

Materials Selection for High Temperature Neutron Scattering Sample Containers

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ABSTRACT

High temperature powder neutron diffraction experiments are conducted at sites including the Spallation Neutron Source and the High Flux Isotope Reactor at Oak Ridge National Laboratory to analyze the atomic structure of materials under operational conditions. Sample environments for these experiments can reach 1600 °C under vacuum conditions. Titanium alloy lids and flanges, which cap vanadium sample canisters, are observed to experience grain growth and bond after thermal cycling above 700 °C, reducing canister reusability, increasing operation costs, and presenting safety concerns. Additionally, molybdenum screws, which join the lids and flanges during experiments, embrittle and break during removal after high temperature experiments. Microscopic analysis shows the beginning of diffusion bonding, a solid-state welding process, at interfaces between the lids and flanges. Alternative processes and designs intended to create diffusion barriers at the interface or reduce the thermal stress are proposed to prevent diffusion bonding and improve the usability by increasing the maximum service temperature of the sample canisters.

I. INTRODUCTION

A. High Temperature Powder Neutron Diffraction

High temperature powder neutron diffraction measurements are valuable to obtain detailed information about the atomic structure of materials as a function of temperature for analyzing materials including catalysts [1], solid oxide fuel cells [2], and ceramic membranes [3] under their operation conditions. Although useful, high temperature experiments have many challenges; factors like eutectic formation, thermal cycling embrittlement, and sample vaporization must be considered when designing experiments. Eutectic formation will lead a material system to melt at

a lower temperature than its constituent elements. Phase diagrams should be consulted to determine if eutectics or phase transformations occur. High temperatures and thermal cycling can lead to unanticipated failure of sample canisters through strength reduction or thermal embrittlement. Under vacuum conditions, the potential exists for samples to vaporize at high temperatures, which can remove the sample from the path of the beamline [4].

B. Furnace Environment

In high temperature measurements at the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL), ILL neutron scattering furnaces, developed by the Institut Laue-Langevin (ILL) [5], are used to heat powder samples to temperatures up to 1600 °C under vacuum conditions ($\sim 2 \times 10^{-5}$ torr). A cross-sectional schematic of an ILL furnace is shown in Fig. 1; powders are contained in sample canisters that are attached to a central rod, and top loaded into the furnace. In these diffraction experiments, neutrons pass through the furnace components and sample canister on route to the powder. Although components in the path of a neutron beam can be easily fabricated out of materials including aluminum and stainless steel, these metals produce diffraction peaks in the data which can obscure information from superimposed peaks from the sample. The most suitable materials for furnace components and sample canisters should have low coherent and incoherent scattering lengths, in order to reduce the Bragg diffraction and background signals [7].

C. Sample Canisters

Vanadium is often used for cells in neutron experiments because of its low coherent scattering cross section of 0.0184 b [8], but alternative materials designated as null-scattering alloys can be created by producing an alloy from two metals with coherent scattering lengths of opposing signs in a proportion that minimizes the scattering length. One example is the Ti68Zr32 alloy (TiZr).

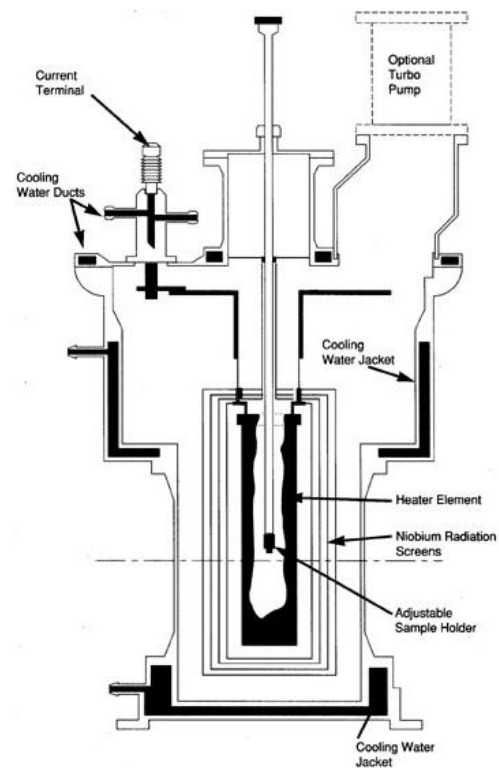


Fig. 1 Cross sectional schematic of an ILL high-temperature furnace [6]

In this alloy, titanium's negative scattering length of -3.438 fm [8] is exactly matched by zirconium's positive scattering length of 7.16 fm [8] to produce no Bragg diffraction peaks that could superimpose on the data, while retaining a high mechanical strength compared to other null-scattering alloys and low neutron absorbing materials [7].

The current high-temperature furnace canister system used at ORNL is based on the vanadium sample cans for powder samples developed by the National Institute of Standards and Technology (NIST). The canister system is comprised of five main components, each shown in Fig. 2: (1) the canister body, (2) the collar or flange, (3) the lid, (4) nuts, screws, and washers, and (5) a stick adapter to join the canister to the loading rod depicted in Fig. 1. These components are made of vanadium (1), the Ti-6Al-4V (Ti-64) alloy (2,3), molybdenum (4), and niobium (5); boron nitride (BN) can also be used as a lid material, as depicted in Fig. 2. Although the lid and flange are fabricated with six holes for screws, only three sets of molybdenum nuts, screws, and washers are used to join the lid and flange assembly during measurements to reduce costs. Depending on the specific component, desired properties for canister materials include compatibility with the vanadium body (2), high maximum service temperatures (1-5), low neutron cross-section (1), low reactivity (1-5), similar thermal expansion coefficients to other components (1-5), and reusability after thermal cycling (1-5). Values for mechanical and thermal properties of the materials used in the canister assembly are given in Table 1 in the appendix. Influencing the desire for reusable

