THE WELDING AND BRAZING OF THE REFRACTORY METALS NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN — A REVIEW*

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SUMMARY

This review covers the present and future problems in the development and welding of niobium, tantalum, molybdenum and tungsten and their alloys. Their metallurgical characteristics are discussed together with the influence of impurities and alloying elements on mechanical properties, alloy development and weldability. Other factors briefly discussed are availability, high temperature strength, ductility and oxidation resistance.

The general problems which will be met when welding these materials are described together with means of assessing weld quality. Information on the welding and brazing of each material and its alloys is assessed in order to define lines of research. Most reported work has been carried out in the United States and the outline research programme is drawn up as a basis for work in the United Kingdom.

It is the opinion of the authors that a welding research programme must be included as an integral part of the development of refractory metal alloys.

I. INTRODUCTION

Modern technology, particularly in the sphere of missiles, aero-engines and aircraft, demands metals and alloys capable of service at high temperatures. The alloys based on the readily available metals iron, nickel and chromium are already being used near their useful limits and attention is accordingly being directed to less-common metals which may have the desired properties. Prominent among these less-common elements are the refractory metals, niobium, tantalum, molybdenum and tungsten, which form a closely related section in Groups Va and VIa of the Periodic Table. For brevity these materials are referred to hereafter by their respective chemical symbols (Nb, Mo, Ta and W).

These four metals all have the body-centred cubic structure and Table I lists the more important of their properties, together with those of some more common metals for comparison. All four are characterised by very high melting points, high to very high densities, low specific heats and low coefficients of thermal expansion; Nb and Ta have rather low thermal and electrical conductivities, Mo and W rather high. The latter pair also have high elastic moduli, but Ta has a moderate and Nb a low value. In relation to their densities, the moduli of Nb and Ta are very low, that of W low but that of Mo high.

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TABLE I

PHYSICAL PROPERTIES OF METALS

Property	*Mg*	*Al*	*Cu*	*Ni*	*Fe*	*Ti*	*Cr*	*Nb*	*Ta*	*Mo*	*W*
Melting point (°C)	650	660	1083	1453	1535	1660	1850	2468	2996	2620	3410
Density (g/cm³)	1.74	2.70	8.94	8.9	7.86	4.51	7.1	8.57	16.6	10.2	19.3
Thermal conductivity (cgs. units)	0.35	0.57	0.92	0.21	0.17	0.04	0.16	0.13	0.13	0.35	0.40
Specific heat (cgs. units)	0.24	0.21	0.09	0.11	0.11	0.13	0.11	0.06	0.04	0.06	0.03
Coeff. of thermal expansion (10^{-6}/°C)	25.7	24.0	16.4	13.3	11.9	8.9	6.5	7.2	6.5	4.9	4.3
Elastic modulus (10^6 lb./in.²)	6.5	10	17.5	30	29	15	36	14	27	46	59
Resistivity ($\mu\Omega$-cm)	4.4	2.7	1.7	6.8	9.7	48	21	14.5	13.1	5.3	5.3

The following factors should be taken as the criteria for the suitability of an alloy for high temperature applications[1]:

(1) metallurgical characteristics
(2) availability
(3) high temperature tensile strength
(4) ductility
(5) formability
(6) oxidation resistance
(7) weldability
(8) coatability

It is not relevant to the present report to discuss all these in detail but a full discussion of item 7 also involves items 1, 2, 3, 4, and 6, especially item 1, since nearly all the problems encountered in welding these metals arise from their metallurgical characteristics. Early investigations into the weldability of these metals were nearly all discouraging and have already been reviewed[2-7].

2. EFFECT OF METALLURGICAL CHARACTERISTICS ON MECHANICAL PROPERTIES

The four metals all possess the body-centred cubic structure which has one unfortunate characteristic, a well-marked transition from ductile to brittle behaviour[8]. The effect can most easily be shown by means of notched bar impact tests, carried out over a range of temperature. If the energy for fracture is plotted against temperature, a graph of the type shown schematically in Fig. 1 is obtained. There is a large decrease

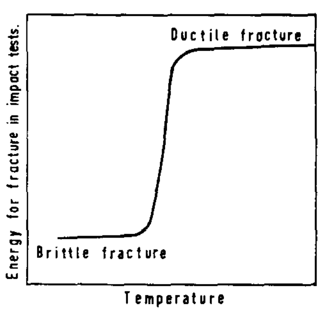


Fig. 1. Effect of temperature on energy required for fracture in impact tests.

