Brazing Molybdenum and Tungsten for High Temperature Service

Ti-65V, pure vanadium, and V-50Mo appear to be excellent brazing materials but must be diluted with base metal to inhibit the formation of Kirkendall voids

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ABSTRACT. Investigations have been conducted to develop vacuum brazes for molybdenum and tungsten which can be used in seal joint applications up to 1870 K (1597 C, 2907 F). Joints were attempted in molybdenum, tungsten and tungsten-molybdenum. The braze materials included: Ti-10Cr powder, Ti-30V wire, Ti-65V wire, V wire, Ni electroplate, MoB-50MoC powder mixture, V-50Mo powder mixture, Mo-15MoB powder mixture, Mo-49V-15MoB powder mixture.

Braze temperatures ranged from 1900 K (1627 C, 2967 F) to 2530 K (2257 C, 4095 F), and leak-tight joints were made with all braze materials except Ti-10Cr. After heat treatments up to 1870 K (1597 C, 2907 F) Kirkendall voiding was found to cause leakage of some of the joints made with only substitutional alloying elements. However, adding base metal powders to the braze or narrowing the root opening eliminated this problem. Kirkendall voiding was found not to be a problem when interstitial elements were a major ingredient in the braze material.

Shear testing of Ti-65V, V, MoB-50MoC and V-50Mo brazed molybdenum at 1670 K (1397 C, 2547 F) indicated strengths equal to or better than the base metal. Ti-65V, V-50Mo and MoB-50MoC brazed joints were exposed to basalt at 1670 K (1397 C, 2547 F) for 3 h without developing leaks.

Introduction

In fabricating structures of molybdenum and tungsten, one is commonly faced with the problem of making joints which are strong, leak-tight, and capable of maintaining integrity at high temperature over long periods of time. Welding of these refractory metals is possible, but it requires highly sophisticated methods such as electron beam or laser welding. Also, special grades of metal purity are required for good welding results. We find, for example, that it is necessary to use low carbon or TZM molybdenum to obtain crack-free weld joints in this material consistently.

Brazing can sometimes offer an attractive alternative to welding, and it can, in some cases, yield joints which are superior. Also, the complexity of the joint design and the purity level of the base metal are not as important in brazing molybdenum and tungsten as compared to that required for welding.

We have been involved with the problem of joining molybdenum and tungsten over the past several years in conjunction with the development of several high temperature devices. Originally, the work was aimed at developing brazing methods for spacecraft mini-thrusters and rock melting drills (Subterrenes). Recently, however, emphasis has shifted to applications in heat-pipe cooled nuclear reactor systems to be used for electrical power generation in space. These brazing methods were identified for molybdenum joining in the mini-thruster development. These alloys include Ti-21V-25Cr, Ti-42.5Zr-15Ta, and V-20Ta-25Nb which were used to braze molybdenum foam successfully to molybdenum sheet at 1825, 1957, and 2175 K (1552 C/2826 F, 1802 C/3276 F, and 1902 C/3455 F) respectively. Canonico, et al. have conducted extensive investigations into the use of the first two alloys for brazing of high temperature materials. A typical joining problem in the Subterrenes, for example, that was solved by brazing with pure titanium or vanadium was the sealing of threaded joints against molten basalt intrusion. In this example, the brazed joint had to be resistant to chemical attack by molten basalt which happens to be one of the most aggressive siliceous melts.

This paper summarizes the results of a screening study of vacuum furnace brazing of molybdenum and tungsten aimed primarily at the Subterrene application—but, however, with rather broad implications. We were aiming to develop brazing methods that could be used to make joints that would be useful at temperatures as high as 1870 K (1597 C, 2907 F) for 1000 h or more. These investigations included making trial brazes with nine different braze materials, high temperature aging of the joints, high temperature compatibility tests with basalt, and high temperature shear testing. The brazing trials, high temperature aging, and compatibility tests were accomplished with a cup specimen, while the shear tests were performed on butt joined plates.