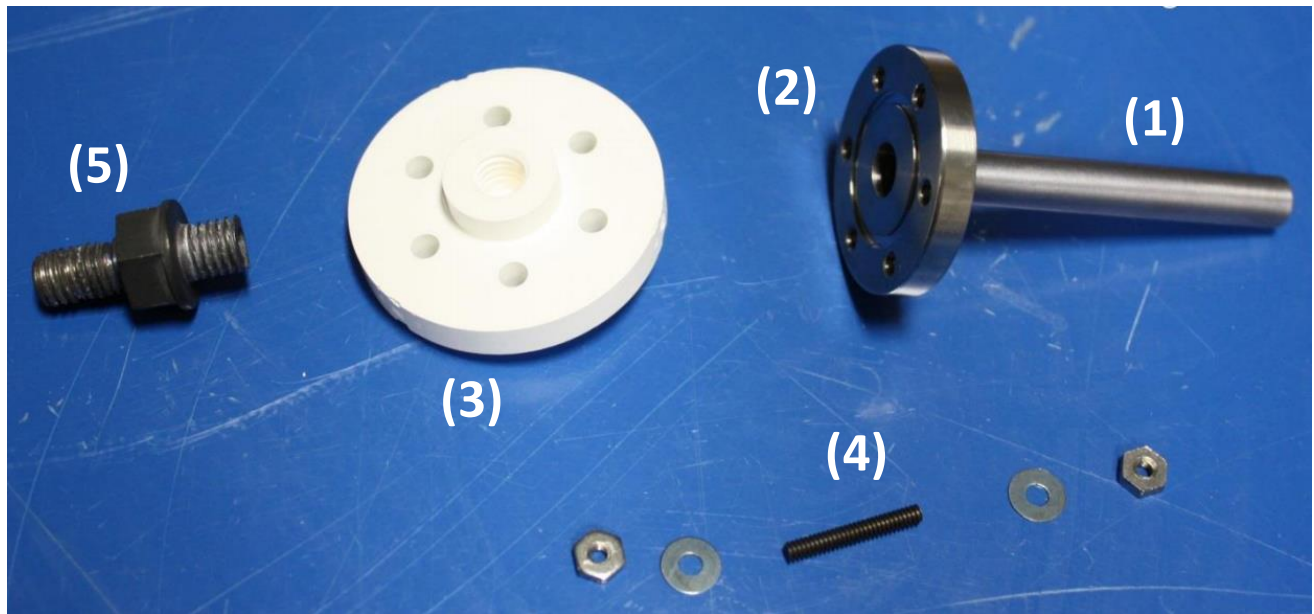


Fig. 2 Components of the high temperature powder canister system: (1) canister body (vanadium), (2) canister collar (Ti-64), (3) lid (boron nitride), (4) screws, washers, and nuts (molybdenum), and (5) stick adapter (niobium) [9].

components is the cost of materials and processing; currently, the SNS has an annual budget of ~\$120,000 for replacing these canister systems. The canister body and collar are manufactured by and purchased from MTI Albany. The canister costs have risen from ~\$150 to ~\$750 per unit, an increase that could be influenced by the economics surrounding the mining of vanadium-containing ores. 90% of the world's vanadium supply is controlled by 3 countries: China, Russia, and South Africa, with China mining more than half the world's supply. Enhanced environmental regulations, primarily in China, have contributed to increases in price, as many producers close or continue mining operations at reduced levels [10, 11]. The effect of COVID-19 on processing, distribution, and shipping is unlikely to improve this situation. Additional sample canister costs include the in-house machining of Ti-64 and BN lids, which cost ORNL \$35 and \$100 each, respectively, to machine. A set of three molybdenum nuts, screws, and washers are currently bought for \$45 from their manufacturers, Thermo Shield and Extreme Bolt and Fastener.

D. Canister Design Rationale

1. Vanadium

The sample canister body is composed of vanadium due to its minimal contribution to the neutron scattering measurements, high-temperature stability, and low reactivity. Vanadium's low coherent scattering cross-section results in minimal detectable Bragg peaks from the canister material in neutron diffraction measurements compared to canisters composed of metals such as aluminum, which has a coherent scattering cross-section of 1.495 b [8]. A vanadium canister may obscure some weak signals in neutron diffraction data, however, from incoherent scattering because of its incoherent scattering cross-section of 5.08 b [12]. It has a high melting temperature, 1910 °C, that exceeds the maximum temperature of the ILL furnaces used for the sample environment. Vanadium canister embrittlement has been observed over 1200 °C, which could limit its use or reusability more than its melting temperature [13]. Vanadium is also relatively resistant to eutectic formation [4] and does not experience any phase changes in its elemental state prior to melting. The metal is known for rapid oxidation at temperatures above 675 °C; with the formation of this oxide, rapid attack or catastrophic oxidation may occur above 650 °C in materials in contact with this oxide layer [14]. Despite the primarily optimal properties for our application, vanadium is expensive and difficult to work or join to other materials [15]. It is unlikely, however, that a comparable replacement for a lower cost will be identified. Null-scattering alloys with maximum operation temperatures up to 1600 °C are difficult to find; regardless of phase transitions that can

occur far below their melting point, these materials can begin melting below the melting temperature of their component elements depending on the specific composition and phase diagram. TiZr, for instance, begins melting around 1550 °C [16], despite titanium melting at 1688 °C and zirconium melting around 1860 °C. As with vanadium, many of these null-scattering alloys have additional problems; TiZr is also challenging to work and bond to other materials [15].

2. *Ti-6Al-4V*

The flange and lid are made of Ti-6Al-4V (Ti-64) because of the material's high melting temperature of 1688 °C, compatibility with vanadium, and comparative price to vanadium. Titanium alloys can be electron-beam welded to the vanadium canister body and have a close thermal expansion coefficient to the metal ($\Delta\alpha = 0.2 \times 10^{-6} \text{ K}^{-1}$) [17, 18], preventing major thermal stresses from forming during temperature cycling that could contribute to weld failure in experiments. While Ti-64 is not inexpensive, it is more affordable than vanadium. Whereas the vanadium sample canister body and welded Ti-64 flange currently cost upwards of \$750 to purchase from MTI, the Ti-64 lid costs \$35 to machine in-house. The material does have several drawbacks; the maximum working temperature of Ti-64 for structural applications is 300-400 °C, which can be increased by improved cooling designs, surface coatings, or a combination of different materials [19]. Cooling designs are largely impractical for this application, but coatings and multi-material solutions may improve the poor high temperature mechanical properties. These properties decrease rapidly at elevated temperatures; the yield strength of the alloy drops to 1 MPa by 1200 °C [20]. Ti-64 also has poor machinability [21], begins to recrystallize at 700 °C, and will begin to oxidize at 1200 °C [18].

3. *Molybdenum*

The flange and lid assembly of the canister is joined by molybdenum screws, nuts, and washers. Molybdenum, a refractory metal, is used because of its high temperature properties. It has a maximum service temperature that exceeds the temperatures seen in the testing environment, as seen in Table 1, because it retains its stiffness and strength at high temperatures better than metals like Ti-64 [22]. It is easily machined to the required tolerances and has a low thermal expansion so the screws will not deform under high temperatures.

4. *Boron Nitride*

Since the working temperature of Ti-64 is low compared to the temperatures of the testing environment, BN is sometimes used as the lid material. BN is an inert ceramic that will not activate

in the neutron beam. Its maximum working temperature is around 4 times that of Ti-64 (Table 1) because of its high temperature stiffness and strength, and the ceramic is readily machinable to the required tolerances. Additionally, it does not require heat treatment or sintering after machining. Its low thermal expansion (Table 1), even at extremely high temperatures, ensures little to no deformation. Each BN lids costs ~\$100, accounting for in-house machining costs.

E. Design Challenges

After experiments at elevated temperatures ($>700\text{ }^{\circ}\text{C}$) using Ti-64 lids, ORNL staff members have observed grain growth in the Ti-64 canister components, and the Ti-64 lid and flange begin to bond, preventing the removal of the lid for sample removal. These components can only be subsequently separated using excessive force, which breaks the can and renders it unusable for future experiments. An inherent safety concern is present in this scenario as the sample, in the form of powder, is still contained in the canister after irradiation and breaking the canister in an uncontrolled manner can lead to powder dispersal. While BN lids are an attractive alternative to Ti-64 lids, specifically at extremely high temperatures to prevent bonding the lid and flange, their application is limited due to their low hardness. Their screw threads deform easily, rendering them only single-use options. Although they are expensive to replace after each experiment, it is more cost-effective to replace a single BN lid (\$100) rather than the entire canister system (\$750+) if the Ti-64 lid and flange assembly bond.