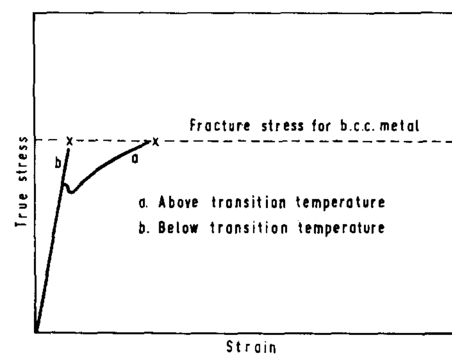


Fig. 2. Schematic stress–strain curves for body-centred cubic metals above and below transition temperature.

in energy absorption over a narrow temperature range and, coincident with this, there is a change in the type of fracture, from tough to brittle. The temperature at which this occurs is not a fixed property of the material but varies with strain rate, triaxiality of stress, alloying, impurities, heat treatment and method of fabrication. Similar results are obtained in tensile tests by plotting the elongation against test temperature, but the transition temperature is much lower than in impact test. At the same time as the ductility falls, the yield strength and tensile strength increase. It is this increase in yield strength which is usually considered to be the cause of the loss in ductility. This is most easily pictured by means of a Ludwig diagram (Fig. 2). A metal starts to deform plastically when the stress reaches the yield point; then the stress continues to rise until the fracture stress is reached, when the metal breaks. At a low enough temperature the fracture stress is reached before the yield stress and the metal breaks without any plastic deformation.

The increase of yield stress is itself due to Cottrell locking of interstitial solute atoms (usually impurities). The movement of solute atoms is associated with thermal fluctuations which are reduced as the temperature decreases so that anchoring is stronger and the yield strength higher. The sizes of the holes in the lattice in which the solute atoms sit are, therefore, important and those metals with large lattices (and hence holes) show no or very low transition temperature. Such metals are sodium, potassium and Ta. Cold working also lowers the transition temperature, by producing more dislocations and breaking others away from solute atoms, but annealing will raise the temperature again. Obviously the removal of the interstitial atoms is a better solution.

It is, therefore, rather misleading to quote transition temperatures for the refractory metals without giving details of the method of testing, purity etc., but in round figures pure Ta is ductile even in liquid hydrogen, Nb shows a transition at −200°C, Mo at −45°C to 40°C and W at 175° to 455°C[9]. Figure 3 shows some results obtained on recrystallised materials[10]. The parameter in this instance is the reduction in area in tensile tests. The purity of the metals was not reported but was probably better than that of most commercial metals.

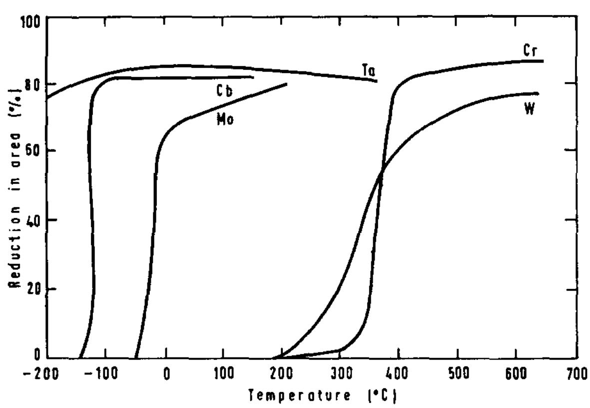


Fig. 3. Tensile transition ranges for recrystallised refractory metals[10].