Cup Brazing and Evaluation

Braze trials were accomplished by making joints between a disc fitted into a sleeve in the manner illustrated.
in Fig. 1. The braze material was placed at the root opening of the joint in the bottom of the cup. This meant the braze had to flow around a corner which was considered to be a rather rigorous test of capillary flow of the molten braze. Some of the sleeves had a 45 deg chamfer machined on the inside at the root opening of the joint to allow for easier entry of the braze material.

The first step in evaluating the as-brazed joints was to subject the cups to a helium leak check; then some cups were sectioned longitudinally and examined metallographically. The remaining cups were heated either empty or containing basalt to obtain some indication of high temperature performance under simulated service conditions.

All brazing was performed at Advanced Technology in Pasadena, California, using a resistance heated, high temperature vacuum furnace capable of maintaining a vacuum of 0.013 Pa (10⁻³ torr) or better while at temperature. Prior to assembly of the cups for brazing, all parts were vapor degreased and cleaned with acetone. One or more assemblies were placed in the furnace hot zone for brazing in a position that allowed viewing of braze flow on at least one of the samples. Melting and flow were observed through a Leeds-Northrup optical pyrometer that was used also for braze temperature measurements.

During each braze cycle, the furnace temperature was raised slowly to avoid thermal shocking of the parts and to maintain the desired vacuum. After flow was observed, the furnace temperature was typically increased 40 K before holding some period of time to allow the braze material to flow into the joint. The joints were visually inspected under X 20 magnification and helium leak tested with a Veeco leak detector after brazing. If the braze material did not flow uniformly through the joint, a second braze cycle was run with the cup inverted and the braze material placed at the root opening on the bottom of the cup.

A summary of the results of the braze trials and the aging and compatibility testing is presented in Table 1. The aging treatment involved heating brazed cups (empty) at either 1670 (1397 C, 2547 F) or 1870 K (1597 C, 2907 F) in a vacuum or a helium atmosphere for 3 h, while the compatibility testing was performed by heating cups filled with Jemez basalt* in a helium atmosphere for the same time and temperature. Helium leak testing and metallography were used to determine the effects of the simple heat treatment on the brazed joints; however, the compatibility tested cups were visually examined for basalt leakage prior to metallographic examination. The brazing procedures and results for each braze material are detailed below.

**Ti-10Cr**

Trial brazes were made between a molybdenum sleeve and disc and a molybdenum sleeve and tungsten disc using a Ti-10Cr alloy powder as the braze material.

All the joints tried with this alloy leaked helium. Metallurgical examination revealed that most of the braze filler metal had flowed out of the joint during the braze cycle. Because of a manufacturing error, the root opening of these joints had been made twice as wide as the desired 0.025 to 0.051 mm (0.001 to 0.002 in.), probably allowing the braze metal to flow through and out of the joint.

Because the braze filler metal that remained in the joint contained microcracks that traversed the width of the joint, titanium-10 wt% chromium was not considered to have reasonable potential as a braze filler metal for either tungsten or molybdenum. For this reason it was dropped from consideration and further testing.

**Ti-30V**

Both Mo-Mo and Mo-W brazes were made with this filler metal. All of the Mo-Mo joints brazed with titanium-30 wt% vanadium leaked helium.

*Jemez basalt has a typical composition of 50% SiO₂, 17% Al₂O₃, 29% CaO, 8% FeO, 6% MgO, 4% Na₂O, 3% Fe₂O₃, 2% TiO₂, and 1% H₂O.

However, when the disc was made of tungsten and the sleeve made of molybdenum, the joints were leaky-tight.

This braze material flowed well into both types of joints and produced a good filler on the inside of the cups. On the other hand, microcracks and porosity in the Mo-Mo joints were observed in the filler metal which was the probable cause of the leakage. As can be seen in Fig. 2A, these defects are absent from the Mo-W joints. However, heating these Mo-W joints brazed with Ti-30V at either 1670 K (1397 C, 2547 F) or 1870 K (1597 C, 2907 F) for 3 h in a vacuum caused both voids and microcracks to form in the filler metal. The voids developed as a consequence of the well known Kirkendall Effect because the intrinsic diffusivities of the base metals are several orders of magnitude less than those for the braze elements. This joint degradation, which can be seen in Fig. 2B, caused it to leak helium.