Another observed challenge with the current canister system concerns the molybdenum screws, which embrittle after repeated thermal cycling. When the embrittled molybdenum screws are subjected to torque during canister disassembly, they often break, causing them to become stuck inside their holes. To prevent the screws from sticking inside the lid, smaller diameter screws are presently used to facilitate removal, which addresses neither the embrittlement nor cost concerns.

F. Solution Scope

While many aspects of the current canister design could be addressed, this project will predominately focus on the lid/flange interface. This area is defined by the bonding of the two Ti-64 components, and the molybdenum screws' tendency of brittle fracture. These are the two most common failure modes within the current canister design. The single most important factor to finding a solution is the operating temperature. Experiments performed at the SNS and HFIR commonly exceed $700\text{ }^{\circ}\text{C}$ and can be run at temperatures up to $1600\text{ }^{\circ}\text{C}$. Materials used for the

canister should be able to operate up to the maximum of the temperature range, behaving consistently across the entire range. Driving factors for this project are rising material costs with a stagnant budget and single use nature of canisters heated above 700 °C. This single use nature increases the number of canisters that need to be purchased. The solution should therefore improve on at least one if not both of these areas, reusability or initial cost, leading to a decrease in the lifetime cost. The solution should be reusable to the point that any higher upfront costs are offset, or should a single use model still be implemented, the initial cost of the canister should be lowered. Components should be readily available, machinable, or able to be prepared with a lead time less than a month. A proposed intermediary should be able to be easily applied or implemented and require minimal maintenance through its service life. Any proposed solution will still likely utilize the vanadium canister body, as comparable materials are unlikely to be found for a lower cost. Compatibility with vanadium, including weldability and thermal expansion behavior, is therefore an important constraint, particularly for flange materials. All possible solutions should at least maintain, if not improve, the inherent safety of the system. Thermal embrittlement or high temperature strength reductions of selected materials should not threaten the structural integrity of canisters.

II. Ti-64 LID/FLANGE BOND INVESTIGATION

A. Microscopy

To investigate the bonding phenomena, two Ti-64 bonded sample canisters were provided by ORNL Neutron Science staff members (Dr. Michelle Everett, a Scientific Associate for the Nanoscale-Ordered Materials Diffractometer, and Ms. Rebecca Mills, a Technician with the SNS and HFIR Sample Environment High Temperature Team). The specific firing schedules for the two provided canisters were unknown. The degree of bonding could not be determined upon initial visual inspection, and both canister lids had molybdenum washers adhered to the surfaces. The one distinguishing factor between the lids was that one appeared to have undergone significant grain growth, which was visible macroscopically and is shown in Fig. 3. To further investigate the interface, samples were prepared by cutting cross-sections perpendicular to the interface. These were mounted in epoxy, polished, and examined via scanning electron microscopy and optical microscopy. During the polishing process, the grain growth sample experienced significant pullout



Fig. 3 Comparison of Ti-64 lids from sample canisters used in high-temperature experiments at the SNS

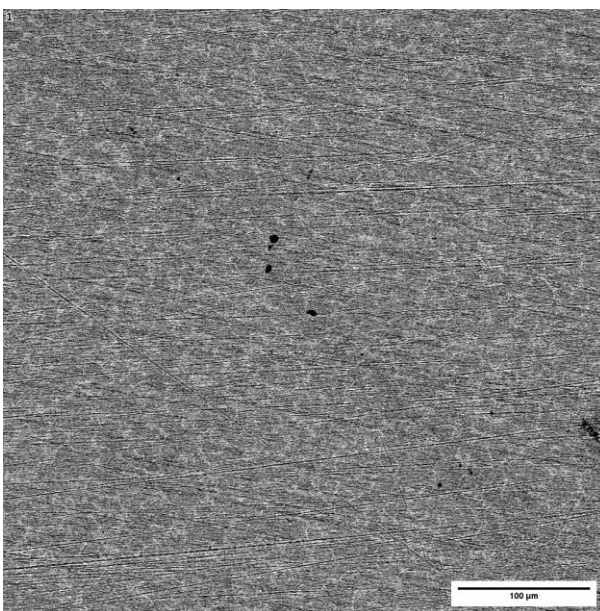


Fig. 4 SEM image of the Ti-64 lid that showed little grain growth from thermal cycling during experiments

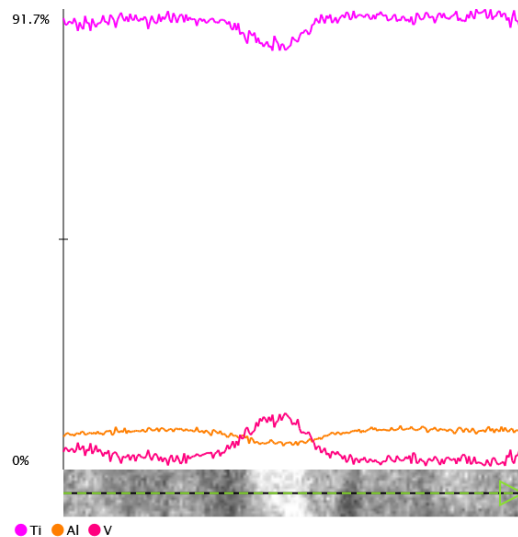
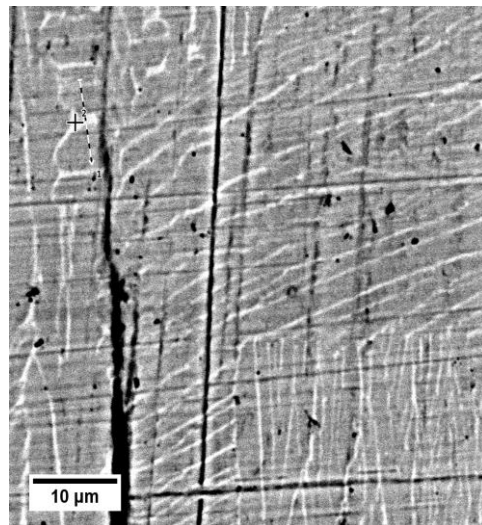


Fig. 5 SEM image and elemental analysis of “wood-grain” vanadium diffusion in the Ti-64 lid showing grain growth

during the final stages, resulting in visible scratches.