2.1. *Effect of impurities*

The embrittling effect due to the raising of the transition temperature by interstitial oxygen, nitrogen and carbon has already been described in Section 2 above, but there may be additional effects. A good example is the case of Mo where if sufficient oxygen is present to exceed the solid solubility limit and form grain boundary oxide films, the metal will be even more brittle[11,12]. The degree of brittleness will be partly controlled by the structure: in a heavily cold worked structure, the oxide will be finely distributed throughout the metal and the room temperature ductility will be good; if the material is recrystallised, the oxide will concentrate in the grain boundaries as thin films, reducing the room temperature ductility to zero. If heated rapidly to a high enough temperature (above 2120°C), pores will be formed since MoO_3 is volatile below the melting point of Mo itself. Even on slow heating above this temperature, embrittlement still occurs as a eutectic is formed between Mo and MoO_2 which wets and penetrates grain boundaries. However, heating to between 1950° and 2120°C is claimed to spheroidise the oxide without forming boundary films, making the material ductile. This subject is discussed at greater length in Section 2.3. below. An alternative approach is to getter the oxide by an alloying addition. The oxide produced must not form grain boundary films and the alloying element must comply with certain other requirements discussed in Section 2.2. below.

In the case of Nb and Ta, hydrogen is also a harmful impurity and can cause severe embrittlement[7]. It is therefore as essential to protect these metals from hydrogen as from oxygen or nitrogen: if pick up of hydrogen occurs it can be removed by a vacuum heat treatment. Hydrogen is not a source of trouble in Mo and W and calls for no special precautions[6].

2.2. *Effect of alloying additions*

Alloying additions made to the refractory metals can be divided into two classes, those intended to neutralise the effects of interstitial impurities and those intended to improve the mechanical properties (some elements fall into both classes).
The latter class can be further subdivided according to the mechanism of strengthening, *i.e.* dispersion hardening, solid solution hardening or strain hardening. There is also for Mo and W one apparently unique addition — rhenium which, while falling into both these classes, also improves the ductility and transition temperature directly[8].

2.2.1. Neutralising additions. In most cases neutralising additions act by gettering the interstitial impurities in the form of oxides, nitrides or carbides[13,14]. The neutraliser must meet certain requirements: (1) it must have a high affinity for the impurity; (2) it must have a high melting point; (3) the compounds formed with any impurities should be capable of spheroidisation and must not form grain boundary films; (4) such compounds must themselves have high melting points; (5) they must not react

TABLE II

APPLICATION PROPERTIES OF PURE METALS

Property	*Units*	*Nb*	*Ta*	*Mo*	*W*
Stiffness/weight ratio*	10^6 in. at 25°C	48	45	125	72
Recrystallisation temperature	°C	975–1150	1100–1400	1150–1200	1200–1650
Brittle-ductile transition temps					
(a) Tensile	°C	−200 to −75	Below −196	−46 to +38	150 to 450
(b) Notch impact	°C	—	Approx. −150	260–480	—
Resistance to thermal shock**	10^5	9	15	32	41

* Given by: Young's modulus/density.
** Given by: Thermal conductivity × U.T.S. (lb./in.^{2}) at 1000°C/coeff. of expansion × Young's modulus × density × specific heat. Units as in Table I.

with the base metal or with any oxides etc. of the base metal to form low melting point eutectics; (6) they must not be volatile at welding temperatures.

Most of the work so far has been concentrated on Mo in which oxygen is the most deleterious impurity. Despite the fact that carbon is an impurity it is also a deoxidiser in that it will remove oxygen by the formation of carbon dioxide. In theory, this should be a particularly useful method for sintered metal since the carbon dioxide should be able to escape during sintering. In practice, deoxidation is not completed during the sintering, so that it continues during welding, causing porosity[13]. However commercially pure Mo (whether sintered or arc cast) contains carbon as a deoxidiser. The optimum excess of carbon is not known, indeed there are conflicting reports[15,16]. Since the excess carbon can be present as a network of Mo carbide, this will reduce the ductility. An initial increase of ductility with increase of carbon was reported[15], but another set of results showed a continual drop in ductility with increase of carbon content[16].

The best deoxidiser so far appears to be titanium, particularly if weldability is being considered[13,14,16,17]. It complies with the requirements outlined above, but again there are conflicting reports of how much should be added and what are the effects on mechanical properties[16,17]. The only commercially available Mo–titanium alloy contains 0.5% titanium which was reported to be the optimum composition[17]. However, another report asserts that this concentration is too low and that 0.7% is necessary[16]. Such differences may well be due to other factors, such as method of production and fabrication and also carbon content[18]. The effect of titanium on the ductility is also not clear, as at least one team found that the ductility was no better at room temperature than that of pure Mo[16]. However the transition temperature does appear to be reduced[17]. Zirconium and hafnium are also possible deoxidants with the required properties[14]. Aluminium, Nb and Ta have been tried as deoxidants without success: welds in alloys containing these metals all showed cracking and porosity[13]. The reasons are not clear but aluminium and aluminium nitride boil below the melting point of Mo, and a low melting point eutectic can be formed. Tantalum oxide decomposes at 1470°C and the oxides of Nb melt below 1780°C, perhaps forming eutectics or boundary films: — quite possibly in this particular case deoxidation was incomplete. Rhenium also has some deoxidant properties, at any rate in large amounts, but this is not its main function[8].

