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FUSION WELDING OF REFRACTORY METALS

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Abstract

The refractory metals of Groups VB and VIB and their alloys display a variety of unique physical and mechanical characteristics in addition to their high melting points. In turn, these characteristics make these materials strong candidates for severe service and specialized applications. However, these materials also present a variety of challenges with respect to both fabrication weldability and the in-service behavior of weldments, many of which are related to the dominant effects of interstitial impurities. This work reviews current understanding of the physical and joining metallurgy of these metals and their alloys with emphasis on fusion welding. Of specific interest are the role of impurities and alloy chemistry in fabrication and service weldability, the material processing route, *eg*. vacuum melting *vs*. powder metallurgy, the importance of welding process procedures and variables, weldment mechanical properties, and fracture behavior. Specific examples from the various alloy systems are used to illustrate general metallurgical and joining characteristics of this class of materials.

Introduction

The term refractory metal is generally reserved for those elements in Groups VB and VIB of the periodic table which have melting points exceeding 2000°C. This includes the metals in periods 5 and 6 of those groups; niobium, tantalum, molybdenum, and tungsten. The metals vanadium and chromium, which are also from Groups VB and VIB, have significantly lower melting points, have not found wide application as the basis for alloy systems, and are thus not normally considered as members of this class of materials. The metals iridium and rhenium, although refractory in terms of their melting points, are relatively scarce and have not found as wide a range of applications as the Group VB or VIB metals. They are not included in this review.

As their name implies, many of the initial uses for the refractory metals were those applications requiring high temperature service. For example, tungsten and its alloys have been used for many years in lamp filaments and electrodes for gas-tungsten arc welding. Other early applications for the refractory metals were in electron tube components such as heater filaments, grids, and electrodes. More recently, however, refractory metals have been used in a variety of other industries and structural applications. In general, the use of these alloys can be roughly divided among applications in the aerospace and nuclear industries, the electronics industry, chemical process industries, and other special applications. Examples of many of the applications for the refractory metals can be found in reference (1).

While the variety of applications has increased, the number of alloys based on the refractory metals has also increased. In turn this increase has resulted in the availability of alloys with a wide range of properties. Taken as a group, however, these alloys present similar challenges with respect to fabrication weldability and the service behavior of weldments. Consequently, in addition to normal alloy selection criteria, ease of fabrication is often a major consideration in determining the suitability of refractory metals relative to other alloy systems, or in selecting one refractory alloy over another. In this work the physical metallurgy of the refractory metals and alloys is considered with respect to its influence on fusion welding behavior.

Pure Metals The metals considered in this work all have the body-centered cubic crystal structure and melting points above 2000°C. The metals are generally produced as powders which are subsequently consolidated by melting or powder metallurgy techniques. Both vacuum arc and electron beam melting can be used, although electron beam melting is generally reserved for niobium and tantalum. Sheet bar and solid rounds suitable for final processing are then produced by extrusion or hot forging of the ingots or powder compacts (1). Strain hardening is the principal strengthening mechanism for the pure refractory metals. Thus, in terms of high temperature applications and fusion welding processes, recovery, recrystallization, and grain growth behavior are important characteristics of these materials. These are discussed in subsequent sections.

Alloys In common with other metallic systems, alloying is a principal method for tailoring the properties of refractory metals. Consolidation of alloys is accomplished through methods similar to those used for the pure metals. The compositions of several commercially important refractory metals are listed in Table I.

As with the pure metals, a principal strengthening mechanism in the refractory alloys is through strain hardening. Therefore, a primary aim of alloying is to retain the worked structure by stabilization of dislocation substructures, increasing recrystallization temperatures, and retarding grain growth. Further strengthening of the refractory alloys is achieved through solid solution strengthening and dispersion hardening (either through precipitation processes or mechanical alloying). Alloying elements are also used to enhance specific properties such as atmospheric corrosion resistance. Additions of reactive elements (*eg*. Ti, Zr, and Hf) reduce the sensitivity for embrittlement by oxygen, nitrogen and hydrogen as well as provide a means for precipitation hardening and grain size control. For an informative and interesting discussion of strengthening mechanisms in refractory metals the reader is referred to early reviews by Chang (2) and Wilcox (3). A review of recent refractory metal and alloy development can be found in ref.(4).

Welding Processes The refractory metals are commonly fusion welded by gas-tungsten arc welding (GTAW), electron beam welding (EBW), and laser beam welding (LBW) (5). The choice of welding process is often governed by the ability of the process to maintain the highest purity in the welding environment, and for this reason other welding processes such as shielded metal arc are not used. Compared with other alloy systems, the total production volume of refractory metal structures is small, so that other higher production rate processes are usually not considered. Specific considerations regarding welding process and parameter selection are presented in subsequent sections.

Table I. Compositions of some commercially important refractory metal alloys (1).

Alloy Designation	Nominal Composition (wt%)
Mo-0.5 Ti	Mo-0.5Ti-0.02W
TZM	Mo-0.5Ti-0.1Zr-0.02W
Mo-30W	Mo-30W
Mo-Re alloys	Mo-50Re most common
Nb-1Zr	Nb-1Zr
FS-85	Nb-27.5Ta-11W-1Zr
SCb-291	Nb-10Ta-10W
Cb-752	Nb-10W-2.5Zr
B-66	Nb-5Mo-5V-1Zr
C-103	Nb-10Hf-1Ti
C-129Y	Nb-10W-10Hf-0.15Y
"63" Metal	Ta-2.5W-0.15Nb
Ta-10W	Ta-10W
T-111	Ta-8W-2Hf
T-222	Ta-10W-2.5Hf-0.01C
Thoria Dispersed W	W-1ThO$_2$, W-2ThO$_2$
W-Mo alloys	W-2Mo and W-15Mo most common
W-Re	W-1.5Re, W-3Re, W-25Re most common
Doped W	50 ppm Si, 90 ppm K, 15 ppm Al, 35 ppm O

Fabrication and Service Weldability

Thermal Requirements The thermal requirements for producing fusion welds in the refractory metals, and indeed all materials, are governed by the thermophysical properties of the material. In this respect the refractory metals differ from one another as well as from other, more common, structural materials. Table II compares several important thermophysical properties of the refractory metals with those of common structural alloys. An obvious feature of this comparison is the significantly higher melting points of the refractories relative to the other alloys. As a first assumption, the high melting points would appear to indicate that welding heat input requirements should exceed that required for the more common alloys. Simple comparison of melting temperatures does not, however, provide a complete picture of the thermal requirements for producing welds in the refractory metals and a more rigorous analysis must include the heat capacity, latent heat of fusion, and thermal conductivity for the various materials. These properties are also shown in Table II. Note that many of the thermophysical properties of Table II are given in volumetric terms. The data are presented in this manner since, in general, welded structure design is based upon weld volume (as it is reflected in penetration or load capacity requirements). The volumetric heat capacities of the refractory metals near room temperature are similar and are low in comparison with common alloys. These values are somewhat misleading since heat capacity tends to increase with increasing temperature and the rate of change with temperature varies among the metals. Similarly, the enthalpy of fusion is not, in itself, a completely reliable indicator of the relative heat input required to melt a given volume of material. The second to last column of Table II shows the calculated enthalpy required to heat each material from room temperature to its melting point plus that required for melting on a volumetric basis. Niobium is seen to be similar to A36 steel while tantalum has somewhat higher thermal requirements and molybdenum and tungsten require significantly higher heat inputs. Clearly, these thermal requirements influence the choice of appropriate welding processes for the refractory metals.