Scanning electron microscopy and energy dispersive x-ray spectroscopy (EDS) were used to further examine any change in grain structure and to determine a baseline composition. While the surface shown in Fig. 4 had little change compared to non-cycled Ti-64 lids, the lid shown in Fig. 5 experienced an increase in grain size (consistent with macroscopic observation) and a variation in composition, which is most likely from a phase change. A partial section of the phase diagram for Ti-64, Fig. 6, shows an α to β transition at approximately 1000 °C. The bright “wood-grains” seen in Fig. 5 were shown to contain ~11 wt.% vanadium, which closely matches beta phase

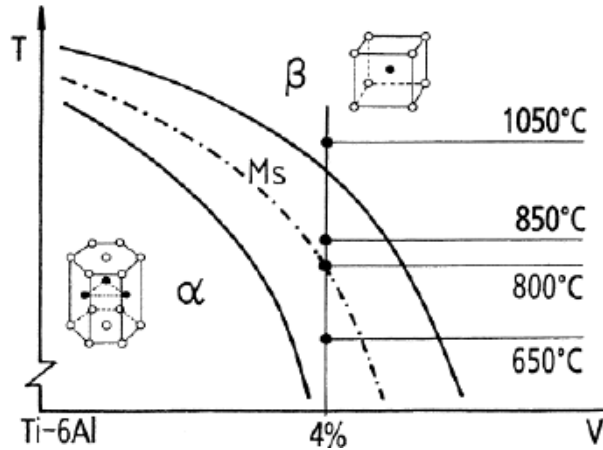


Fig. 6 Phase diagram for Ti-6Al with varying vanadium content [23]

composition at room temperature. Also, as shown in the continuous cooling transformation (CCT) diagram in Fig. 7, Ti-64 results in an $\alpha+\beta$ phase when heated to around 1300 °C and cooled at 10 °C/min (the approximate cooling rate used by the SNS). EDS was done across the lid, starting at the center and moving radially outward. It indicated the vanadium concentration was highest in the center, around 11.5 wt.%, and decreased to the alloy's nominal composition closer to the edge. While this supports that diffusion from the canister body was at work within the vanadium-Ti-64 system, further measurements using an electron microprobe could be used to get a more precise visualization of the diffusion.

Once it was determined that vanadium was diffusing into the Ti-64, the molybdenum was examined using the same technique. According to the binary titanium-molybdenum phase diagram, Fig. 8, molybdenum may experience similar diffusion into the Ti-64 as vanadium. The holes where the molybdenum screws were placed and the areas where the molybdenum washers stuck were examined using EDS. Even at the edge of the hole, no signs of molybdenum diffusion into the Ti-64 lid material were detected. To ensure complete accuracy, this would also require using an electron microprobe.

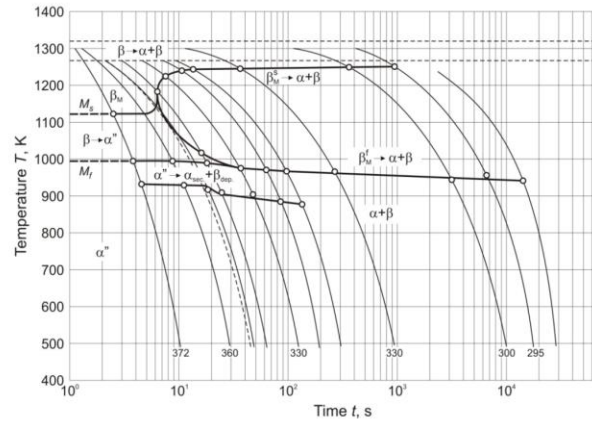


Fig. 7 CCT diagram for Ti-6Al-4V [24]

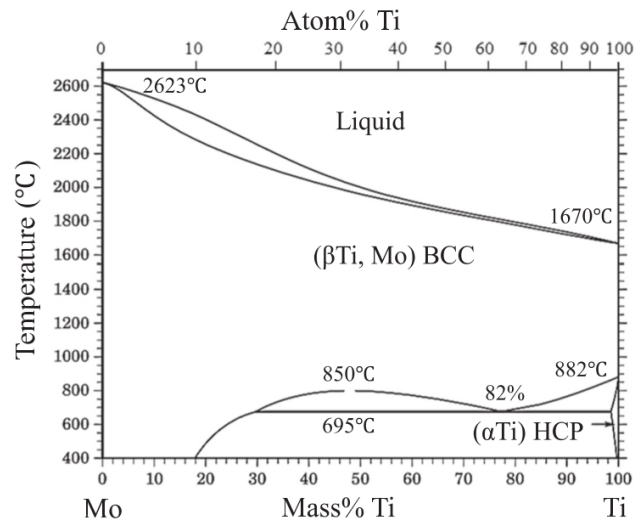


Fig. 8 Mo-Ti binary phase diagram [25]

Optical microscopy was performed on the two lids to analyze the bond. In the sample that showed substantial grain growth and vanadium diffusion, the Ti-64 components were visually estimated to be 75-90% bonded while the other sample was estimated to be 20-30% bonded, as can be seen in Fig. 9. The observed diffusion, grain growth, and increase in bonding were all likely due to a higher operating temperature. These observations suggest the canisters are initiating welds through diffusion bonding.

B. Diffusion Bonding

Diffusion bonding is a high temperature solid-state welding technique used to join similar or dissimilar metals. Atoms diffuse between contacted surfaces under pressure and at elevated temperatures to join the materials. Three components are required for the process. The first is the plastic deformation of the surface under an applied load, which decreases interfacial void space between the surfaces. The load typically causes stresses below the yielding point of the welded material. The second requirement is high temperatures, which, combined with the load, contribute to increased creep and the migration of grain boundaries, further decreasing voids [26]. The bonding temperature often ranges between 50-90% of the melting temperature [27], which accelerates diffusion between surfaces and causes an expansion of the materials, increasing the acting contact area. The third component is the diffusion of material across the interface, forming the bond [26].

Multiple variations of diffusion bonding have been identified depending on criteria including atmosphere, source of pressure, heating and cooling, and system concept [26]. ORNL's neutron scattering sample canisters are observed to initiate solid phase diffusion bonding, a process

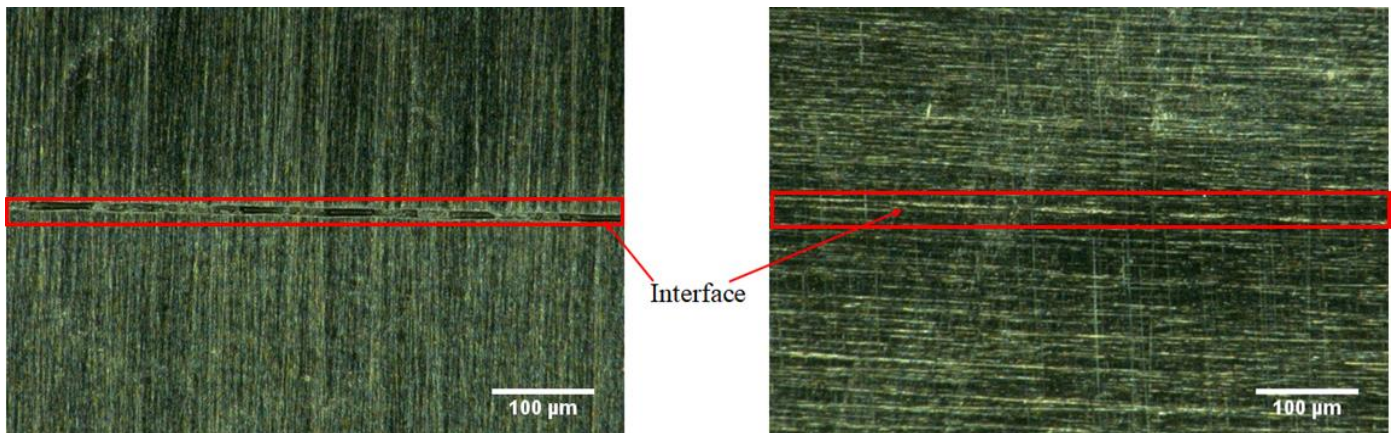


Fig. 9 Optical images of the two lid-flange interfaces: 20-30% fusion (left) and >90% fusion (right)