There has been no *ad hoc* investigation of additions to remove nitrogen or carbon from Mo, since they are less serious in their effects than oxygen. However, it seems very probable that titanium or zirconium also getter nitrogen and they will certainly form carbides.

There has been no investigation of the possibilities of adding neutralisers to W. However, in view of the close similarity to Mo similar conclusions probably apply.

In the case of Nb, nitrogen has a greater embrittling effect than oxygen. The resuirements are the same for the neutralising additions as in the case of Mo and the same three metals titanium, zirconium and hafnium appear to offer the best properties[19]. All Nb alloys investigated contain zirconium and/or titanium, although not necessarily just as a neutralising addition (Table III). There has been no published investigation of the concentrations necessary for gettering the nitrogen or oxygen but ½–1% is generally favoured.

Ta has an even higher tolerance for interstitial impurities than Nb[7] but as very

TABLE III

COMPOSITIONS OF SOME ALLOYS UNDER DEVELOPMENT[9]

		Nominal composition
Nb base	100 Nb	0.036 O 0.019 N 0.024 C
	FS 80	0.75 Zr
	FS 82	33 Ta 0.75 Zr
	Cb 65	7 Ti 0.8 Zr 0.11 O 0.02 N 0.075 C
	Cb 74	10 W 5 Zr 0.12 O 0.02 N 0.03 C
	Cb 752	10 W 2.5 Zr
	F 48	15 W 5 Mo 1 Zr 0.1 C
	F 50	15 W 5 Mo 5 Ti 1 Zr 0.05 C
	D 31	10 Mo 10 Ti 0.05 O 0.07 N 0.06 C
	D 41	20 W 10 Ti 6 Mo
	Cb Ta W Zr	24 Ta 10 W 1 Zr
	C 103	10 Hf 1 Ti 0.5 Zr
	D 14	5 Zr
	D 36	10 Ti 5 Zr
Ta base	100 Ta	0.004 O 0.003 N 0.004 C
	Ta–10 W	10 W 0.0045 O 0.0015 N 0.001 C
	Ta–10 Hf 5 W	10 Hf 5 W
	Ta–30 Cb 7.5 V	30 Nb 7.5 V
Mo base	100 Mo	0.01–0.03 C
	Mo 0.5 Ti	0.5 Ti 0.02–0.05 C
	TZC	1.25 Ti 0.15 Zr 0.15 C
	TZM	0.5 Ti 0.08 Zr 0.02–0.08 C
	Mo–0.05 Zr	0.054 Zr 0.024 C
	Mo 0.5 Zr	0.5 Zr 0.02 C
	Mo 25 W	25 W 0.11 Zr 0.05 C
	Mod TZC	1.27 Ti 0.29 Zr 0.3 C
	Mo 1.5 Cb	1.5 Nb 0.25 C
W base	100 W	0.002–0.005 O 0.0015–0.004 N 0.0004–0.005 C
	W 1ThO_2	1 ThO_2
	W 2ThO_2	2 ThO_2
	W 10Mo	10 Mo
	W 15Mo	15 Mo
	W 25Mo	25 Mo
	W 0.38TaC	0.38 TaC

little attention has been directed to Ta alloys, there has been no investigation of neutralising additions. However, it seems certain that titanium, zirconium and hafnium would again be the best choice.