In fusion welding, thermal conductivity is also an important factor affecting heat input requirements. Thermal conductivity becomes increasingly important at low travel speeds where heat conduction into the base material acts to reduce the relative quantity of heat available for melting. In addition, the high thermal conductivity of the Group VIB metals results in a tendency for large weld beads at low travel speeds and promotes a wide heat-affected zone (HAZ). The high thermal conductivities must also be carefully considered in fixture design and materials selection. For a given fixture design, the fixture is likely to be subjected to significantly higher temperatures for those materials with the highest melting points and highest thermal conductivities (*eg.* Mo and W). High thermal conductivity is also a consideration in applications where temperature sensitive components are located near the weld zone.

The coefficients of thermal expansion of the refractory metals are substantially lower than those for other structural materials (Table II). These low expansion coefficients imply that joint and fixture design are less stringent for the refractory metals since weld restraint is generally related to the amount of shrinkage encountered during weld cooling. However, it is important to note that the temperature range over which shrinkage occurs is much larger for the refractory metals, so that the total strains involved may be substantial. In addition, as will be seen in subsequent sections, as-solidified (*ie.* fusion zone) and recrystallized (*ie.* HAZ) refractory metals often display comparatively limited ductilities. Further, the strength levels in the weld zone are often dramatically lower than that for wrought base metals, so that that shrinkage strains are essentially accommodated entirely in the weld zone. The net result of the preceding considerations is that, in spite of the low expansion coefficients, the refractory metals are generally very sensitive to joint and fixture design. Low restraint joint designs which serve to minimize the flow of heat into the base metal, such as standing edge welds, are thus preferable and often required.

Table II. Thermophysical properties of the refractory metals compared with several common structural materials (6,7).

Metal or Alloy	Melting Point or Range (°C)	Density at 20°C (g/cm^3)	Thermal Conductivity (W/m·K) (a)	Coefficient of Expansion (μm/m·K) (a)	Mean Specific Heat (J/cm^3·K) (a)	Enthalpy of Fusion (J/cm^3) (b)	Enthalpy of Heating + Melting (J/cm^3) (c)
Niobium	2467	8.6	54.1	7.2	2.31	2711	9885
Tantalum	2980	16.6	57.6	6.5	2.36	2264	10917
Molybdenum	2615	10.2	137	5.1	2.56	4159	13624
Tungsten	3387	19.3	174	4.5	2.66	3689	15043
ASTM A36	1478-1516	7.86	51.2	12.1	3.82	1940	9500
AISI 304	1400-1455	8.0	16.3	17.3	4.02	2230	9330
IN718	1260-1336	8.19	11.4	13.0	3.56	2530	9800

(a) Mean values for the temperature range 20-100°C.
(b) Values for alloys are estimates.
(c) Values calculated for heating from room temperature to melting using temperature dependent heat capacities and include heat of fusion.

The high melting points of the refractory metals also have an indirect influence on fusion welding behavior through their influence on the method of consolidation. Because of the difficulties and expense associated with melt processing of high temperature alloys, many of these materials are processed by powder metallurgy techniques. As will be discussed in subsequent sections, the fusion welding of powder metallurgy alloys is generally inferior to melt processed versions.

Weld Defects - Solid State Cracking A principal form of welding defect in the refractory metals is weld cracking. Typically, weld cracking in the refractory metals occurs in the form of centerline separation and an example of this type of defect is shown in Fig. 1. The micrograph shows the as-welded surface of the fusion zone of a butt weld in 0.5 mm thick molybdenum sheet. Although some relief is seen at the column boundaries of the solidification structure, the cracking is concentrated entirely at the weld centerline. The cracking shown in Fig. 1 is intergranular and in general a variety of factors can influence the tendency of these materials to form cracks during welding. The first of these factors was mentioned in the previous section and involves the relationships between shrinkage stresses and differences in strength between the wrought base metal, the recrystallized HAZ, and the as-solidified fusion zone. Figure 2 shows the yield and tensile strengths for the tantalum alloy T-111 as a function of temperature (8) and is representative of the behavior of the refractory metals in general. In essence these curves approximate the instantaneous tensile properties of the various zones of a weldment during cooling (with the recrystallized curves representing the fusion zone plus HAZ and the stress relieved curves representing the base metal). As shown, at temperatures below approximately 1500°C, the strength levels for recrystallized material are significantly below that of the strain hardened. If the weld joint is heavily restrained most of the shrinkage strain must be accommodated in the fusion zone and HAZ, with the possible result that the ductility of the material is insufficient to completely accommodate this strain. In reality the situation is more complex since there can be significant differences in the strength of the fusion zone compared with the HAZ and strength differences across the HAZ. The strength differences between the fusion zone and HAZ result from the strong grain size dependence of yield and tensile strength in the body-centered cubic metals and the refractory metals in particular. This dependence is illustrated for niobium in Fig. 3, where increases in grain size of a factor of 10 result in yield strength decreases on the order of 40-50%. Therefore, neglecting other possible strengthening mechanisms, in many cases the deformation can be concentrated principally in the fusion zone.

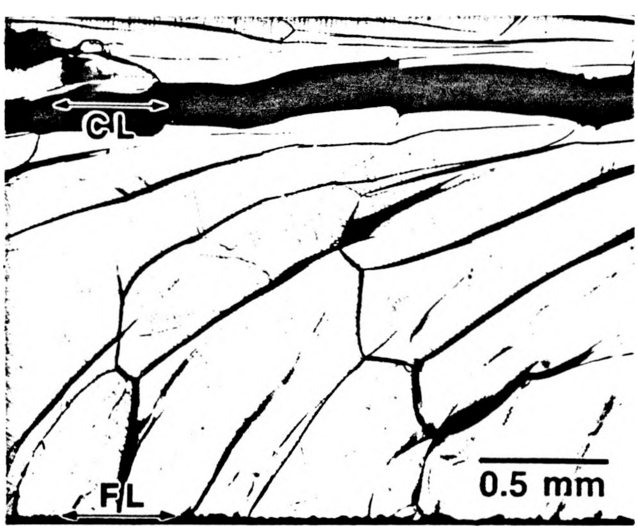

Figure 1. Micrograph of as-welded surface of butt weld in 0.5 mm thick Mo sheet illustrating a centerline crack. CL and FL indicate weld centerline and fusion line, respectively.