primarily conducted in vacuum or under an inert gas atmosphere at relatively low pressures (3-10 MPa) to form components for aerospace and nuclear applications. The technique requires a smooth surface finish due to the reduced pressure relative to other diffusion bonding methods. Finishes better than $0.4\text{ }\mu\text{m}$ are advised, and the interface is recommended to be cleaned as thoroughly as possible to reduce weld contamination. Welding at higher pressures through hot isostatic pressing can be done with finishes rougher than $0.8\text{ }\mu\text{m}$, which allows for more complex geometries to be welded [28]. The high concentration of voids seen across the weld interface of the Ti-64 lid and flange can likely be attributed to the surface finish of the components, which was determined through surface topography measurements with a 3D roughness reconstruction software on a Phenom SEM to be $6\text{ }\mu\text{m}$, as seen in Fig. 10. Although such surface roughness would not be conducive to strong bonds in a system where welding is desired, the onset of diffusion bonding still renders the canister unusable by requiring destructive separation to remove samples. Increasing the roughness of the lid or flange surface would likely reduce the strength of the weld but not completely avoid bonding, based on testing by Kadhim et al. with copper and nickel bars [29]. Diffusion bonding conditions like bonding temperature, holding time, diffusion behavior and pressure are some of the factors to consider when evaluating ways to prevent diffusion bonds. Bonding temperature and holding time depend on the requirements of the specific scattering experiment, so reducing pressure is an ideal parameter to consider initially. In the sample canisters,

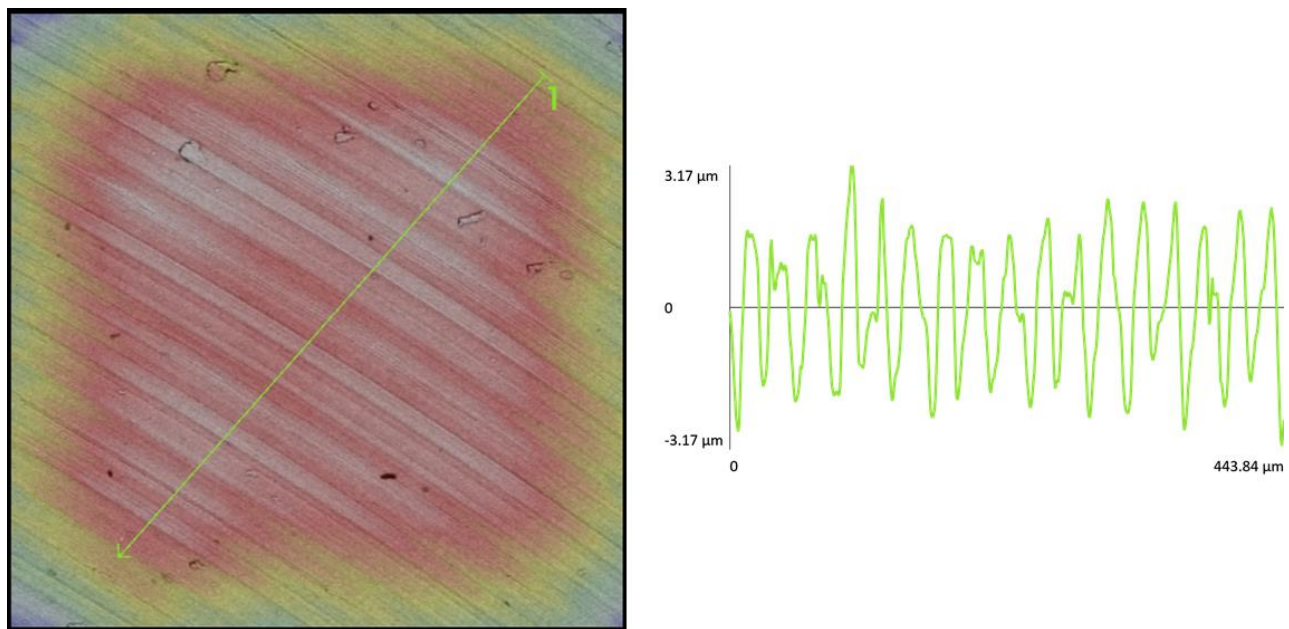


Fig. 10 Surface roughness measurements across the machined surface of the Ti-64 lid

a small physical load is exerted through the hand-tightening of the molybdenum screws when the system is sealed. When the canisters are heated, the primary load is applied through thermal stress from differential thermal expansion. Molybdenum, a low thermal expansion metal, is used as a fixture for the relatively high thermal expansion Ti-64 lid and flange assembly. The lid and flange are restrained from expanding fully when heated, creating thermal stresses that cause plastic deformation of rough surface ridges and ensure the two components stay in close contact during the experiments.

1. Thermal Stress Estimate

The thermal stress concentrations across the interface between the lid and flange at elevated temperatures were estimated using finite element analysis (FEA) of a model of the sample canister in Autodesk's Fusion 360. As the temperature increases during experiments, it is important to note that the thermal and mechanical properties of the materials in the canister will change, especially for Ti-64. While molybdenum is a refractory metal capable of being used in structural applications at elevated temperatures, Ti-64 rapidly loses strength and stiffness in the temperature range between 500 and 700 °C.

Thermal stress concentrations at the interface between the lid and flange are shown in Fig. 11 at 500 and 1000 °C. Stress is heavily localized around the screw holes, where the expansion of the lid and flange is most restrained, and varies across the rest of the surface; at 500 °C, most of the stresses at the interface range between 8 and 13 MPa, but decrease at 1000 °C to between 4 and 8 MPa. By 500 °C, the yield strength in the molybdenum screws has been exceeded and minor

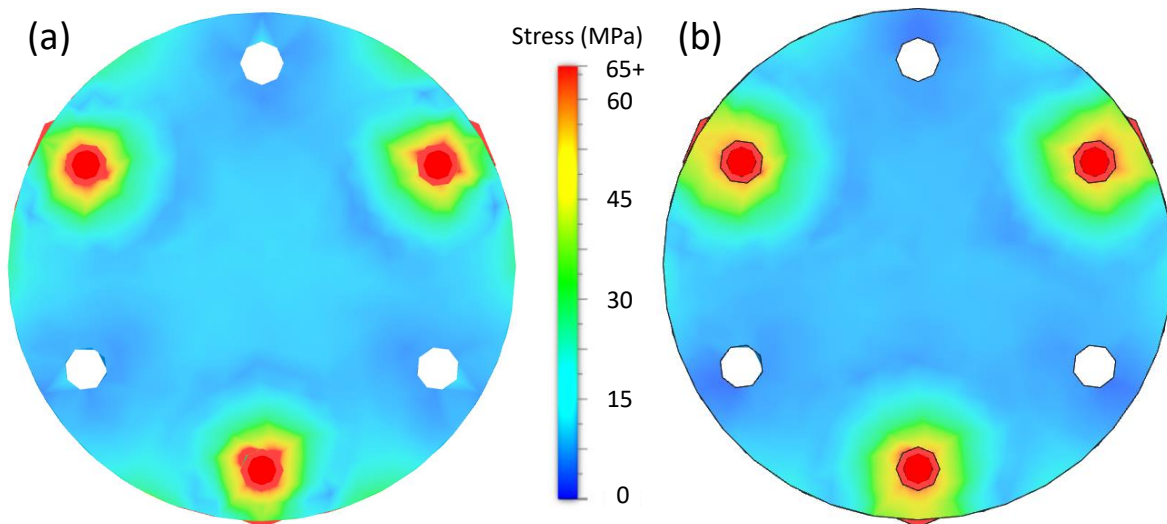


Fig. 11 Thermal stress concentrations across the interface between the canister lid and flange at (a) 500 °C and (b) 1000 °C.

