Compatibility of Brazed Joints With Potassium and Vacuum

When tested at 1500F for joining refractory metals, brazing filler metal Ti-28V-4 Be performs satisfactorily and shows good compatibility with potassium and vacuum

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ABSTRACT. Approximately one dozen of the most promising brazing filler metals developed at Oak Ridge National Laboratory for joining refractory metals were examined for compatibility with potassium and vacuum. These compositions have shown good wettability and flow characteristics and their strength and aging effects have been previously studied. This paper investigates the environmental effects of high vacuum (< 5 x 10^-8 torr) and exposure to the corrosive media of an alkali metal, potassium, in both the liquid and vapor states.

Eight filler metals from the V-Ta-Nb and the V-Ta-Ti systems with brazing temperatures in excess of 3200 F were tested at 1700 F for 1000 hr. All exhibited excellent corrosion resistance to the boiling liquid potassium and vapor environments. No metallographically detectable corrosion of the brazes was observed in either the brazing filler metal or at the filler metal-base metal interfaces. These brazes also withstood exposure to vacuum and no observable evidence of volatilization was found.

Five lower melting brazing filler metals were tested for 1000 hr. at 1500 F. Two of these (Ti—28 wt % V—4 wt % Be and Zr—19 wt % Nb—6 wt % Be) exhibited very good resistance to potassium, both liquid and vapor. No evidence of corrosion was apparent in the brazes or at the braze metal-base metal interfaces. The Ti-V-Be joint was also unaffected by the high vacuum exposure; however, the Zr-Nb-Be brazed joints showed evidence of possible loss of a constituent.

The resistance of the Ti—40 wt % Zr—15 wt % Fe filler metal to all of these environments is questionable. Evidence was found that suggests that constituents have been lost from the braze after testing in all environments.

The Zr—48 wt % Ti—4 wt % Be and Zr—46 wt % Ti—4 wt % V filler metals were not able to withstand 1500 F exposure for 1000 hr. Exposure to liquid or vapor potassium resulted in portions of the filler metal being removed. Examination of the specimens indicated that this was probably a result of incipient melting of the braze at 1500 F. Also, after testing in high vacuum one or more constituents had apparently been lost and embrittlement of the brazing filler metal had occurred. The embrittlement of the Zr-Ti-Be sample appeared to be more severe.
Introduction

The aerospace and nuclear fields have created a need for new brazing filler metals that are capable of joining advanced materials, such as the refractory metals, for service applications involving severe environmental conditions. Brazing offers many advantages over fusion welding for many of these applications, particularly in those where complex and intricate components are to be joined. In typical applications such as the fabrication of heat exchange devices and nuclear fuel elements, the physical act of performing the work using conventional welding operations can produce insurmountable problems. However, by using brazing, such components can be much more readily fabricated. Brazing also overcomes the metallurgical problems frequently encountered in joining dissimilar materials.

In advanced nuclear and space concepts utilizing brazed joints of refractory metals, the environment surrounding the joint may be alkali metal (in either the liquid or vapor state), high vacuum, or high-purity inert gas. Corrosion or selective vaporization are factors to be evaluated in brazing filler metal selection. Consideration must also be given to service temperature and strength requirements.

The purpose of this investigation was to examine approximately one dozen of the most promising brazing filler metals which have been developed at Oak Ridge National Laboratory for joining refractory metals. These compositions have been shown to have the ability to readily wet refractory metals and to have adequate flow characteristics on Nb—1% Zr base metal (Nb—1% Zr has been used extensively as the structural material for high-temperature liquid-metal applications). Although studies on strength and aging effects have been previously conducted, one area that had not been adequately investigated was the effect of exposure to high vacuum and liquid metals such as potassium.

Materials and Brazing Procedure

The Nb—1% Zr was used as the base metal throughout this investigation; it has good corrosion resistance to potassium and is readily brazed by the filler metals under study.

Each brazing filler metal was used to fabricate a tee-joint made of 1/2 in. wide x 3 in. long x 0.050 in. thick strips of base metal. Approximately 1 g of brazing filler metal was placed on each end of the tee-joint on opposite sides of the vertical member. The brazing filler metals used in this investigation were divided into three groups and are listed in Table 1. The first two groups are comprised of high melting alloys (flow temperatures greater than 3200 F) from the V-Ta-Nb system and the V-Ta-Ti system, respectively. The third group is composed of a variety of lower melting alloys (flow temperatures less than 2300 F). The higher melting groups were corrosion tested at 1700 F (925 C), while the lower melting group was tested at 1500 F (815 C). The duration of all tests was 1000 hr. Within the lower temperature test group, three of the brazing filler metals were tested at a temperature that was within 350 F of their original brazing temperatures. This is significant since one
of these materials (Zr—48 wt % Ti—4 wt % Be) has a remelt temperature on tantalum of approximately 200°F lower than its original brazing temperature.3

Potassium was chosen as the alkali metal for this test since, like sodium, it has many properties that are advantageous in space-nuclear applications.4 Potassium has a relatively low melting point of 147°F (63.7°C) and a boiling point of 1407°F (764°C). It is one of the lightest metallic elements, having a density of 0.876 g/cm³ at 1292°F (700°C), and it has a low thermal neutron absorption cross section. All of these factors, coupled with its excellent heat transfer capabilities, make potassium an attractive reactor coolant.