2.2.2. *Strengthening additions.* Apart from their function as neutralisers, titanium, zirconium and hafnium also act as strengtheners, in conjunction with carbon[9,20–22]. A fine dispersion of carbides gives some increase in strength in both Nb and Mo, without much affecting the ductility. In Mo the recrystallisation temperature is also raised while the transition temperature is not substantially altered and may even be lower under some circumstances[9]. This method of hardening is not used for

TABLE

MECHANICAL PROPERTIES AND SOME PRICES OF METALS

Alloy	Condition*	U.T.S. (tons/in.²) at, °C						
		1095	1205	1315	1370	1650	1925	2205
Nb base								
Pure Nb	2	4.4	4.1					
FS80	1	~8.8	—					
FS82	1	13	5.7					
D14	2	14	—	—	5.3			
D36	2	10						
D31	1	13	12					
Ta base								
Pure Ta	2	—	4.4	—	3.1	1.3		
Ta–10 W	1	—	30	—	9.7	4		
Mo base								
Pure Mo	1	20	—	5.7				
Mo–0.5 Ti	1	25	16	8.4				
Mo–0.5 Ti–0.8 Zr	1	—	—	—				
W base								
Pure W	1	—	—	—	22	8.8	4.4	2.9
$W–1ThO_2$	1	—	—	—	22	16	13	6.2
$W–2ThO_2$	1	—	—	—	16	13	12	7.7

Ta or W. However, the latter can be hardened by a dispersion of thorium dioxide or tantalum carbide[9].

Greater strengthening can be obtained by solid solution additions. The refractory metals are all fully soluble in each other, and most high strength alloys are therefore based on additions (often large) of one or more of the other refractory metals to the base metal, frequently with a large addition of titanium, zirconium of hafnium (with or without carbon) as well.

Typical compositions of refractory metal alloys are given in Table III. Table IV gives details of those commercially available. These alloys are all American; there is no information on any alloys other than these being available in the United Kingdom or the Continent.

A Mo alloy which is unlikely to be produced commercially in the near future but which none the less has some ideal properties is that containing 50 wt. % of rhenium[8]. This alloy possesses a remarkable combination of high-temperature strength with low-temperature ductility and a very low transition temperature. This is due to a particular twinning mechanism of deformation which occurs more readily the lower the temperature and the faster the strain rate, and which prevents the yield stress from rising (see Section 2.). The strain hardening coefficient is also low (comparable to those of Nb and Ta), unlike those of Mo, which is high, and rhenium, which is the highest known. A globular mixed oxide is formed so that embrittlement from this cause is also eliminated. Similar, though less marked, effects are found in W – rhenium alloys. It is therefore unfortunate that rhenium should be scarce and correspondingly costly (about £300 per lb. in the U.K.). Unless the supply of rhenium can be increased the use of these alloys is likely to be confined to vital military applications.

D ALLOYS COMMERCIALLY AVAILABLE [9,86,87]

100 h stress rupture (tons/in.^{2}) at, °C							
1095	1205	1315	1370	1480	*Source*	*Production method*	*Approximate price for 1 sq.ft. 0.064 in. sheet*
1.4					U.S.	Electron-beam melted	£131
8.5					—		
7.9					—		
5.3	2.2				U.S.	Arc-cast	£95
—					U.S.	Arc-cast	£95
8.8					—		
					U.S.	Electron-beam melted	£110
5.7	—	—			U.K.	Sintered	£13
15.2	7.9	4.4			—		
13					U.S.	Arc-cast	£53
—	—	—	9.7	4.8			

* 1 = Wrought or stress-relieved; 2 = Recrystallised

2.3. *Heat treatment*

Heat treatments can be divided into two types, pre-weld and post-weld. The former are usually intended to produce optimum properties in the base metal and not to improve the weldability; normally they have no effect on the weld properties since in the weld area all effects of heat treatment are removed by the high temperatures reached. However, some attention has been given to the possibility of improving the properties of Mo sheet by heat treatment[11,12]. As already discussed (Section 2.1) recrystallisation is usually harmful since the ductility is sharply reduced. How-

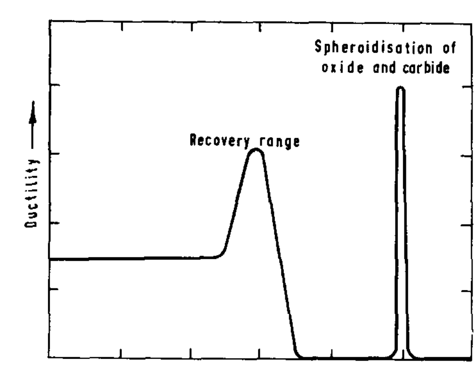


Fig. 4. Effect of annealing temperature on the ductility of molybdenum[6].