A secondary phase, which can be seen in Fig. 2B, precipitated in the braze material during the heat treatments. These second phase particles are probably the α-titanium-vanadium phase because the electron microscope indicated that they contained mostly titanium with a small amount of vanadium.

Jemez basalt was observed to attack the Ti-30V brazed Mo-W joint severely during the 3 h exposure at 1870 K (1597 C, 2907 F). As can be seen in Fig. 2C, the molten basalt intruded into the joint, and the cup was observed to have leaked basalt during the test. Furthermore, it appears that the braze material that has diffused into the base metals promotes grain boundary attack in both molybdenum and tungsten.

This braze material was judged to have marginal utility as a high temperature braze for molybdenum and tungsten primarily because of its propensity to form Kirkendall voids in service. Consequently, no further trial brazes or testing were conducted with Ti-30V.

**Ti-65V**

As will be noted in Table 1, all the cups brazed with the titanium-65 wt% vanadium alloy wire were helium leak-tight. This braze material flowed into both Mo-Mo and Mo-W joints very well and formed a uniform fillet. However, cups with the narrower root opening (0-0.013 mm, 0.0005 in.) were brazed a second time because the filler metal did not flow uniformly through the joint on the first try.

The microstructure of the as-brazed Ti-65V filled joints was very similar to the Ti-30V as-brazed joints—Fig. 2A.
Microcracks were also observed in the as-brazed Ti-65V joints with the wider root opening (0.051-0.102 mm, 0.002-0.004 in.), but they did not cause the cup to leak. These wider joints did not receive the 40 K over temperature treatment during brazing, so the filler metal was not as well alloyed with the base metal.

Heating the brazed joints in a vacuum for 3 h at 1870 K (1670 K, 2547 F) or at 1870 K (1670 K, 2547 F) caused Kirkendall voids to form in the joints, but only the 1870 K heat treatment caused the cup to leak. Cracking of the braze filler metal in the wider root opening joints was also observed after the 1870 K heat treatment similar to that seen in Fig. 2B in a similarly heat treated Ti-30V brazed Mo-W joint. As can be seen in Fig. 3A, no cracking was seen to result from a similar 1670 K (1397 C, 2547 F) heat treatment of a narrow root opening joint.

A secondary alloy phase like that seen in Fig. 2B was seen in the center of a 1670 K (1397 C, 2547 F) heat treated Ti-65V joint with a wide root opening which, as with the Ti-30V joints, was found to contain mostly titanium with a small amount of vanadium. The presence of this secondary phase suggests a eutectoid decomposition is taking place in the Ti-V alloy system that is not indicated in any of the accepted binary phase diagrams, but it has been suggested.8 Efimov, et al. have observed a similar alloy decomposition in studies on the Ti-V

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Table 1—Cup Brazing and Evaluation Summary

<table>
<thead>
<tr>
<th>Composition</th>
<th>Melting point or range, °K</th>
<th>Form used</th>
<th>Metals joined</th>
<th>Radial root opening, mm</th>
<th>Brazing conditions</th>
<th>Helium leak test results</th>
<th>Basalt compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-10Cr&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1830-1880</td>
<td>Disc</td>
<td>Mo</td>
<td>0.051-0.102</td>
<td>1970</td>
<td>F&lt;sup&gt;5&lt;/sup&gt;</td>
<td>Heated through</td>
</tr>
<tr>
<td>Ti-30V</td>
<td>1880-1890</td>
<td>Sleeve</td>
<td>Mo</td>
<td>0.051-0.102</td>
<td>1970</td>
<td>F</td>
<td>Leaked</td>
</tr>
<tr>
<td>Ti-65V</td>
<td>1920-1990&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Wire</td>
<td>Mo</td>
<td>0.051-0.102</td>
<td>1930</td>
<td>P&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No leakage</td>
</tr>
<tr>
<td>V-50Mo</td>
<td>2200</td>
<td>Wire</td>
<td>W</td>
<td>0.051-0.102</td>
<td>2240</td>
<td>P&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No leakage</td>
</tr>
<tr>
<td>MoB-50MoC</td>
<td>2225-2480&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>Wire</td>
<td>W</td>
<td>0.051-0.102</td>
<td>2330</td>
<td>P&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No leakage</td>
</tr>
<tr>
<td>Mo-15MoB&lt;sub&gt;5&lt;/sub&gt;</td>
<td>2225</td>
<td>Wire</td>
<td>W</td>
<td>0.051-0.102</td>
<td>2425</td>
<td>P&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No leakage</td>
</tr>
<tr>
<td>Mo-49V-15MoB&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1825-2225</td>
<td>Wire</td>
<td>W</td>
<td>0.051-0.102</td>
<td>2325</td>
<td>P&lt;sup&gt;5&lt;/sup&gt;</td>
<td>No leakage</td>
</tr>
<tr>
<td>Ni</td>
<td>1995-1730</td>
<td>Electroplate</td>
<td>Mo</td>
<td>0.051-0.102</td>
<td>1970</td>
<td>F</td>
<td>Leaked through</td>
</tr>
</tbody>
</table>

