks added to the thickness and decreased the stresses at the interface. Disks as thin as 0.30 mm (12 mils) were sufficient. The application of the $MoSi_2$ slurry coating on both faces of the $MoSi_2$ disk was found to be necessary.

Photomicrographs taken of the bonding interface (Fig. 2) show a thin bonding layer appeared between the TZM and the $MoSo_2$ slurry coating. The photomicrograph of the TZM bonded to the $MoSi_2$ disk where no slurry was used (Fig. 3), shows bonding occurred only along contact points at the surface. The $MoSi_2$ disk was 60% dense, so $\leq$ 60% of the surface of the TZM was in contact with the $MoSi_2$. In contrast with the bond interface present where the slurry was applied (Fig. 4) a continuous bond interface existed. The thick, bonded interface that results can resist the thermal expansion differences.

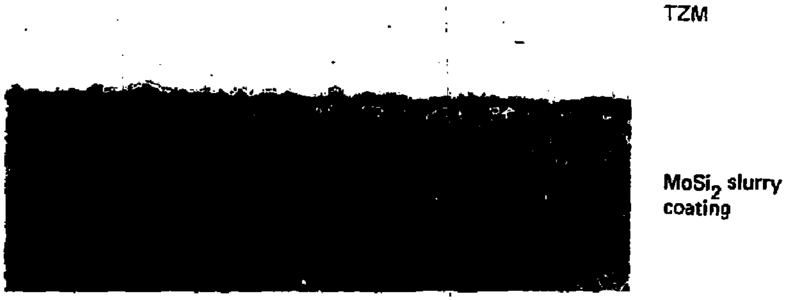

Fig. 2. Bonding interface between TZM and slurry-coated $MoSi_2$.

Fig. 3. Bonding interface between TZM and a 60% dense $MoSi_2$ disk.

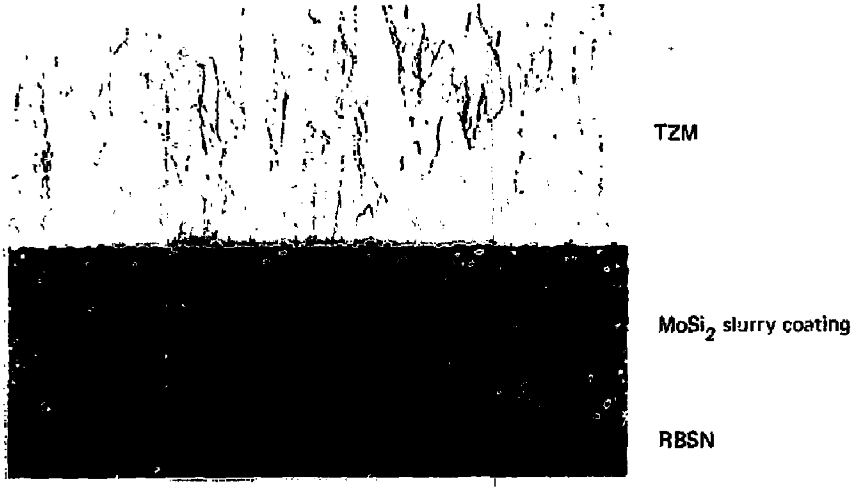

Fig . Bonding interface between TZM and slurry coated $MoSi_2$ after etching.

Bonding occurred over a range of temperatures. For each temperature there was a corresponding pressure that had to be applied perpendicularly to the layered coupons to achieve a bond within a reasonable time ($\leq$ 4 h). The relationship between temperature and pressures is plotted in Fig. 5. At low temperatures, high pressures are required for bonding; fabrication processes at these conditions are not practical. At temperatures above 1300°C, the rate of recrystallization of the TZM becomes the limiting factor.

In the photomicrograph of the unetched sample heated to 1300°C (Fig. 2), the $MoSi_2$ is almost at full density. In the sample etched to bring out the grain structure of the TZM, the etchant had severly attacked the $MoSi_2$ (Fig. 4). The grain structure of the bonded TZM appeared similar to the as-received TZM. If any recrystallization of the TZM had occurred at 1300°C, it was not evident from the microstructure (see Table 1).

Table 1. Vickers microhardness values on TZM samples in various conditions.