ever, heating to high temperatures can restore some ductility, as shown schematically in Fig. 4. The temperature range for this restoration of ductility is very narrow; between 1950° and 2120°C has been quoted[11,12]. In this range, spheroidal oxide particles are formed which have no embrittling effect: grain growth is rapid. Above this range, intergranular oxide precipitates are formed which again reduce the ductility to zero and also prevent grain growth: these films are probably a eutectic of Mo and MoO_2. Below 1950°C, no oxide is visible but there is no ductility. The range 1370°–1650°C has also been quoted as giving some ductility[23], and there is no apparent reason for the disagreement between the two sets of results. Electron beam annealing in vacuum (but only for a few seconds) also produced an improvement in ductility at annealing temperatures of 750–1000°C, followed by a fall at higher temperatures, with a slight rise at 2100°C in one sample but not in another[24]. However, if the suggested explanation of spheroidisation of oxide is correct, annealing times of more than a few seconds would probably be needed. It is not known whether welds in material so treated are ductile: the temperatures reached in the weld zone are higher than the 2120°C quoted above, but the times involved are short and the benefits of the heat treatment may be retained in the heat-affected zone, if not in the weld metal.

It has also been suggested that some purification may be obtained by heating above 1900°C in high vacuum[25]. A sample of rod heated at 2100°C for 12 h in a vacuum of $5 \cdot 10^{-5}$ torr was recrystallised but was ductile with a transition temperature of −90°C. However, this may well have been due to the spheroidisation of oxide rather than to any purification, although other workers have claimed that the oxygen and nitrogen contents are reduced[23]. If true, the benefits of such a treatment would be felt in the weld metal, as well as the heat affected zone.

There has been no investigation of the effects of high temperature vacuum heat treatment on W, but similar effects seem likely.

Post-weld heat treatments are usually aimed at improving the ductility of the weld, either by reduction of residual stresses or by modification of the metallurgical structure of the weld metal (the latter applying only to alloys).

Provided the recrystallisation temperature of the parent metal is not reached, stress-relief may sometimes prevent cracking in welds of Mo of marginal purity, particularly if the weld is not allowed to cool to room temperature before the stress relief[15]. The recrystallisation temperature is not, of course, a fixed point but after a heavy reduction temperatures of 1,000°–1,200°C have been quoted[26]. The Mo–0.5% titanium alloy has a higher recrystallisation temperature, whilst that of very pure Mo is lower. In practice, and on complex structures, stress relief will probably be desirable for all of these materials.

The subject of post-weld heat treatment for alloys has not been explored, but it seems certain that for many alloys such a treatment will be needed to restore or improve the mechanical properties in the weld area. It has already been established[27] that the Nb alloys D31 and F48 (Table III) require treatment at 1150° and 1290°–1370°C respectively (Section 7.3.1. below).

3. AVAILABILITY

None of these metals is in plentiful supply and they are consequently expensive (some estimates of cost are given in Table IV). Of the four pure metals Mo is the easiest to obtain, followed by Ta, Nb and W. However, the position is complicated by the fact that several production methods for each metal are employed, with quite a wide variation in the properties of the metal produced. Originally the only method was by sintering powder compacts (in hydrogen or vacuum) which gave material with a fairly high interstitial impurity level, too high for Mo or W produced in this way to be weldable. Material of better quality is produced by arc melting the sintered metal either in vacuum or inert-gas, but since this is an extra operation such material is more costly. Electron-beam melting has also been used to produce high quality material, but such material again is in short supply.

At present good quality Mo, Nb and Ta can be obtained in sheet form but W cannot. However, it has recently been forecast that high quality W sheet will soon be available in the United States[28].

It is not clear which alloys will be available. The only commercially available Mo alloys are Mo–0.5% Ti and TZM (Table IV). There appear to be four commercial Nb alloys in the United States, FS80, FS82, D14 and D36, and one Ta alloy. There are no commercially available W alloys, with the possible exception of those containing thorium dioxide.

Many other alloys, particularly of Nb and Mo, are being investigated in the United States and some of these have reached the stage of pilot production but it is impossible to predict the availability of such alloys. In the United Kingdom, work so far on alloys has been very limited. At the present stage, significant batch to batch variations can be expected, which will complicate any investigation.