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<sup>6</sup> All compositions in wt%.
<sup>5</sup> Estimated temperature.
<sup>bc</sup> Helium leak rate specification: P = 1.0 X 10<sup>-6</sup> std cm<sup>3</sup> He/s < F.
<sup>b</sup> Brazed twice.
<sup>273 K = 0 C = 32 F.</sup>
binary system which they attribute to the influence of impurities.

Molten basalt attacked the braze material and surrounding base metal to some degree, but it did not leak through any of the joints tested. Joints were tested for compatibility with basalt to as high as 1870 K (1597 C, 2907 F). Basalt was observed to intrude into the joints having the wider root opening as can be seen in Fig. 3B, but basalt intrusion was not seen in the narrower joints.

Ti-65V has been judged to be a suitable braze for molybdenum and tungsten if the service temperature is kept below about 1670 K (1397 C, 2547 F). Also, these data indicate the root opening should be kept between 0.013 and 0.051 mm (0.0005-0.0015 in.) for best performance. The root opening was not optimized in this study.

Vanadium

Because of our prior success with vanadium braze sealing of Subterrene rock melting drills, we decided to perform a more systematic evaluation of this braze material by making cups of both molybdenum and tungsten. Braze flow was first observed at the melting point of vanadium, 2200 K (1927 C, 3501 F). All the trial joints brazed with pure vanadium were leak-tight; however, this filler metal appeared to have difficulty penetrating even the wider root opening (0.051-0.102 mm, 0.002-0.004 in.) W-W joints. Consequently, the narrower root opening Mo-Mo joints were brazed a second time with braze material placed on the outside of the bottom cup. Both tungsten and molybdenum appeared to be wetted very well by molten vanadium and consequently tended to form small fillets. A typical as-brazed microstructure of a W-W joint is seen in Fig. 4A.

Heating the wider W-W joint at 1870 K (1597 C, 2907 F) for 3 h in a helium atmosphere caused it to leak helium because, as can be seen in Fig. 4B, microcracks and Kirkendall voids formed in the filler metal during the heat treatment. No voids or cracks were observed in the filler metal of the narrower Mo-Mo joint after 3 h at 1670 K (1397 C, 2547 F) in helium, and this joint was still leak-tight after the heat treatment.

Both joint types were found to be contaminated with impurities after the simple heat treatments. The vanadium in the W-W joint appeared to pick up oxygen during the heat treatment as evidenced by an increase in hardness from 290 to 1000 DPH. This is the probable cause of the cracking seen in the filler metal in Fig. 4B. An electron microprobe analysis of the filler metal in the Mo-Mo joints revealed the presence of significant amounts of carbon which apparently was picked up during the brazing. Brazing and the 1670 K (1397 C, 2547 F) heat treatment of the Mo-Mo joints yielded a 50-50 molybdenum-vanadium alloy at the center of the joint. Grain growth across the original interface also was observed indicating that significant interdiffusion between the braze and the base metal had occurred.

Only the W-W joint brazed with pure vanadium was tested for compatibility with basalt. After 3 h at 1870 K (1597 C, 2907 F) in contact with molten basalt, the filler metal and surrounding base metal were attacked severely as can be seen in Fig. 4C. Basalt also was observed to have leaked through the joint during the test.