yielding is observed. The development of additional thermal stresses is reduced by the deformation of the bolts, keeping the stress concentrations across the interface relatively constant as temperature increases. At elevated temperatures ($< 700\text{ }^{\circ}\text{C}$), the thermal stress is restrained by the weakened mechanical properties of Ti-64 rather than the deformation of the screws. By $1000\text{ }^{\circ}\text{C}$, the Young's modulus and yield strength of the titanium alloy has decreased to around 15 GPa and 13 MPa, respectively, causing the lid to deform rather than cause further plastic elongation in the screw.

The pressures estimated across most of the interface are consistent with the pressure range for solid-phase diffusion bonding. Considering Lee et al. observed void-free bonding in Ti-64 pressure vessel components after being held at $875\text{ }^{\circ}\text{C}$ and 4 MPa for 1 h [30], diffusion bonding is expected at these pressures, despite the surface roughness of the lid, when combined with the long dwell times (1-4 h) and repeated thermal cycling across multiple measurements during individual experiments.

2. Preventing Canister Bonding

a. Pressure Reduction

Because pressure is a required component of diffusion bonding, reducing pressure at the lid and flange interface could prevent or delay the onset of welding. To decrease applied pressure, the thermal expansion difference should be reduced, which can be done by changing the component materials or by altering the design of the canister. Swapping the molybdenum screws with Ti-64 fasteners may prevent thermal stresses and bonding. Although the high temperature strength and stiffness of Ti-64 normally limits the application of the alloy for screws above $500\text{--}700\text{ }^{\circ}\text{C}$, the only stresses on the bolts should be caused by the weight of the canister. Another potential design change is replacing the current system with the lid and flange assembly in Fig. 12, based off the POWGEN AutoChanger can assembly [31] and using a screw-based design to avoid the need for separate joining components.



Fig. 12 Canister lid and flange assembly, provided by ORNL, using screw threads to join the Ti-64 lid and flange rather than Mo screws.

b. Oxide Coatings

Another way to prevent diffusion bonding would be to separate the surfaces with an intermediate diffusion barrier to prevent contact. Unfortunately, titanium alloys react with nearly all but the most stable elements [32]; while this allows for a wide range of diffusion-based surface treatments to enhance the properties of titanium components, it makes it difficult to prevent unwanted diffusion bonding. Any coating that relies on a chemical reaction during application is likely to react with the other titanium component during an experiment. While a joint formed under these circumstances is weaker than a Ti-Ti solid-state bond, intermediate layers with the highest probability of success will likely utilize an unreactive interlayer.

Oxide coatings are a common diffusion barrier for other metals; diffusion bonding is commonly done in a vacuum or inert-gas atmosphere to avoid high-temperature oxidation, and surfaces are often cleaned and deoxidized prior to diffusion bonding. Titanium, however, is one of the metals most commonly joined in industry through diffusion bonding. The metal has a claim as the easiest of common structural materials to weld by the process because of titanium's ability to dissolve its own oxides around normal bonding temperatures [33]. For many metals, surface oxides can be mitigated in diffusion bonding through increased plastic deformation, although some metals may require high pressures before disrupting an oxide. Films on aluminum alloys can only be bypassed with loads up to 40% the yield strength of the material [34], so it can be preferable to use a method like transient liquid phase diffusion bonding to join such materials. Titanium avoids requiring such practices; diffusion bonding of Ti-64 is often carried out between 850 and 950 °C [30], while TiO_2 , the primary stable titanium oxide at room temperature, decomposes into suboxides including Ti_2O_3 , TiO , and Ti_3O_5 above 180 °C, all of which dissolve into titanium above 400 °C under high vacuum conditions [35]. For this reason, methods to increase the thickness of the oxide layer on the surface of the lid and flange through thermal or electrochemical processes are unlikely to prevent welding, but they may be investigated for thoroughness. Although the lid and flange may both bond to the thick oxide coating of the other component, titanium oxide layers are known to be brittle and susceptible to damage from mechanical impact, preventing them from significantly improving wear resistance in other applications. The bond could potentially be broken, but the reusability of an oxide coating is questionable. A thicker coating, however, is more likely to only increase the time required to initiate bonding. Changing the material of the lid to a different refractory metal with a more stable oxide film would likely not improve canister performance;

many of these metals, including tantalum, tungsten, and niobium, have a high solubility for interstitial contaminants, rendering them prone to joining by diffusion bonding [36]. They also do not have a close enough thermal expansion coefficient to titanium to avoid increasing internally generated pressures.

c. Nitride Coatings

Along with oxides, nitrides are commonly used as both corrosion protection coatings and diffusion barriers. The two most common nitride diffusion barriers are TiN and TaN, but other refractory metal nitrides like WN, NbN, and MoN are also used [37]. Although gas nitriding of the Ti-64 lids may be the most convenient approach to apply an intermediate nitride layer to the canister system [32], nitrogen from the TiN layer that forms at the surface begins to diffuse into titanium between 405 and 475 °C. In multi-layered TiN/Ti/TiN thin film samples, major reactions were observed above 505 °C that led to grain structure modification and growth in thickness of the central Ti layer due to diffusion from the other layers [38], suggesting a TiN layer would react with both the flange and the lid. These reactions were observed at the nanoscale, however, while TiN layers 2-15 µm thick have been easily produced through gas nitriding [32]. The effectiveness of a TiN film at preventing bonding should be tested, due to its ease of application and lack of specialized equipment required for gas nitriding, but a different diffusion barrier like TaN, formed through chemical vapor deposition [39], may perform better.

d. Misc. Ceramic Coatings

Nonreactive ceramic coatings like BN may also perform better as an intermediate layer than titanium oxide. Near-net shape titanium components for aerospace applications can be produced through a combined diffusion bonding/superplastic forming (DB/SPF) method. Multiple titanium sheets are placed in layers into dies, heated at elevated temperatures, and injected with an inert gas at low pressures, typically 0.7-1.4 MPa [33, 40]. A stop-off or release agent like BN or Y₂O₃ is placed on the sheets to prevent bonding in certain locations. The uncoated regions bond together, after which gas is blown between the sheets, causing the coated portions to expand and take on the form of the die [40, 41]. The ceramic agents are often suspended in acrylic binders and may be bought in an aerosol or brush-on form from manufacturers like ZYP Coatings. Initial testing of a ZYP aerosol BN coating by the ORNL sponsors of this project around 700 °C were unsuccessful at preventing bonding, despite ZYP's BN coating's maximum service temperature in vacuum being listed as 1400 °C (Y₂O₃ has a maximum service temperature of 1500 °C in vacuum with

carbon, and 1900 °C without carbon). Pressures during DB/SPF are less than the thermal stresses estimated at the interface between the lid and flange; the high localized pressure around the screw holes may be sufficient to bypass the coatings, so a stop-off agent may perform better when combined with a pressure-reducing canister design. Additional testing is also needed to determine the appropriate layer or thickness of coatings. Coating the surface of the canister flange or lid with a layer of ceramic powder like Al_2O_3 or ZrO_2 could create a cheaper layer thick enough to mitigate the diffusion of oxides into metal, but would likely be messier than an acrylic binder coating and risk contaminating the neutron diffraction sample.