4. HIGH TEMPERATURE TENSILE STRENGTH

Some figures for the high temperature tensile strength of the pure metals and of the alloys are given in Table IV. The strength of the pure metals depends on whether they have been cold worked or not and whether they are being tested above or below the recrystallisation temperature. Of the pure metals Nb and Ta are weak and alloying improves the strength considerably. At the moment, the most effective method for strengthening Ta appears to be by solid solution hardening with quite large additions of W, Nb etc.[20]. A similar conclusion applies to Nb, although in this case titanium is frequently added to improve the oxidation resistance and workability. Pure Mo and W are much stronger, and less spectacular increases are obtained by alloying.

In the U.S.A. certain targets have been set for the mechanical properties of alloys. An extract from these is shown in Table V[29]. In all cases except Ta, the alloys were divided into two classess, "fabricable" and high strength. The former covers the requirement for wide thin gauge high quality sheet, with good weldability, the latter for sheet with very high strength at elevated temperatures. It was considered that Ta alloys would meet both requirements. The only pure metal included is W, as it was felt that the other metals were insufficiently strong for high temperature structural applications.

5. DUCTILITY

It is extremely difficult to define the term "adequate ductility". The ductility measured in a uniaxial tensile test may bear no relation to that in service, where the strain rate and stress pattern are probably very different. However, most people would agree that the material should behave in a ductile and not a brittle manner, which implies that the transition temperature must be low, even if they cannot agree

TABLE V

AMERICAN REFRACTORY METAL ROLLING PROGRAMME TARGET PROPERTIES[29]

Property	*F.Mo*		*H-S.Mo*		*F.Nb*		*H-S.Nb*		*UD.W*		*H-S.W*			*Ta*		
RT tensile OC	10		2		15		10		2		2			15		
elongation (%) CR	10		2		15		10		—		—			15		
Elevated temperature tensile properties (OC):																
Temperature (°C)	1095	1315	1315	1650	1095	1315	1205	1425	1650	1925	1650	1925	2205	1315	1650	1925
Tensile strength (tons/in.²)	33	22	33	11	22	9	22	11	9	4	16	12	7	16	11	7
0.2% proof stress (tons/in.²)	27	16	27	7	18	7	18	7	7	3	11	8	4	12	7	4
Recrystallisation (OC) 50% by metallurgical observation:																
Time (h)	1		1		1		1		1		1			1		
Temperature (°C)	1425		1760		1315		1540		—		1870			—		
Transition temperature (OC), 4T bend (°C)	−40		RT		−73		−40		150		150			−196		
Bend ductility RT																
Base metal	1T		4T		1T		4T		4T(150°C)		4T(150°C)			1T		
Welded (longitudinal test)	4T		—		2T		6T		—		—			2T		

F = fabricable, H-S. = high strength, UD = unalloyed or dilute, OC = optimum condition, CR = completely recrystallised, RT = room temperature.

on the elongation required. In general terms, Ta has the lowest transition temperature and highest ductility followed by Nb, Mo and W in that order (Fig. 3). The level of impurities has a marked effect, especially on Mo and W and so does the degree of cold work; the transition temperature of commercial Mo is well above room temperature if recrystallised, below it if heavily worked. Alloying usually reduces the ductility, but at operating temperatures the ductility is still high.

Room temperature ductility and transition temperature are among the target properties for the American Refractory Metal Rolling Programme (Table V).

6. OXIDATION RESISTANCE

The oxidation resistance of all the refractory metals leaves much to be desired. They can again be divided into the two pairs of Nb and Ta, and Mo and W. In the case of Nb and Ta, reaction with air starts at temperatures as low as 200° and 400°C respectively[30,31]. The oxide formed is adherent but not protective; it cracks and oxidation proceeds at a linear rate[8]. Small anions such as Mo and vanadium give some improvement. W and Mo behave even worse since the oxide formed is not even adherent but volatile (Mo starts to smoke at 450°C in air and smokes very noticeably at 700°C; W behaves similarly about 200° higher) so that it has no protective effect whatever. A graph of penetration against time for the four metals is shown in Fig. 5[32]. Large additions of nickel reduce attack on Mo, but such additions are undesirable metallurgically[8]. The addition of preferential oxide formers, while beneficial to the metallurgical properties, does not seem to reduce external attack.