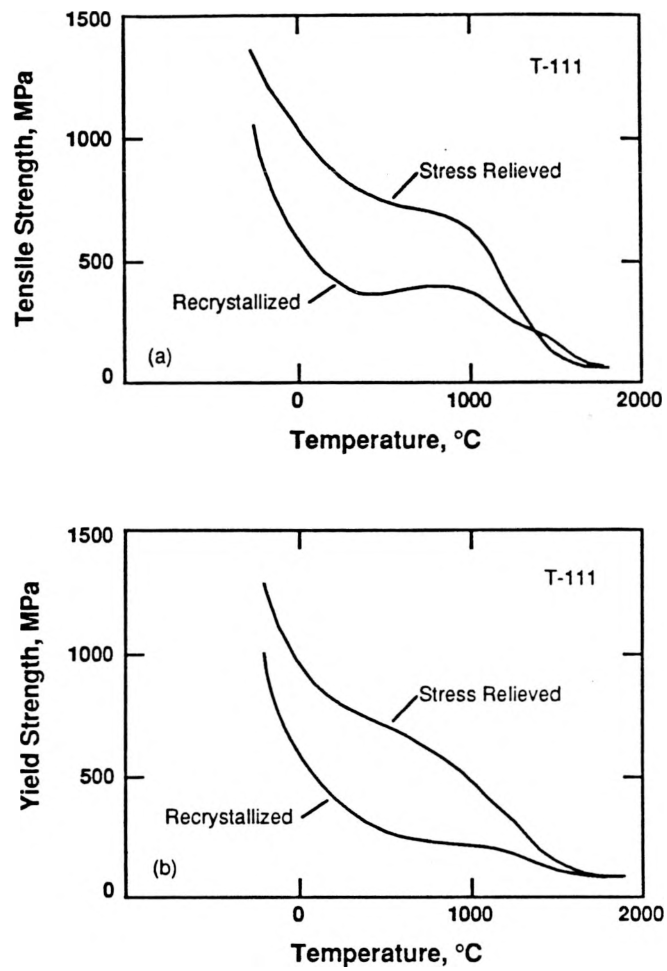

Figure 2. Temperature dependence of (a) yield stress and (b) tensile stress for tantalum alloy T-111 in recrystallized and stress relieved conditions (8).

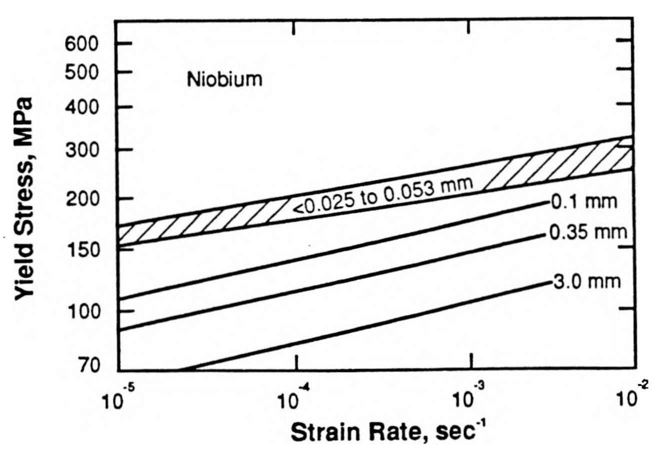

Figure 3. Typical effects of grain diameter and strain rate on the yield stress of niobium (9).

Since there is no nucleation event in fusion welding, the as-solidified grain size in the fusion zone is related to the grain size in the HAZ. Thus, recrystallization and grain growth in the HAZ influences the final grain structure in both the HAZ and fusion zone. This influence can be seen in Fig. 4 which compares the HAZ and fusion zone grain sizes for welds in vacuum arc cast and powder metallurgy molybdenum. In the arc cast molybdenum, grain growth in the HAZ is essentially unrestrained and the fusion zone grain size is large. For the PM material grain growth in the HAZ is restricted by aluminum and calcium oxide inclusions, and a smaller fusion zone grain size results.

As might be expected, recrystallization and grain growth effects are usually more important in pure metals than in highly alloyed materials. Figures 5 (a)-(c) show the effects of alloy additions on the recrystallization behavior and resulting properties for three different types of strengthening mechanisms. The three strengthening mechanisms include solid solution strengthening (Fig. 5(a)), precipitation hardening (Fig. 5(b)), and oxide dispersion strengthening (Fig. 5(c)). For each of the hardening mechanisms the onset and completion of recrystallization is deferred to higher temperatures (and longer times), and for a given thermal cycle higher strengths are observed. In this way, alloying elements generally reduce the tendency for solid state shrinkage cracking since they reduce strain localization in the weld zone. Alloying

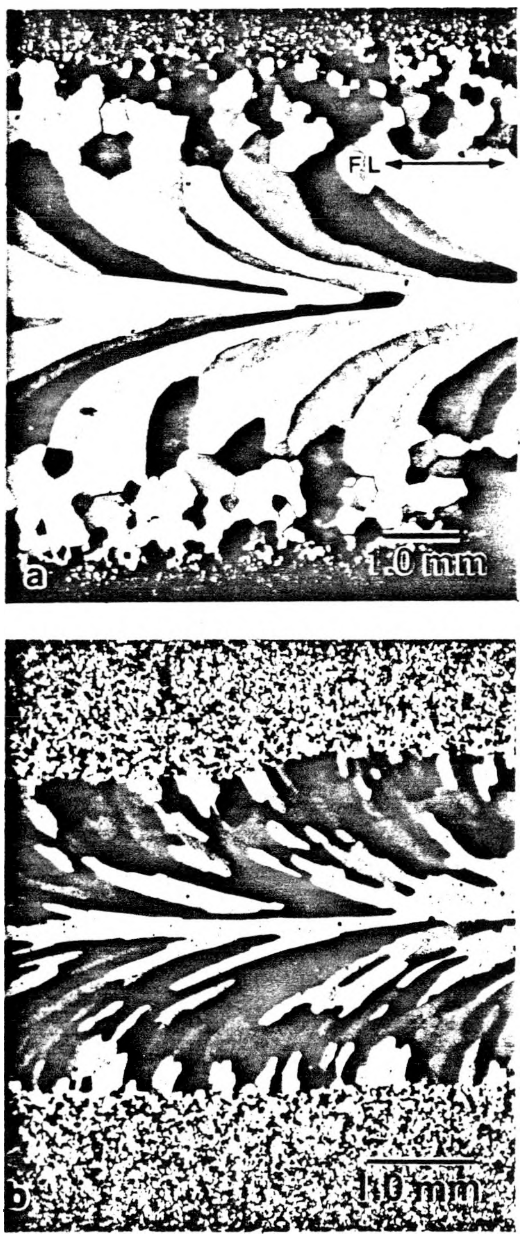

Figure 4. Comparison of grain structure in HAZ and fusion zone of GTA welds in (a) arc cast and (b) powder metallurgy molybdenum. Full penetration welds in 0.5 mm thick sheet.