However, the successful containment of potassium by refractory metals and alloys at temperatures in excess of 1500°F requires high purity of both the potassium and the refractory metal. The corrosiveness of potassium is accelerated in refractory metals by the presence of oxygen,5 and, in view of the high affinity of potassium for this element, the importance of avoiding exposure of the potassium to oxygen cannot be overemphasized. In our experiments, the oxygen level of the potassium was less than 25 ppm.

Test Procedure

The brazing operation was performed in a vacuum furnace, using tungsten-mesh heater elements and an average pressure of 2 × 10⁻⁶ torr. The furnace was brought slowly to brazing temperature, using an upper pressure of 5 × 10⁻⁶ torr as the limiting factor. The actual brazing temperature was maintained for about 1 min, after which the brazement was furnace cooled to room temperature in vacuum.

After the brazing operation, each brazement was cut into 1/2 in. long sections using the spark-discharge machining technique to minimize...
Fig. 4—The Nb—1% Zr brazed with V—20 wt % Ta—30 wt % Ti. No corrosion was observed. Etchant: lactic-nitric-hydrofluoric mixed acid solution.

Fig. 5—The Nb—1% Zr brazed with Ti—28 wt % V—4 wt % Be. The brazed joint successfully withstood all tests. Etchant: lactic-nitric-hydrofluoric mixed acid solution.
Fig. 6—The Nb−1% Zr brazed with Zr−19 wt % Nb−6 wt % Be. Good corrosion resistance and fair thermal stability were evident. Etchant: lactic-nitric-hydrofluoric mixed acid solution.

Fig. 7—The Nb−1% Zr brazed with Ti−40 wt % Zr−15 wt % Fe. The braze fillets were subject to modest deterioration after exposure to potassium, vacuum, and argon. Etchant: lactic-nitric-hydrofluoric mixed acid solution.
vibration and possible cracking of the brazed joint. The four sections of each brazement used in the test were always taken from the center portion of the tee-joint to provide a reasonably consistent fillet size and to eliminate possible end effects.

Four sections of each brazement were used in this investigation, two for potassium exposure (one in liquid and one in vapor as shown in Fig. 1), one for vacuum testing, and one for static argon testing. The container material was Nb—1% Zr in each test conducted. With this method, we could distinguish between the effects of the corrosive medium, evaporation, and any solid-state metallurgical reactions that might occur in the control sample tested in static argon.

The brazements used for vacuum testing were subjected to pressures of approximately 1 x 10⁻⁹ torr at the test temperatures. A pressure lower than approximately 5 x 10⁻⁸ torr is considered to be in the ultrahigh vacuum range and approaches the extremely low pressures one would expect to encounter in space flights. The apparatus used to achieve and maintain the test pressure is shown in Fig. 2. The same equipment was used for testing in static argon.

Test Results

1700F Tests

The higher temperature brazing alloys from the V—Ta—Nb and V—Ta—Ti systems exhibited good brazing properties and very good corrosion resistance to the liquid and vapor environment of the boiling potassium. Metallographic examination of the brazements after testing revealed that the braze joint (including the filler metal, the filler metal-base metal interaction layer, and the base metal) exhibited no detectable attack from the potassium exposure. Also, the brazements in this group all withstood the vacuum exposure, and no observable evidence of volatilization by any of the constituents of the braze filler metal was noted.

As illustrated in Figs. 3 and 4, which are representative samples of the test brazements after environmental exposure at 1700 F, the most apparent changes occurred in the base metal as a result of aging at the test temperature. Also, there was some change in the microstructure of the brazing filler metal due to thermal exposure including the development of a similar epitaxy between the braze metal and the parent metal.

1500F Test

The brazement made using Ti—28 wt % V—4 wt % Be as the brazing filler metal exhibited good filleting and minimal base metal dilution and, in general, was sound. Samples from this brazement performed exceptionally well under all of the environmental exposures without any apparent adverse results. No significant volatilization of the alloy constituents was noted after vacuum exposure and no corrosive effects were observed after testing in potassium. This is illustrated in Fig. 5. The blackening of the brazes in the photomicrographs is from the etchant and is not due to a bad braze.

The test brazements using Zr—19 wt % Nb—6 wt % Be and Ti—40 wt % Zr—15 wt % Fe as filler metals were slightly cracked in the fillets in the as-brazed condition. Subsequent environmental exposure resulted in intergranular diffusion of the brazing filler metal constituents into the base metal (Figs. 6 and 7). After testing in potassium, the Zr-Nb-Be brazed joint suffered considerable microstructural cracking. The sample of the Ti—Zr—Fe brazement tested in potassium vapor (Fig. 7) contained a very wide and distinct diffusion band around the braze joint. The samples were apparently not corroded by the potassium per se; however, the thermal exposures in argon, vacuum, and potassium all created sufficient constituent loss to cause severe cracking and microstructural disintegration within the braze as seen in Fig. 8.