These data indicate that pure vanadium is a suitable filler metal for the brazing joining of molybdenum or tungsten if the service temperature does not exceed 1670 K (1397 C, 2547 F). Above this temperature, void formation and coalescence is expected to cause joint leakage and weakening. The root opening has not yet been optimized, but the recommended value ought to be between 0.013 and 0.051 mm. An upper temperature limit for the use of this braze material in contact with siliceous melts was not established in this study.

V-50Mo

Any molybdenum-vanadium interface is primed for Kirkendall voiding because of the large difference between the intrinsic diffusivities of these two elements. The self-diffusion data of Pavlinov and Bykov indicate the intrinsic diffusivity of molybdenum at 1670 K (1397 C, 2547 F) is \(1 \times 10^{-13} \text{cm}^2/\text{s}\), while the intrinsic diffusivity of vanadium at the same temperature is reported to be \(8 \times 10^{-13} \text{cm}^2/\text{s}\).

Thus, in order to reduce the voiding problem in vanadium brazed molybdenum during high temperature service, it was decided to try to braze molybdenum cups with a mechanical
The braze material was prepared by premixing and ball milling —325 mesh pure metal powders together using pure ethanol as a carrier. The braze material was placed in the bottom of the cup for the first brazing cycle, and because the braze material did not flow uniformly through the joint on the first try, the cycle was repeated with the cup inverted and the braze material placed on the outside of the bottom of the cup. In both cycles, the furnace temperature was raised to 2530 K (2257 C, 4095 F) before being turned off. Of the four cups brazed with V-50Mo, only one leaked helium, and that failure was due to a cracked sleeve rather than a braze joint failure.

Cups were heated in a vacuum at both 1670 K (1397 C, 2547 F) and 1870 K (1597 C, 2907 F) for 3 h without developing leaks. In fact, these heat treatments improved the joints by causing significant interdiffusion to take place between the braze material and the base metal. As can be seen in Fig. 5, grain growth across the original interdiffusion zone, and the grain boundaries of the base metal to a depth of about 1.6 mm (0.06 in.) were seen in the electron microprobe to have a composition close to Mo,C. The second phase seen at the midplane of the joint in Fig. 5 were also analyzed with the electron microprobe to have a composition close to Mo,C. The second phase present was molybdenum carbide. However, as we shall see, sound joints were made with the MoB-50MoC mixture.

The braze material used consisted of premixed and ball milled —325 mesh MoB and MoC powders slurred with pure ethanol. Braze flow was observed at 2290 K (2017 C, 3663 F) with molybdenum cups when exposures were only about 70 K above the MoB-Mo eutectic temperature given by Shunk. After flow was observed, the temperature was raised to 2330 K (2057 C, 3735 F) before the furnace was turned off. It was found that the braze material “attacked” the molybdenum base metal somewhat, but it wetted and flowed well through the joints making the four tries leak-tight. This “attack” appears to be due to a eutectic reaction with the base metal. This reaction probably could have been reduced significantly if the pure molybdenum had been added to the braze material as originally intended.

Cups brazed with this material were found to be leak-tight after heating at 1670 K (1397 C, 2547 F) and at 1870 K (1597 C, 2907 F) for 3 h in a vacuum. Also, this braze material was not attacked by molten basalt during a 3 h exposure at 1670 K (1397 C, 2547 F). Neither heat treatment caused a significant change in the microstructure of these joints.

The photomicrograph seen in Fig. 6 is representative of both the as-brazed and the heat treated cups (empty). The braze material penetrated the grain boundaries of the base metal to a depth of about 1.6 mm (0.06 in.) producing grain boundary precipitates that were analyzed with electron and ion microprobes to have a composition close to Mo,C. The second phase particles seen at the midplane of the joint in Fig. 6 were also analyzed with
the microprobes and were found to have a composition close to Mo$_3$B.

There was little evidence of mixing of the carbide and boride phases in these specimens. The equilibrium phase in this situation according to Goldschmidt$^{10}$ ought to be Mo$_2$CB, so it appears that equilibrium was not achieved in these joints. As expected, this braze material did not cause the formation of Kirkendall voids during heat treatment.