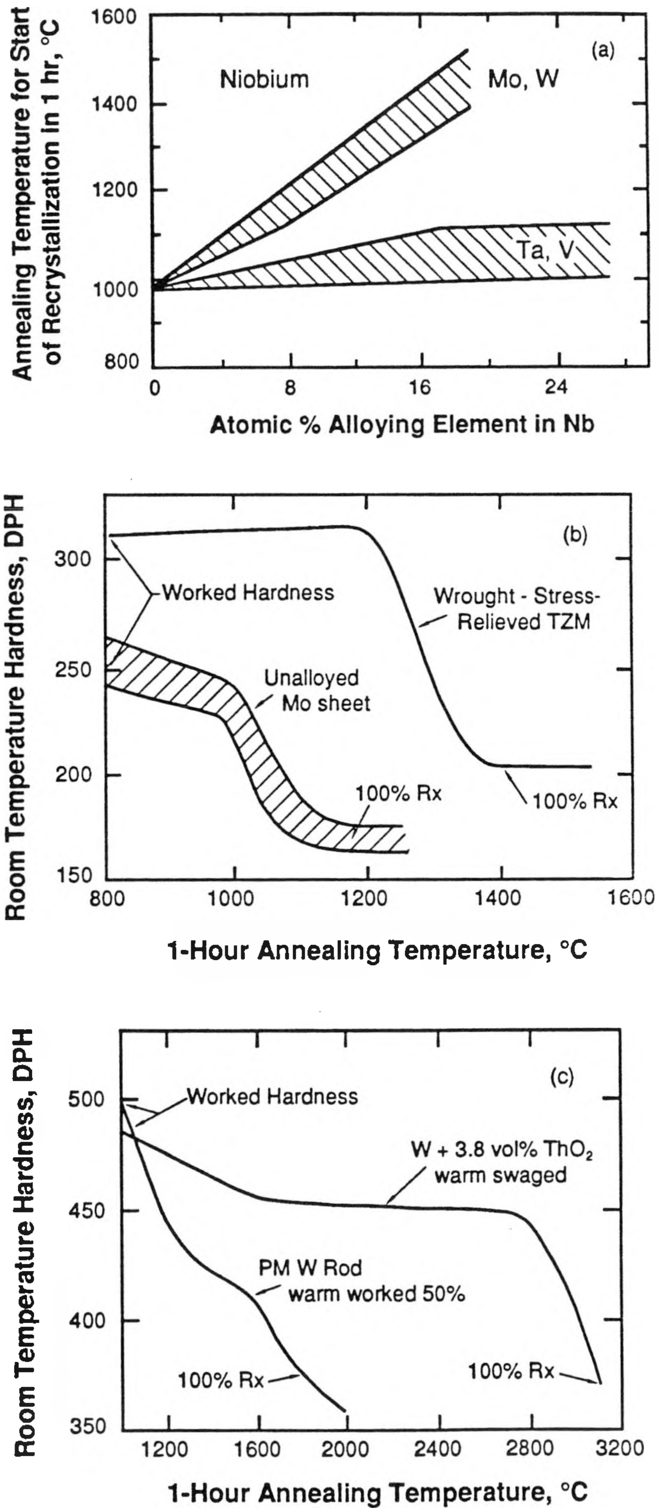

Figure 5. Influence of (a) solid solution additions, (b) precipitation, and (c) dispersed particles on the recrystallization behavior of refractory metals (3).

elements can, however, have adverse effects on the solidification characteristics (*eg*. hot cracking) tendency of the refractory metals. Pulsed welding processes have been shown to result in refinement of weld zone grain sizes (11). However, pulsed processing generally reduces the level of weld restraint required for solid state weld cracking (increased thermal shock) and is likely to increase the incidence of hot cracking.

The localization of shrinkage strains in the fusion zone is a further illustration of the importance of fixture design in the fabrication weldability of the refractory metals. As mentioned previously, heating of fixtures can be significant for those metals with high melting points and high thermal conductivities. As a result, it is generally desirable, and often imperative, to utilize fixture materials and designs which have a minimal contribution to strains in the weld zone.

Strain localization has been cited as a principal cause for the apparently low ductility of welds in refractory metals (12, 13). Since the weld zone is of appreciably lower strength than the base metal, transverse tensile tests (which include base metal) of weldments under nominal strain rates result in abnormally high strain rates and lower apparent ductilities in the weld zone. Both joint design and location within welded structures must therefore be considered in this light.

Ductile to Brittle Transitions The fabrication and service weldability of the refractory metals are strongly influenced by their tendency for brittle behavior with decreasing temperature. This tendency is shown in Figs. 6 and 7 in terms of reduction of area in tensile tests. The temperature associated with the transition depends on a variety of factors, including testing conditions (stress state, strain rate), microstructure (degree of cold work, grain size, grain shape, orientation) and the content of interstitials and substitutional alloying elements (10). As a general rule, alloys which display tensile ductile to brittle transitions near or above room temperature are likely to be strongly susceptible to cracking in the weld zone.

Low temperature slip in the refractory metals is similar to iron, and occurs in ⟨111⟩ directions. However, the refractory metals (except tungsten) slip on fewer planes having a ⟨111⟩ direction. The slip planes for iron are the {110}, {112}, and {123} planes, whereas slip in the refractory metals generally occurs exclusively on {110} (although tantalum and tungsten also display a limited ability to slip on {112}). Cleavage fracture in the refractory metals is also similar to iron, with a {100} family of planes being operative. Tantalum and molybdenum also cleave on {110} and {111} (10). Because of the similarity between iron and the refractories in terms of crystal structure, slip, and cleavage fracture, the underlying mechanisms responsible for ductile to brittle transitions are also similar (see for example reference 14). The subtle differences between iron and the refractories in these same terms cause the refractories to be generally more susceptible to problems (such as weld cracking) associated with ductile to brittle transitions. In terms of service behavior, the increased grain size of the weld zone (both fusion zone and HAZ) indicates that the weld will likely have a transition temperature exceeding that of the base metal (14). A similar generality also holds for fracture toughness, so that the design of refractory metal structures must reflect this reality.

It is important to note that the refractory metals, and in particular molybdenum and tungsten, can also fail by grain boundary fracture. This mode of failure is more insidious than cleavage fracture since it generally occurs at lower stress levels and often before any appreciable (and in many cases measurable) plastic deformation. For fusion welding, intergranular failure is particularly severe since the weld centerline often consists of a grain boundary oriented perpendicular to the transverse shrinkage stresses. Grain boundary failure at the weld centerline is seen in the molybdenum weld of Fig. 1.