III. PROPOSED EXPERIMENTAL PROCESS

A. Gas Nitriding

The thickness of a TiN layer formed on a titanium alloy through gas nitriding is dependent on nitriding time and temperature [42]. Although the process can take 1-100 h depending on the desired layer thickness [32], 1-10 μm thick layers can be formed by nitriding between 900 and 1100 °C in less than 10 h [42]. Prior to coating, the surface of the components should be cleaned by a technique such as ultrasonic cleaning to remove contaminants that can form brittle hydride phases during nitriding [43]. Gas nitriding should be conducted in a furnace capable of holding a nitrogen atmosphere; the air should be evacuated and refilled with nitrogen gas three times, before heating the components to 1000 °C for 5 h. After initial review of the effectiveness of the intermediate layer at preventing diffusion bonding, nitriding parameters can be customized.

B. Anodizing

Anodizing involves electrode reactions combined with titanium and oxygen ion diffusion, driven by an electric field, to form an oxide coating at the surface of a component [44]. The properties of an anodized oxide coating are determined by electrochemical parameters (voltage, anodizing time, current density), electrolyte specifications (pH, temperature), alloy composition, and surface conditions. The natural oxide film on titanium is 2-7 nm thick; traditional anodizing commonly results in an oxide layer up to hundreds of nanometers [45, 46], while more complicated methods like anodic spark deposition (ASD), that requires a dielectric breakdown to keep the oxide growing, can form coatings up to hundreds of micrometers [47].

Oxide thickness is linearly dependent on cell voltage in traditional anodic oxidation, where thicknesses between 15-30 and 150-300 nm have been formed with voltages ranging between 10

and 100 V with an acidic electrolyte [46]. Although a variety of electrolytes can be used, anode oxidation could be performed in a strongly alkaline solution to produce a coating up to a few micrometers; anodizing in acidic, neutral, or mildly basic solutions forms only comparatively thin coatings less than 200 nm [48]. The technique involves creating a current flow between the titanium component and a counterelectrode, which causes Ti atoms to form Ti^{4+} cations that combine with oxygen anions from the electrolyte solution to form a TiO_2 layer [45]. The oxide has a higher resistivity than the electrolyte and metallic components of the anodizing setup, so will continue to grow until the electric field can no longer drive ions through the coating [44]. Similar to gas nitriding, a chemically clean surface is required for successful anodizing. The components should be cleaned through ultrasonic cleaning, and then etched or deoxidized with a solution like NH_4HF_2 or HF to improve anodizing uniformity.

If the diffusion bonding is still observed in samples anodized at voltages up to 100 V, a thicker oxide layer formed through ASD may be investigated. When the breakdown voltage of the coating is passed, the oxide continues to grow but increased gas evolution and sparking is observed. The current concentrates in small areas in the oxide, characterized by defects or localized stress states. The electric field increases rapidly in these locations and causes atom ionization. Electric discharges between the weak spaces create sparks, whose energies damage the oxide and create microcracks and porosity [44, 45, 47]. In ASD, a metal ion from the electrolyte solution (such as phosphorus, silicon, or aluminum) is incorporated into the oxide [45]; doping the coating with a specific element could help prevent diffusion bonding. Success may also be found by oxidizing one component of the canister while nitriding the other, although the oxidized component may not be reusable for multiple thermal cycles.

C. Alternative Surface Treatments

The intentional formation of oxide layers (aside from anodization), and the use of intermediate materials can also be used to reduce diffusion bonding. The high temperature requirement and the affinity of titanium to diffusion bond eliminates most metals (and all polymers) as possible intermediaries. A thin, native oxide layer is typically present within titanium and its alloys which lends itself to the corrosion resistance at low temperatures ($<550\text{ }^\circ\text{C}$) [49]. Because of titanium's tendency to dissolve its oxide, this film cannot act as an effective diffusion barrier. A possible solution is to create a thicker coating, on the order of multiple micrometers, by applying an Al_2O_3 or ZrO_2 powder coating on the lid and flange components. This layer could be added prior to

experiments and fired to avoid contaminating the experimental sample with loose powders. As seen in Fig. 13, the aluminum from Al_2O_3 has been shown to diffuse hundreds of micrometers in titanium during diffusion bonding, so the dissolution of the oxide layer is likely unless a macroscopic oxide layer on the order of millimeters is applied. Lower levels of diffusion than that seen in Fig. 13 are expected, as no pressure will be applied during the firing step and experiments will have shorter dwell times than 100 h. A sufficiently thick enough ceramic layer may prevent diffusion bonding, although may be cracked by the stress at the interface.

Companies like ZYP also make ceramic paints that could be applied to the system in varying thicknesses as a barrier to bonding.

Commercially available coatings include BN and Y_2O_3 , which are rated up to between 1400 and 1900 °C in vacuum environments and are known to be relatively inert to titanium alloys (as demonstrated by the nonreactive BN canister lids). This coating solution would be easily applied, as it can be sprayed on or brushed and fired at low temperatures to remove organic binders. The coating can be removed easily through mechanical means for minimal maintenance between experiments. Solid intermediates can also be used. Quartz wool is used as insulation in furnaces and would therefore be rated to the necessary temperature. Other benefits would be its ease of use, and reusability.

D. Surface Roughening

Surface mapping was used to determine that the roughness of the Ti-64 lids was about 6 μm as shown in Fig. 10. As stated previously, diffusion bonding has three requirements: (1) pressure, (2) temperature, and (3) ability of the material to diffuse across the interface to form the bond. If

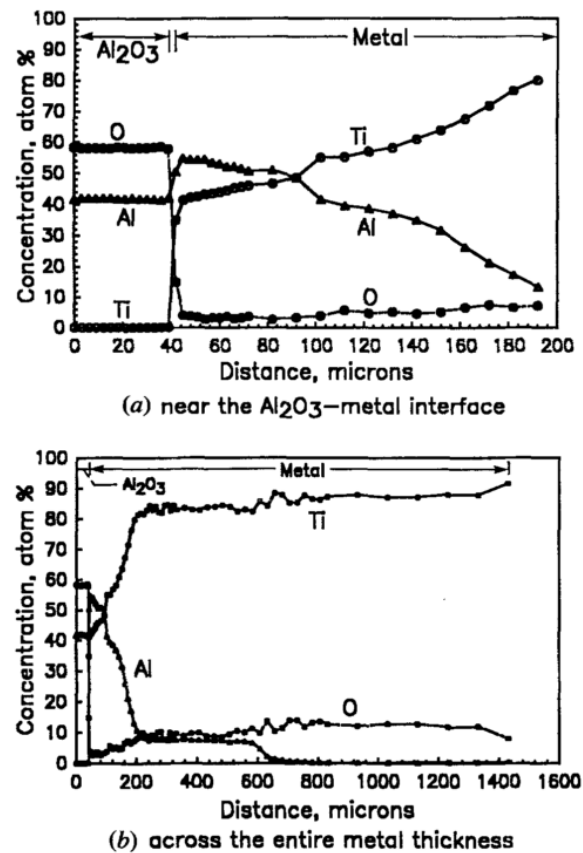


Fig. 13 Concentration profiles of Ti, Al, and O across the Al_2O_3 -metal interface of an Al_2O_3 /Ti diffusion couple bonded at 1200 °C for 100 h near the interface (a) and across the entire thickness of the Ti sample (b) [50]