It would appear that the MoB-MoC braze system shows excellent potential for joining molybdenum and possibly tungsten, especially for high temperature applications. We have not even begun to optimize the formulation of the braze material in this study, and it is not clear that powder mixtures represent the best form for the braze. A pre-alloyed powder might be a better form, but Mo$_2$CB would appear to be impractical because of its high melting temperature, $\approx 3075$ K (2802 C, 5076 F).$^{14}$

Mo$_{15}$MoB$_2$

This braze material was formulated to contain 14.8 wt% MoB$_2$ plus molybdenum in order to form the lowest melting eutectic in the Mo-B system which, according to Shunk,$^{15}$ melts at 2323 K (2052 C, 3726 F) and has a eutectic composition at about 3 wt% boron.

In the interest of economy and expediency, molybdenum and MoB$_2$ powders were premixed and ball-milled together rather than pre-alloying. The ethanol slurred mixture was placed in the bottom of a cup which had a sleeve with a chamfer at the bottom of the disc well. The molybdenum cup was set in the vacuum furnace on a hearth of tungsten powder and after evacuating the furnace, the temperature was raised until the braze was observed to flow at 2425 K (2152 C, 3906 F). This temperature was held for 10 min.

This braze material produced a leak-tight joint even though a few gaps were seen in the metallographic section of the joint. As can be seen in Fig. 7, the joint formed with this braze material is hardly detectable. This indicates considerable interdiffusion took place across the original interface during the rather long braze period. Grain growth across the original interface is further evidence of significant interdiffusion.

No heat treating or compatibility tests were performed on Mo$_{15}$MoB$_2$ brazed joints. This joint would probably perform very much like the MoB-50MoC brazed joints relative to the lack of degradation due to void formation with time at high temperature because boron is expected to diffuse predominately by the interstitial mechanism in molybdenum.$^{15}$ As we found late in this study, this type of braze material is not original with us as it has been previously recommended for brazing both molybdenum and tungsten.$^{15}$

Mo$_{49}$V$_{15}$MoB$_2$

In order to find a lower braze temperature than used for the Mo$_{15}$MoB$_2$ system, a braze material was formulated to contain 48.5 wt% vanadium, 14.8 wt% MoB$_2$, and the remainder molybdenum. This was an attempt to form a Mo-V-B ternary eutectic that would melt between the vanadium-boron binary eutectic temperature, $1825$ K (1552 C, 2826 F) and the molybdenum-boron binary eutectic temperature, $2323$ K (2050 C, 3722 F).

According to Elliott$^{11}$, the V-B eutectic composition occurs around 4 wt% boron. Again in the interest of economy and expediency, powders were premixed and ball-milled together. A pure ethanol slurry of the mixture was placed in the bottom of the chamfered molybdenum cup. Braze flow was not observed until the Mo-B binary eutectic temperature was reached. Then the furnace temperature was held constant at $2325$ K (2052 C, 3726 F) for 7 min.

The cup was helium leak-tight as-brazed, but metallographic examination of the joint revealed many gaps between the disc and sleeve. As can be seen in Fig. 8, the areas where the original 0.013-0.025 mm (0.0005-0.001 in.) root opening is filled with braze material are so well bonded that remnants of the original interface are practically impossible to see in the microstructure of the joint. Interdiffusion during the rather long braze period has contributed significantly to the bonding.

Indications of incomplete alloying of the mixture were seen on the bottom of the cup at and at the entrance of the joint. Eutectic like structures were analyzed with an electron microscope and found to be approximately MoVB. A single-phase metallic appearing structure found in the same location was analyzed to contain 29 wt% vanadium and the remainder molybdenum but no boron. It appears from this resultant inhomogeneous braze filler metal that pre-alloying of this system would be advised.

Neither heat treating nor basalt compatibility testing was conducted on this type of joint. High temperature degradation because of interdiffusion between the braze material and base metal is not expected to be a problem here.
Nickel is a classical “activator” for diffusion bonding molybdenum bars together end-to-end as well as a recommended braze material for both molybdenum and tungsten. In this study we attempted activated diffusion bonding molybdenum and tungsten discs into molybdenum sleeves using nickel deposited as a 10 μm thick electroplate on the disc.