Interstitial Impurities To a large extent, the fabrication weldability of the refractory metals is dominated by the interaction of these materials with impurity elements. In particular, those elements of

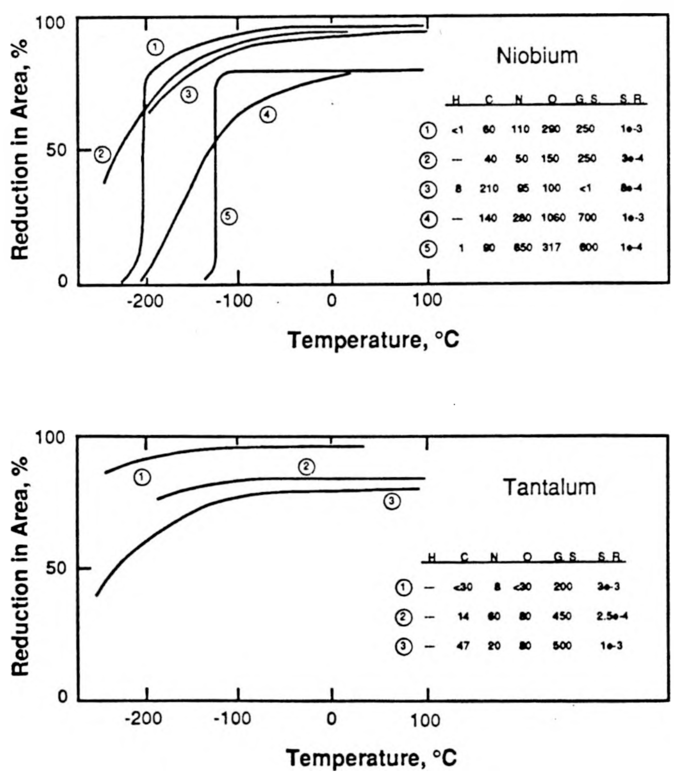

Figure 6. Ductile to brittle transition behavior of recrystallized Group VB metals as a function of composition (10). G.S. indicates grain size in grains/mm. S.R. indicates strain rate in sec^{-1}.

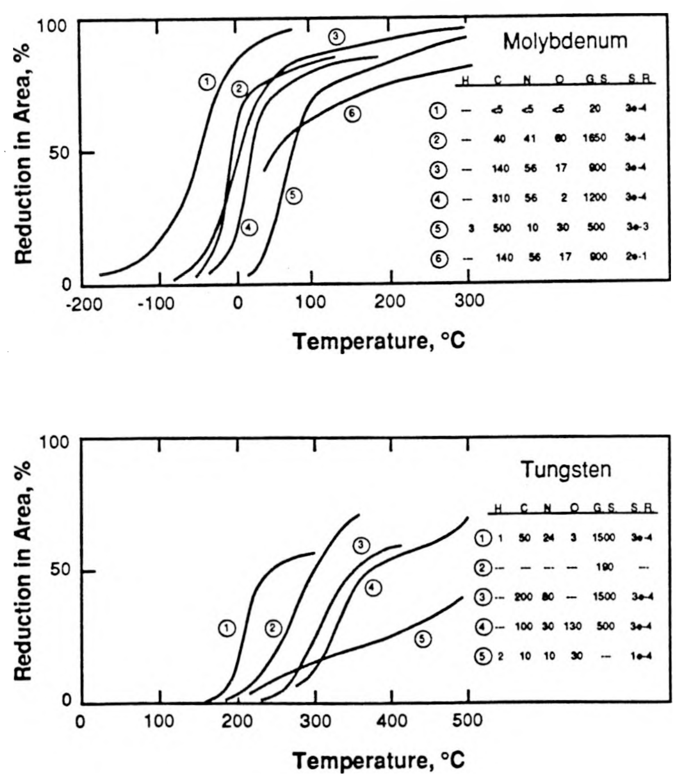

Figure 7. Ductile to brittle transition behavior of recrystallized Group VIB metals as a function of composition (10). G.S. indicates grain size in grains/mm. S.R. indicates strain rate in sec^{-1}.

Groups IIIA to VIA (*eg*. C, N, and O) which dissolve interstitially are of primary importance. Broadly, the most significant influence of these elements is related to their strong tendency to reduce the ductility and fracture toughness of the refractory metals. Among the various base metal systems, different elemental impurities and impurity levels are important, but the basic effects are similar. The impurity elements are also significant because they are common in, and difficult to exclude from, raw materials, fabrication environments, and service environments. Thus, these impurities can be incorporated into the refractory metals during primary consolidation, fabrication, or the service lifetime of the alloy.

The effects of interstitial impurities on the behavior of the base refractory metals are illustrated in Figs. 6 and 7. The data contained in Figs. 6 and 7 are from numerous sources and should be viewed with some caution since, as mentioned previously, there are numerous variables included in the curves. Thus, although the effects of interstitial elements are included, so are the effects of grain size, strain rate, and possibly orientation (since this is often not reported). Chemical analysis of interstitials at low levels in high melting point materials is also difficult (15), so that the reported concentrations of impurities can vary depending on the analysis method used. Nevertheless, the curves of Figs. 6 and 7 show that for a given refractory metal, a wide range of ductile-brittle transition temperatures are possible. In terms of alloy acceptance criteria for welded and other applications, it is clear that composition variations must be carefully considered.

With respect to interstitial impurities, it is difficult to assess from Figs. 6 and 7 the effects of a particular species either by itself or in conjunction with other impurities. Through experiments using high purity alloys doped with individual impurities, it has been observed that there are a number of impurities that result in brittle behavior. Discussion of the effects of each of these species in each of the base materials is, however, beyond the scope of this report. The general behavior of interstitial impurities in the refractory metals can be illustrated by the oxygen-niobium and hydrogen-niobium systems as shown in Fig. 8. Both oxygen and hydrogen increase the transition temperature of niobium. Interstitial impurities reduce the ductility of the refractory metals through several distinct mechanisms including; solid solution strengthening, precipitation of secondary phases, and grain boundary segregation.

Solid solutions of interstitial impurities increase the ductile to brittle transition temperature principally through elevation of the yield strength. In it simplest terms, a ductile to brittle transition temperature can be thought of as the temperature at which the stress required for yielding exceeds that for initiation of cleavage fracture. Since the yield stress of body centered cubic metals has a large temperature dependence, increases in the yield stress through other mechanisms (such as solid solutions) tend to increase the temperature at which the yield to cleavage strength ratio approaches unity.

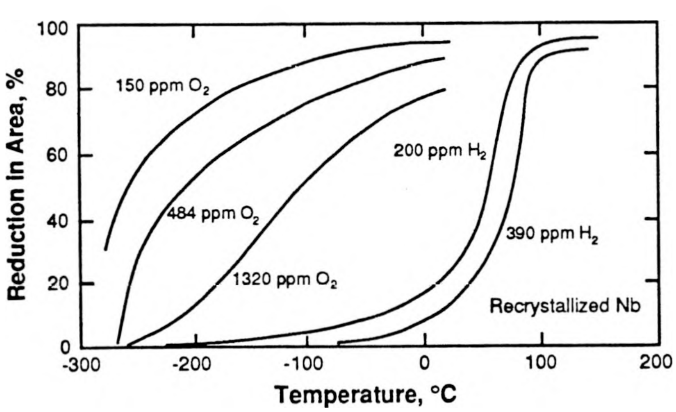

Figure 8. Effect of hydrogen and oxygen on the ductile to brittle transition of unalloyed niobium in the recrystallized condition (10).