The brazing filler metals Ti—46 wt % Zr—4 wt % V—4 wt % Be and

Fig. 8—Higher magnification view of the vacuum-exposed Ti-Zr-Fe braze shown in Fig. 7. Exposure to the 1500 F test temperature has resulted in degradation of the joint. Etchant: lactic-nitric-hydrofluoric mixed acid solution
Fig. 9—The Nb—1% Zr brazed with Ti—46 wt % Zr—4 wt % V—4 wt % Be and tested in different environments. Severe attack and/or disintegration of the braze occurred during testing. Etchant: lactic-nitric-hydrofluoric mixed acid solution.

Fig. 10—The Nb—1% Zr brazed with Ti—48 wt % Zr—4 wt % Be and tested in different environments. The brazed joint was severely deteriorated as a result of the tests. Etchant: lactic-nitric-hydrofluoric mixed acid solution.
Ti—48 wt % Zr—4 wt % Be, shown in Figs. 9—11, exhibited good wetting and flow characteristics, and base metal dilution was minimal. No intergranular reaction with the base metal was noted as a result of the braze cycle. The initial brazing temperatures of the Ti—46 wt % Zr—4 wt % V—4 wt % Be and Ti—48 wt % Zr—4 wt % Be filler metals, 1740 and 1830 °F, respectively, are relatively close to the 1500 °F test temperature utilized in these experiments. Therefore, it is not surprising that the thermal exposures resulted in constituent loss from the braze fillet into the environment, diffusion into the base metal, and in some cases, incipient remelting of the braze. The exposure of these alloys to potassium produced almost total deterioration of the fillet. In a subsequent experiment, as-cast buttons of these filler metals were exposed to potassium in individual Nb—1% Zr containers at 1500 °F for 500 hr. Post test examination revealed complete dissolution of the buttons and deposition of the alloy on the container wall.

**Summary**

Table 2 is a summary of the results of this investigation. All the brazing filler metals tested at 1700 °F withstood the stated test environments without any adverse effects.

Of the alloys tested at 1500 °F, one (the Ti—28 wt % V—4 wt % Be alloy) performed satisfactorily under all the test conditions. In the Ti—Zr—Fe and Zr—Nb—Be systems, the integrity of the brazes was severely diminished after testing at 1500 °F in argon, vacuum, and potassium. The specimens brazed with Ti—48 wt % Zr—4 wt % Be and Ti—46 wt % Zr—4 wt % V—4 wt % Be filler metals were severely degraded by the test environments at 1500 °F for 1000 hr. However, because of their excellent ability to braze most refractory metals, these last-mentioned compositions are very attractive for lower temperature applications.

**Acknowledgments**

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**References**


**Table 2—Results of Metallographic Examination of Brazed Joints**

<table>
<thead>
<tr>
<th>Composition, wt-%</th>
<th>Brazing temperature, °F</th>
<th>Test temperature, °F</th>
<th>1000 hr in test environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-25 Ta-25 Nb</td>
<td>3400</td>
<td>1700</td>
<td>Good, some alloying base metal</td>
</tr>
<tr>
<td>V-30 Ta-30 Nb</td>
<td>3500</td>
<td>1700</td>
<td>Braze unaffected, diffusion layer in base metal</td>
</tr>
<tr>
<td>V-5 Ta-30 Nb</td>
<td>3300</td>
<td>1700</td>
<td>Unaffected</td>
</tr>
<tr>
<td>V-30 Ta-5 Nb</td>
<td>3400</td>
<td>1700</td>
<td>Cracked</td>
</tr>
<tr>
<td>V-30 Ta-5 Ti</td>
<td>3350</td>
<td>1700</td>
<td>Slightly cracked</td>
</tr>
<tr>
<td>V-25 Ta-20 Ti</td>
<td>3350</td>
<td>1700</td>
<td>Incipient melting of braze</td>
</tr>
<tr>
<td>V-20 Ta-30 Ti</td>
<td>3200</td>
<td>1700</td>
<td>Embrittled braze</td>
</tr>
<tr>
<td>V-10 Ta-50 Ti</td>
<td>3200</td>
<td>1700</td>
<td>Eroded braze</td>
</tr>
<tr>
<td>Ti-28 V-4 Be</td>
<td>2280</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Ti-40 Zr-15 Fe</td>
<td>1830</td>
<td>1500</td>
<td>Cracked</td>
</tr>
<tr>
<td>Zr-19 Nb-6 Be</td>
<td>1720</td>
<td>1500</td>
<td>Slightly cracked</td>
</tr>
<tr>
<td>Ti-48 Zr-4 Be</td>
<td>1830</td>
<td>1500</td>
<td>Good</td>
</tr>
<tr>
<td>Ti-46 Zr-4 V-4 Be</td>
<td>1740</td>
<td>1500</td>
<td></td>
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Fig. 11—The Nb—1% Zr brazed with Ti—48 wt % Zr—4 wt % Be and tested in vacuum. Degradation of the joint is evident. Etchant: lactic-nitric-hydrofluoric mixed acid solution.