On the first attempt at brazing cups, the root opening was too large to allow the nickel to operate as a diffusion activator, and it operated as a simple braze. Probably because the plate was so thin, braze flow was never observed and an arbitrary braze temperature of 1970 K (1697 C, 3087 F) was held for 3 min. These joints all leaked helium, but the microstructure seen in Fig. 9 indicates a good joint was formed in some places. This photomicrograph is typical of both Mo-Mo and Mo-W brazed joints.

A second attempt at activated diffusion joining molybdenum discs into molybdenum sleeves proved successful. In this case, the root opening was reduced to less than 0.013 mm (0.0005 in.) and the bonding temperature was reduced to 1785 K (1512 C, 2754 F). All joints were leak tight, and grain growth was observed across the original interface.

Heat treatments were performed only on the cups made in the first attempt. It was done only to see if a 3 hour treatment at 1870 K (1597 C, 2907 F) would cause the joints to seal. This was not successful. In the molybdenum joint, insufficient nickel diffused away from the original interface to solidify all of the molybdenum-nickel alloy that formed during brazing and the heat treatment. The alloy solidified in the Mo-W joint, but excessive Kirkendall voiding on the tungsten side of the joint resulted from the heat treatment and left the joint porous and leaky.

Molten basalt appeared to displace the molten braze material from the Mo-Mo joint and leak through during a 3 h compatibility test at 1870 K (1597 C, 2907 F). However, the Mo-Ni alloy regions bordering the joint were quite resistant to attack by molten basalt. This suggests that a nickel activated diffusion bond between molybdenum would be resistant to attack by molten basalt and similar siliceous melts. We were unable to test this theory on the second trial samples.

**Shear Testing**

Four of the braze materials—Ti-65V, pure V, V-50MoC and MoB-50MoC—were evaluated on the basis of 1670 K (1397 C, 2547 F) shear testing of joints in molybdenum. Vacuum arc-cast, rolled molybdenum plates 3.2 mm (1/16 in.) thick machined into mating halves 8 cm (3/16 in.) long and aligned within ±0.051 mm (0.002 in.) of a line through the hole centers. All specimens were ground to a uniform thickness prior to testing.

The final machining and shear testing were performed at Metcut Research Associates in Cincinnati, Ohio. The tests were performed in a high temperature vacuum furnace equipped with molybdenum resistance heating elements. A Baldwin-Lima-Hamilton, manually controlled, hydraulic testing machine was used for applying the load and measuring the shear strength. Two platinum-rhodium thermocouples were attached to the test section of the specimen for the test, and the specimen temperature was equilibrated to 1670 ± 1 K (1397 C, 2547 F) before the test was initiated. Each specimen was held at the test temperature for about 25 minutes before being pulled to failure at a crosshead speed of 0.02 mm/s (0.0008 in./s). Vacuum of 5 × 10^-6 Pa (0.72 × 10^-4 psi) or better were maintained in the furnace during each test.

Shear strength data for the braze joint specimens are listed in Table 2. Five Ti-65V brazed samples, four pure vanadium, and three each V-50Mo and MoB-50MoC joints were shear tested. Shear yield strengths of all the joints are slightly higher than the value calculated from tensile strength data for molybdenum, about 10 MPa (1450 psi).

As can be seen in Fig. 11, the base metal yielded in three out of the four joint types tested before the joint failed. This indicates some reduction in the thickness of the test sections should have been performed prior to testing in order to maintain pure shear loading in the joint to failure. Perhaps the Ti-65V brazed joint did not yield in

<table>
<thead>
<tr>
<th>Braze material</th>
<th>0.2% yield strength, MPa</th>
<th>Ultimate shear strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-65V</td>
<td>16 ± 2</td>
<td>34 ± 10</td>
</tr>
<tr>
<td>Pure V</td>
<td>14 ± 4</td>
<td>34 ± 5</td>
</tr>
<tr>
<td>V-50Mo</td>
<td>12 ± 1</td>
<td></td>
</tr>
<tr>
<td>MoB-50MoC</td>
<td>17 ± 5</td>
<td></td>
</tr>
</tbody>
</table>

* Joint was substantially stronger than the base metal.