The refractory metals in general, molybdenum and tungsten in particular, have a low solubility for interstitial impurities. Table III shows the estimated interstitial content in solid solution in the refractory metals following cooling from high temperature at moderate rates (10-20 °C/min). These values are derived by assuming that equilibrium concentrations are maintained by precipitation from solid solution until a limiting temperature (corresponding to a solute diffusivity of 10^{-11} cm²/sec) is reached. Below this temperature, the interstitials are considered immobile and remain in solid solution. For commercial purity niobium and tantalum, the interstitial contents (excluding carbon) are usually below saturation. For molybdenum and tungsten, all but hydrogen normally exceed saturation and thus are likely to contain second phase oxides, nitrides, or carbides (or may display significant grain boundary segregation). Supersaturated hydrogen is not retained in molybdenum or tungsten and the hydrides of these metals are unstable.

From the data of Table III it may be inferred that the Group VB metals are less susceptible than the metals of Group VIB to the effects of interstitial impurities. Comparison of Figs. 6 and 7 in terms of the oxygen levels required to effect a similar shift in transition temperature shows that this trend is generally observed.

Table III. Estimated concentrations of interstitial elements in solid solution in the refractory metals following moderate cooling rates (wt. ppm) (16).

Metal	Hydrogen	Carbon	Nitrogen	Oxygen
Niobium	9000	100	300	1000
Tantalum	4000	70	1000	200
Molybdenum	0.1	0.1 to 1	1	1
Tungsten	N.D.	<<0.1	<<0.1	1

Interstitial contents based on estimates of the equilibrium solubility at the temperature where the diffusion coefficient for the interstitial impurity is equal to 10^{-11} cm²/sec. N.D. indicates not detectable.

Grain Boundary Segregation The low temperature brittleness in recrystallized molybdenum and tungsten is often associated with the segregation of impurities (primarily oxygen in molybdenum and phosphorus in tungsten) to the grain boundaries. For molybdenum, the mechanism by which ductility is decreased has been ascribed to two sources. First, in samples where oxygen levels were sufficiently high, oxide precipitation has been observed on grain boundary fracture surfaces either in the form of discrete precipitates (17) or what has been interpreted as essentially two dimensional layers of oxide (18, 19). In either case, the precipitation of grain boundary oxides is thought to promote intergranular failure because of their tendency to initiate grain boundary cracking at low stresses. At somewhat lower concentrations (but still above the bulk solubility limits), oxygen is thought to segregate to molybdenum grain boundaries in monolayer form thereby lowering the grain boundary fracture stress (18-20). Quantitative work in this area was performed by Kumar and Eyre (18) who measured grain boundary fracture stress for oriented bicrystals as a function of segregated oxygen level, as shown in Fig. 9. The segregated oxygen levels were determined by Auger electron spectroscopy (AES) and are plotted in Fig. 9 as a percentage of saturation coverage, where saturation is defined as the final oxygen level of the fracture surface after long term exposure to the vacuum system. The reduction in grain boundary fracture stress due to the oxygen segregation is significant.

The tendency for grain boundary fracture, particularly in molybdenum and tungsten, is intimately related to the fabrication weldability of these metals and to some degree their alloys. For example, the welding process results in recrystallized regions and regions with large grains which are susceptible to this problem. Very large grains, such as those in the fusion zone, have

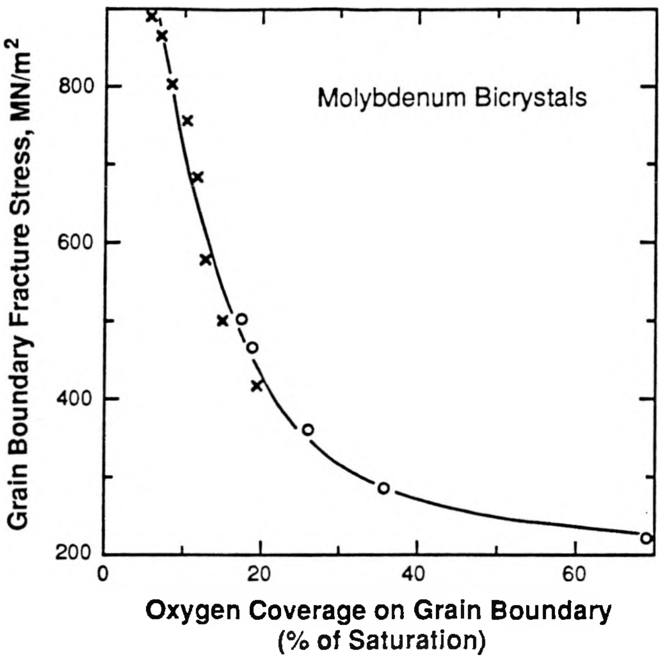

Figure 9. Variation in measured grain boundary fracture stress in molybdenum bicrystals quenched (x) and slow cooled (o) from 1900°C (18).

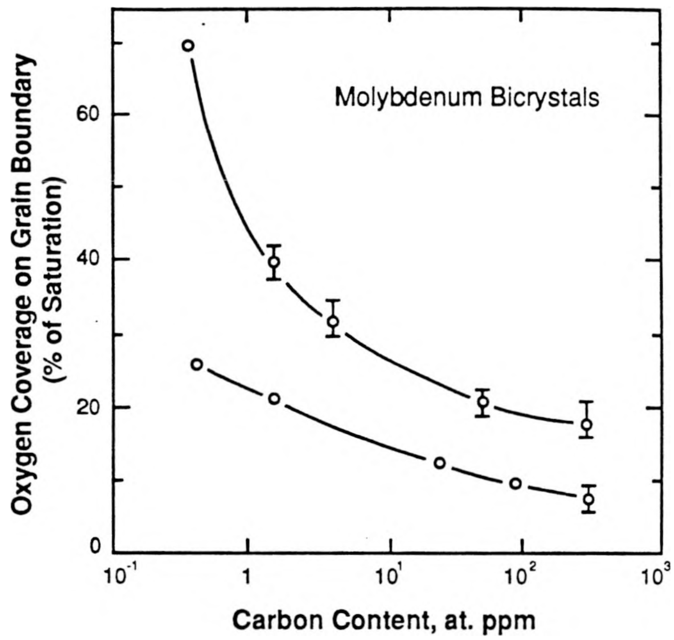

Figure 10. Effect of carbon on degree of segregation of oxygen to molybdenum grain boundaries (18).

comparatively little grain boundary surface area and can therefore be saturated with segregated impurities at lower bulk impurity levels. Further, the welding atmosphere can contribute impurities which increase the tendency for intergranular failure. As a result, control of impurities in the weld environment is of paramount importance. Finally, the nature of the solidification microstructure (Figs. 1 and 4) can result in weld centerline configurations which consist of a single, essentially planar grain boundary traversing the length of the weld. Boundaries of this geometry are particularly vulnerable to the problems associated with segregation embrittlement. The reduction in grain boundary fracture stress due to segregated oxygen is responsible for the cracking observed in the molybdenum weld of Fig. 1. The bulk oxygen content of the material shown in Fig. 1 was deliberately raised to approximately 50 wt. ppm (by annealing in wet hydrogen). The same material prior to wet hydrogen annealing, containing 10-15 wt. ppm oxygen, can be welded under the same conditions without cracking as shown in Fig. 4(a).