Condition of TZM	Indentation load, g	Average DPH value
As-received	100	298
Pressure bonded at 1300°C	100	297
Pressure bonded at 1400°C	100	190
At 10 μm from the 1300°C pressure-bonded interface	25	404
Near 100 μm from the 1300C pressure-bonded interface	25	315

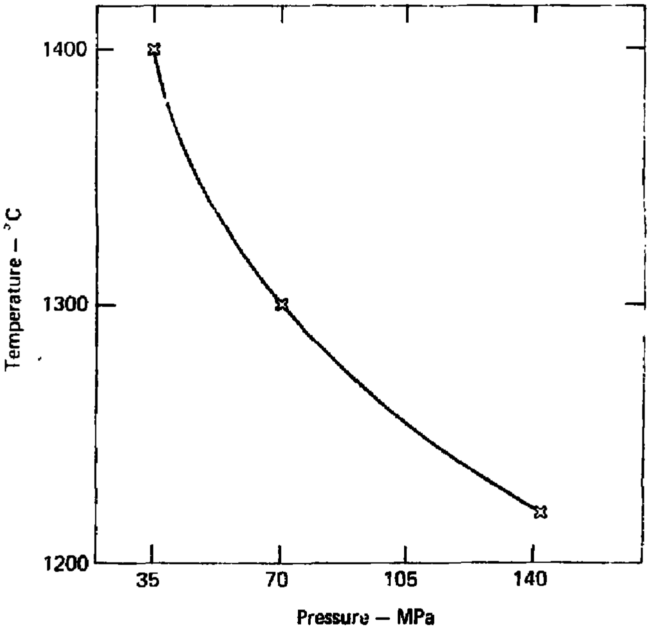

Fig. 5. Conditions under which TZM can be bonded to RBSN in less than 4 h and with a bond strength greater than the strength of RBSN.

The microhardness of the TZM heated to 1300°C showed no significant difference from the microhardness of the as-received TZM. With a 100-g load, a Vickers diamond indentation made perpendicular and parallel to the rolling direction had an average Vickers microhardness of 298 in the as-received TZM. In the sample heat treated to 1300°C, an average hardness of 297 was measured. However, in the TZM that was heated to 1400°C, an average value of only 190 was found. Several Vickers indentations (25-g load) were made in the TZM near ($\sim$10 μm) the bonded interface to get an average value of 404. Further away (>100 μm) from the interface using the same conditions, an average value of 315 was measured. The microhardness of the metal had increased along the bonded interface as expected. No such increase in surface hardness was detected on an as-received TZM specimen.

From the photomicrographs taken of the RBSN – $MoSi_2$ interface (Fig. 6), there appears to be very complete contact of the $MoSi_2$ to the RBSN surface structure. No reaction layer was detected at this interface, although a chemical as well as mechanical bond is expected.

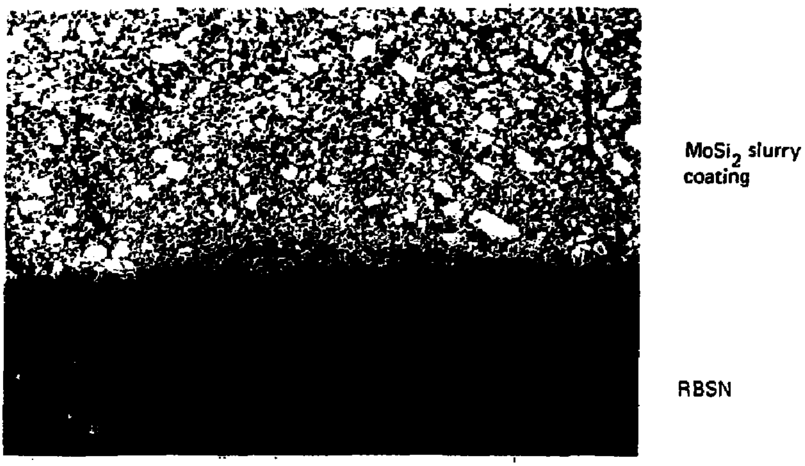

Fig. 6. The bonded interface between RBSN and slurry-coated $MoSi_2$.

CONCLUSIONS

(1) TZM can be bonded to RBSN below 1400°C and 137 MPa with the aid of an intermediate bonding layer of $MoSi_2$.

(2) The best temperature and pressure for bonding is 1300°C and 69 MPa

(3) For the best bonding, the TZM surface should be free of oxide layers and organic films.

(4) The properties of TZM are not significantly affected by pressure bonding at 1300°C. Slightly higher microhardness values were obtained near (100 ≤ μm) the bond interface.

(5) To ensure that the difference in thermal expansion between the RBSN and the TZM does not cause failure during thermal cycling, the $MoSi_2$ layer should be between 0.2 and 0.3 mm thick.

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