**Table 2—1670 K Shear Strength of Braze Joints in Mo**

**Note:** Values are standard deviations of means.

**Fig. 11**—Braze joints in Mo shear tested at 1670K: 1B-Ti-65V; 2B-Pure V; 3A-V-50Mo; 4B-MoB-50MoC.
the base metal enough prior to failure to cause a significant error in the shear strength of this joint.

Figure 11 also illustrates the relative shear strength of the four filler metals tested, in the order of increasing shear strength: Ti-65V, V-5MoMo and MoB-50MoC. These data clearly indicate that these braze materials have as much high temperature strength as pure molybdenum.

Discussion and Conclusion

This screening study has identified several braze materials and procedures that have considerable potential for fabricating joints in molybdenum and tungsten that will be used at high temperatures for extended periods of time. The braze materials include Ti-65V, pure vanadium, V-5MoMo and MoB-50MoC. These data indicate that these braze materials have a beneficial effect on their temperature for a few minutes could hold for a few minutes.

The first three mentioned braze alloys appear to be excellent braze materials, but special processing is required to make them serviceable at high temperatures. These braze alloys must be diluted with the base metal to inhibit the formation of Kirkendall voids, and this may be accomplished by:

1. Pre-alloying the braze material with the base metal.
2. Allying with the base metal by raising the temperature above that at which the braze was seen to flow and hold for a few minutes.
3. Annealing the joint a few degrees below the flow temperature of the braze for a few hours.

A narrow root opening is a prerequisite for the success of the last two processes, but if the root opening is less than about 0.025 mm (0.001 in.), braze flow of these materials will probably be inhibited.

The molybdenum and carbide braze systems appear very attractive. However, our studies did not define the optimum compositions or procedures, even though we had good success making leak-tight and, in one case, demonstrated strong joints. Because of its extreme wetting and flow capabilities, this type of braze could be used in very narrow root opening joints, and holding these joints at the brazing temperature for a few minutes could have a beneficial effect on their strength. It is likely that more uniform filling of the joints could be achieved with these braze materials if pre-alloyed powders were used instead of mechanical mixtures.

This study has demonstrated also that molybdenum joints made with Ti-65V, pure vanadium, V-5MoMo and MoB-50MoC are as strong or stronger than the base metal at elevated temperature. The shear test specimen design used in this study had its shortcomings, but useful data were derived from them. Better shear specimen designs have been described in the literature.

Since molten basalts are representative of the more corrosive siliceous materials, those braze joints which were found to be compatible with molten basalt ought to have equal or better performance in contact with such things as molten commercial glasses. The most resistant joints among those tested were brazed with Ti-65V, V-5MoMo, and MoB-50MoC. Without further testing, it would probably be best to limit the maximum service temperature to 1670 K (1397 °C, 2500 °F).

The excellent results obtained with vanadium as a vacuum furnace brazing material for molybdenum and tungsten suggest that it would also be useful as a filler metal for electron beam welding of these two metals. It ought to be useful in either the pure form or alloyed with either molybdenum or tungsten.

It appears that very high temperature (> 1800 K or 1527 °C) brazing of molybdenum and tungsten is somewhat easier than the medium temperature (1200-1550 K or 927-1277 °C, 1701-2331 °F) brazing used for super-alloys because of factors such as easier wetting and flow which makes pre-placing of the braze materials unnecessary. Also, grain growth across the brazed joint appears easier with molybdenum and tungsten. It appears that good brazing practice for molybdenum and tungsten includes observing the brazing flow or making some trial brazes, which is usually not general practice in medium temperature brazing. If one is accustomed to vacuum furnace brazing super-alloys, the braze of molybdenum and tungsten should give fewer problems.

Acknowledgments

The authors want to thank R. C. DeSilvestri of Advanced Technology for performing the brazing and for suggesting some of the braze systems. Special thanks goes to S. W. Moore of LASI for suggesting the design of the shear test specimen and to E. A. Hakki-la for the electron and ion microprobe analyses.

The work described in this paper was performed under the auspices of the U.S. Energy Research and Development Administration.

References