The importance of the welding environment and procedures with respect to interstitial and segregating impurities cannot be overstated. Although the fabrication weldability of the Group VIB metals is more strongly influenced by these impurities than the metals of Group VB, the service behavior of both groups are affected by their presence. Since these elements can have detrimental effects when present in the ppm range, minimization of their entry into the material during welding is an overriding concern. In practical terms, controlling impurities means controlling all possible routes of entry of these elements into the weld metal. In addition to the welding atmosphere (for which continuously purified inert atmospheres or vacuum are preferable), consideration must be given to materials specifications and acceptance criteria, forming and machining procedures, and pre-weld cleaning methods (which are normally aggressive). Processing procedures are available to reduce the effects of grain boundary segregation and brittleness. For example, oscillation of the electron beam perpendicular to the welding direction has been used to disrupt the centerline geometry (21).

Effect of Carbon The influence of carbon on the toughness (and weldability) of the refractory metals is complex. Carbon has been variously reported to be both embrittling and toughening in the refractory metals. Most early work, for example that of Olds and Rengstorff (17), indicated that carbon decreased ductility and promoted intergranular failure in molybdenum. More recent work (18, 22-24) indicates that carbon, when present in the proper proportions and distribution, is beneficial to ductility and reduces the tendency for intergranular failure. Much of the discrepancy results from difficulties in preparing materials of sufficient purity so that the effects of individual impurities can be isolated. A further complication results from the fact that there can be interactions between the various impurities. Molybdenum provides a good example of these interactions and is discussed here. In molybdenum welds, carbon acts in three principal ways to improve fabrication and service weldability, all three of which are related to improvements in ductility. For molybdenum consolidated by melting techniques, carbon additions improve scavenging of oxygen during melting so that high carbon alloys are generally lower in oxygen. An extension of this effect is that higher carbon contents promote further deoxidation (or at least limit the tendency to pick up oxygen from the welding atmosphere) during fusion welding. Secondly, carbon reduces the free energy of segregation of oxygen in molybdenum (18). The reduction in driving force for segregation is reflected in reduced grain boundary oxygen concentrations at higher carbon contents, Fig. 10. The net result is that for acceptable room temperature ductility in molybdenum, a carbon to oxygen ratio greater than two is desirable (25). Finally, it has been argued (24) that carbide precipitates on molybdenum grain boundaries form low energy coherent interfaces (26) and this further reduces the tendency for intergranular failure by lowering the total grain boundary energy. It is further thought that such precipitaes can also act as dislocation sources (18) An example of a grain boundary carbide showing such interfaces is shown in Fig. 11.

Weld Porosity A common defect encountered in the joining of the refractory metals is weld porosity such as that shown in Fig. 12. Weld porosity is significant for several reasons. First, in cases where porosity is substantial, it can increase the net section stress on a particular plane in the material, thereby lowering the nominal failure stress. Second, depending on their morphology and distribution, pores can act as stress concentrations similar to a notch. Since the refractory metals are generally notch sensitive, pores can

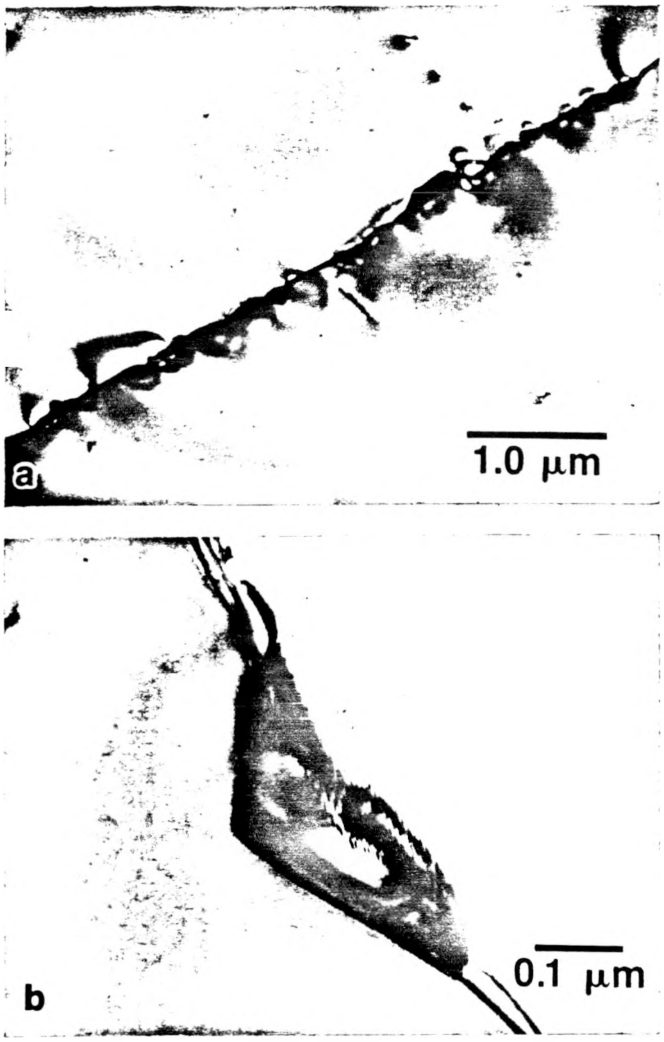

Figure 11. TEM micrographs of grain boundary carbide precipitates in Mo welds showing (a) general distribution of the carbides and (b) partial coherency of a carbide precipitate with one grain.

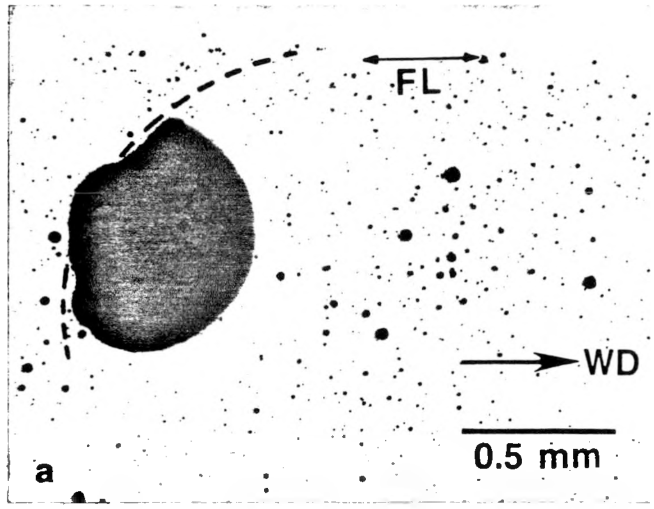

Figure 12. Optical micrograph of GTA weld in PM molybdenum sectioned in the plane of the weld. The micrograph shows an example of both fine and large scale porosity. The dotted line to the left of the pore indicates the approximate position of the solidification front when the pore formed. FL and WD indicate fusion line and welding direction.

Figure 13. TEM micrograph of inclusion in thin foil specimen of powder metallurgy molybdenum sheet. X-ray analysis of the inclusion indicates the presence of Al, Si, Ca, and O (13).

therefore have a detrimental impact on the strain rate and temperature sensitivity of these materials. Pores of sufficiently small size and the proper distribution can act in a manner similar to dispersions or precipitates, thereby elevating yield strength, reducing tensile elongation, and increasing transition temperature (3).