pressure cannot be sufficiently reduced, the ability to diffuse must be limited. One method to do this is to limit the interface contact. A study performed by Somekawa and Higashi on AZ31 (Mg-Al-Zn alloy) showed an almost 1 to 1 increase in required bonding time with increasing surface roughness. Their study showed a 7.5 times increase in bonding time with a 6.75 times increase in surface roughness [51]. Therefore, a possible solution to reduce or eliminate diffusion bonding in the canister system would be to roughen the lids and flanges once received. To experimentally determine the effectiveness of this approach, a series of sandpaper grits would be required. The as-received surface roughness would be roughly equivalent to 3000 grit ($\sim 6 \mu\text{m}$) as shown in Fig. 10. Commercially available sandpaper from a local Lowe's or Home Depot commonly range from 1500 ($\sim 14 \mu\text{m}$) to 40 grit ($>150 \mu\text{m}$). Using the lowest grit to provide the largest scratch sizes would seemingly provide the best results. However, there may exist a point where the scratches no longer impact diffusion bonding and may begin to negatively impact the sample canister system through factors including the tolerance of the parts and the seal between the lid and the flange.

E. Pressure Reduction

In the current canister system, pressure is applied by molybdenum screws holding the Ti-64 lid and flange assembly together. The current design calls for six screws to be used to connect the lid and the flange. However, since a tight seal is not required in the canister, only three screws are used, which coincidentally acts to reduce thermal stresses at the surface from the thermal expansion mismatch of Ti-64 and molybdenum ($\Delta\alpha = 3.8 \times 10^{-6} \text{ K}^{-1}$) [18, 52]. A proposed alternative lid and flange assembly can be seen in Fig. 12. This alternative design addresses the issue of thermal expansion mismatch and eliminates the need for molybdenum screws. Therefore, within the lid/flange section, where diffusion bonding is occurring, the only thermal expansion mismatch that would be present near the interface is between the vanadium canister body and the Ti-64 flange. However, the thermal expansion coefficients of these materials are almost identical ($\Delta\alpha = 0.2 \times 10^{-6} \text{ K}^{-1}$) [17, 18], making the mismatch negligible. This design also ensures a more uniform pressure distribution.

F. Testing

To test these alternative processes and designs, samples simulating the lid and flange assembly will be prepared with the outlined coatings or diffusion barriers and submitted to a furnace run that will simulate high temperature neutron diffraction experiments. The alternative lid and flange

assembly will also be compared to the current design. Each sample will be heated in a vacuum environment to 600, 700, 1000, 1300, and 1600 °C with a 10 °C/min ramp rate. Samples will dwell at each temperature for 2 h before being cooled to room temperature with a 10 °C/min ramp rate. After thermal cycling to each temperature, the design modifications will be characterized for bonding, interface integrity, and size changes, and unbonded canisters will be subsequently tested at the next temperature. Microscopy of any bond canisters should be used to evaluate the degree of bonding and diffusion between the intermediate layers and the Ti-64 components.

IV. CONCLUSION

In this report, the design and materials selection rationale of sample canisters used in high temperature powder neutron diffraction experiments at the SNS and HFIR has been described. The bonding of the lid and flange assembly, observed after experiments above 700 °C, was characterized. The process through which this bonding occurred was determined to be diffusion bonding, a solid-state welding technique. Alternative processes and designs were suggested to improve the reusability of the sample canisters. These proposals have been primarily suggested for ORNL facilities but can likely be applied for use at other neutron diffraction facilities utilizing high temperature powder neutron diffraction if they prove successful. Future developments will be aimed at evaluating the bonding prevention, ease of application, and durability of the processes and designs, potentially during a future senior design project.

APPENDIX

Table 1: Properties of materials used in sample canister assembly

Properties	Vanadium [17]	Ti-6Al-4V [18]	Molybdenum [52]	Niobium [53]	Boron Nitride [54]
Thermal Properties					
T_M (°C)	1890	1610 - 1660	2604 - 2621	2454 - 2466	2282 - 2382
Max. Service Temp. (°C)	380 - 530	350 - 420	866 - 1310	549 - 738	1638 - 1721
Thermal Expansion Coefficient (10^{-6} K^{-1})	8.4	8.6	4.8	7.1	1.2
Recrystallization Temperature (°C)	800-1010	700-750	900-1300	980-1205	N/A
Oxidation Temperature (°C)	675	1200	600	400	430
Mechanical Properties					
Young's Modulus	18.1 - 21.8	16 - 17	45.7 - 48.6	14.5 - 16	6.96 - 7.25
Yield Strength	58 - 76.9 (ksi)	114 - 155 (ksi)	1.03e7 - 1.1e7 (lb _f .ft/lb)	12.3 - 15.2 (ksi)	3.92 - 4.35 (lb _f .ft/lb)
Hardness (HV)	120 - 200	332 - 420	200 - 290	110 - 160	200 - 300
Fracture Toughness (ksi.in ^{1/2})	63.7 - 114	74.6 - 104	18.2 - 36.4	81.9 - 109	4.1 - 5.01
Toughness (ft.lb/in ²)	18.1 - 50.9	28.4 - 54.7	0.642 - 2.14	37.3 - 64.2	0.198 - 0.291
Price					
Price (USD/lb)	141 - 181	9.3 - 10.8	7.26 - 11.8	52.6	16 - 23.5
Price/unit volume (USD/ft ³)	5.32e4 - 6.97e4	2.49e3 - 2.97e3	4.59e3 - 7.59e3	2.83e4 - 2.86e4	2.23e3 - 3.34e3
Neutron-Diffraction Related Properties					
Coherent Cross-Section (b) [8]	V: 0.0184	Ti: 1.485	Mo: 5.67	Nb: 6.253	B: 3.54
		Al: 1.495			N: 11.01
		V: 0.0184			
Incoherent Cross-Section (b) [8]	V: 5.08	Ti: 2.87	Mo: 0.04	Nb: 0.0024	B: 1.7
		Al: 0.0082			N: 0.5
		V: 5.08			
Neutron Activation [55]	Moderately (68.5 m)	Moderately (56.9 m)	Activated (18.5 days)	Moderately (94.9 m)	No (0.186 s)
	V-51: HL 3.75 m	Ti-50: HL 5.8 m	Mo-100: HL 14.6 m	Nb-93: HL 6.2 m	B-11: HL 0.0203 s
		Al-27: HL 2.246 m	Mo-92: HL 6.9 h		
		V-51: HL 3.75 m	Mo-98: HL 66 h		

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