As with other materials, porosity in refractory metal welds can be the result of the welding process parameters (27) or joint preparation procedures (28). For example, impurities in the weld shielding atmosphere which are soluble in the liquid metals but display limited solubility upon solidification can result in porosity. Also in common with other metals, typical impurities in shielding atmospheres which may result in porosity are hydrogen, nitrogen, and oxygen. Improper weld schedule parameters, such as excessive arc length in GTA welding, can also result in porosity. Joint preparation and cleaning procedures are important since they can contribute to increased impurity concentrations in welds (28).

Of greater importance, however, are the effects of materials properties on the tendency for pore formation since these are usually not influenced by process parameters. For the refractory metals, the tendency for pore formation is dominated by the interstitial (*eg*. H, N, and O) content of the alloy. In turn, the interstitial contents of these materials are governed by the the presence of other impurities and the consolidation method for the material (13, 29). In the case of commercial powder metallurgy molybdenum the bulk of the oxygen in the material is present in the form of oxide inclusions such as that shown in Figure 13. These inclusions consist of oxides of aluminum, calcium, or silicon or complex oxides containing several of these elements. At fusion welding temperatures inclusions can either decompose or dissolve in the molten metal, thereby liberating significant quantities of gas into the melt. Since the gaseous species have lower solubilities in the solid than in the liquid, they are rejected into the liquid ahead of the solidification front and the concentration of the gaseous species in the liquid further increases. At some point the solubility in the liquid is exceeded and a gas pocket or bubble is formed. As shown in Fig. 12 the size of gas bubbles can be a significant fraction of the weld pool size and is an indication of a high inclusion fraction. Refractory metals consolidated by melt techniques, *eg*. vacuum arc casting or electron beam melting, have a much lower inclusion content than their powder metallurgy counterparts and display less weld porosity (4, 13). Variations in powder processing methods have also been shown to reduce weld porosity (29).

Hot Cracking The tendency for refractory metal welds to exhibit hot cracking has not been investigated as extensively as other alloy systems, but the potential certainly exists (30). In simplest terms, hot cracking occurs because of the segregation of impurities or alloying elements during solidification. This segregation results in the formation of low melting point eutectic-like constituents which, in turn, remain liquid to temperatures where significant shrinkage stresses are developed. Hot cracking is of concern from both fabrication and service (reliability) standpoints since it can result in low production yields and undetected or subsurface cracks may propagate during service. Because of the high melting points of the pure metals, many of the phases which form in refractory metal systems have melting points below those of the pure metals. Both alloying elements and impurities are important with respect to hot cracking. For example, boron has been observed to increase the ductility of molybdenum (31) and is therefore a potentially useful alloying addition. However, attempts to dope molybdenum welds with boron resulted in the occurrence of hot cracks (32). Figure 14 shows the surface of a weld centerline crack in a molybdenum weld doped with approximately 750 wt. ppm boron. Clearly a liquid phase was present at the weld centerline when cracking occurred. Evaluation of the hot cracking tendency of several niobium and tantalum alloys (30) indicated that alloying elements can also contribute to an increased hot cracking susceptibility.

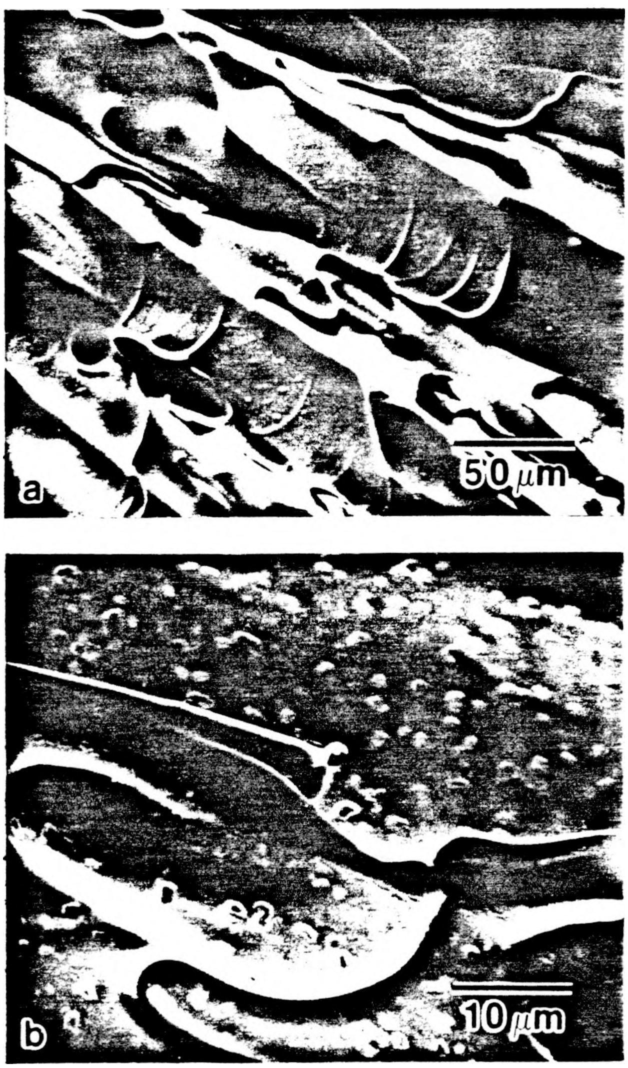

Figure 14. SEM micrographs of surface of weld centerline crack in boron doped arc cast molybdenum weld (32).

Directional Properties As a result of the limited number of slip systems in the refractory metals, a pronounced texture can be developed during mechanical working (33). This texture can have adverse effects on the transverse ductility of the refractory metals. In addition, Wadsworth *et al.* (33) have shown that in molybdenum alloys, cracked carbide stringers are commonly present along grain boundaries, and this further contributes to very poor transverse ductility. With respect to fabrication weldability, the net result of poor transverse ductility is a strong susceptibility to delamination phenomena similar to lamellar tearing in steels (34). Cracking occurs in the base metal and is typically oriented parallel to the fusion line near the edge of the HAZ. Since the problem is related to directional properties of the base metal, it occurs most often in tee and corner joints where the fusion boundary of the weld is parallel to the plate surface. Suitable weld joint design must therefore be used to minimize the opportunity for delamination. Wadsworth *et al.* (33) have developed thermal-mechanical treatments which can also be used to reduce the tendency for this type of defect.

Summary and Conclusions

Fusion welding is a suitable and competitive option for joining the refractory metals and their alloys. Many of the problems associated with fusion welding of these materials are related to the cleanliness of the material and the welding environment. Current alloy production technology and welding practice, if properly applied, are capable of minimizing the effects of impurities. A second principal difficulty associated with refractory metal welding is the formation of weld zones of large grain size and considerably reduced strength relative to the base materials. Although welding procedures can control weld grain size to some degree, further work is needed in the area of alloy development directed at improved resistance to HAZ grain growth. As a result of renewed interest in the refractory metals (4) new alloy types and processing procedures are currently under development. Clearly, research directed at joining of these new alloys is appropriate.

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