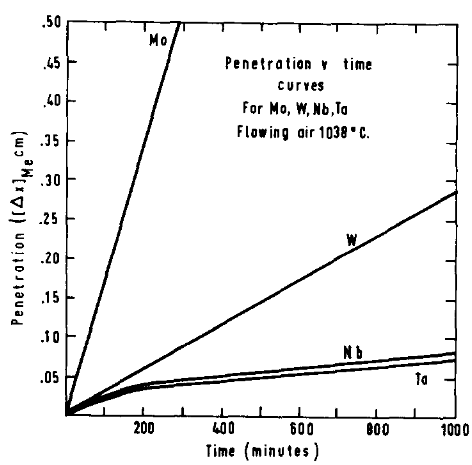


Fig. 5. The oxidation rate of Mo compared with that of W, Nb, and Ta[32].

For a few uses protection may not be required, *e.g.* high in the atmosphere or for missiles which have short life, but for most applications the resistance to oxidation must be increased. Since alloying is of limited use, considerable attention has been paid to coatings on Mo, less on Nb and very little on Ta and W. Examples of such coatings are electroplated nickel and chromium on Mo or metallised silicon–aluminium–chromium or a thin coating of zinc on Nb [10,32]. Ceramic coatings are also being investigated.

It would seem almost impossible to weld parts that have already been coated, since the presence of constituents of the coating in the weld metal would render it completely brittle. The presence of a weld should not, however, prevent a part from being coated.

7. WELDABILITY

This section is divided into sub-sections dealing with the possible joining processes and their characteristics, the assessment of joint properties and heat treatment. The available information on the weldability of the four metals concerned is then reviewed.

7.1. Joining processes

The following are all possible techniques for joining the refractory metals: arc welding, electron-beam welding, resistance welding, pressure welding, ultrasonic welding, friction welding and brazing. It is pertinent to consider the characteristics of each of these processes in turn.

7.1.1. Arc welding. There are only two or possibly three arc welding processes which are suitable for use on the refractory metals. These are the tungsten-arc (TIG) and metal-arc (MIG) inert-gas-shielded processes and possibly the submerged arc process. In the TIG process, an arc is struck between the work and a tungsten electrode in an atmosphere of argon or helium which serves the dual purpose of both carrying the arc and of protecting the weld area from oxidation. Usually inert gas is also supplied to the back of the weld by a grooved backing bar to protect the penetration bead. This bar also assists in the jigging and chilling of the weld: clamp or chill bars are used on the top of the work for the same purpose. Filler wire can be fed into the weld pool if necessary. The MIG process is similar except that the arc is struck between the filler wire and the work. The welding speed is higher in the MIG process and it is more suited to welding plate than sheet. The TIG process is more suitable for sheet, with filler if necessary.

In the submerged arc process the arc is struck between an electrode and the work either in a flux which becomes molten or in a liquid. In the latter case, the chilling is superior, but the protection less good.

Fusion welds in the refractory metals are typical of a pure metal. The grain size in the weld is very coarse, becoming finer as the heat affected zone is crossed, until unaffected parent metal is reached[33] (Fig. 6). Precipitates may or may not be present, depending on the composition. In the fused and recrystallised zones, any beneficial effects resulting from working must be lost.

It has already been pointed out how greatly the impurity level affects the strength and ductility, and also the ease with which oxygen or nitrogen is picked up at high

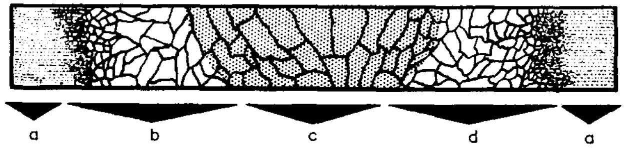


Fig. 6. Grain structure of a typical fusion weld in a refractory metal. (a) Parent sheet unaffected; (b) Heat-affected zone, coarse-grained adjacent to weld zone, fine recrystallised grains adjacent to parent sheet. (c) Very coarse-grained weld zone.

temperatures. Contamination during welding is one of the major problems during fusion welding. The weld pool, the heat affected zone and the back of the weld must all be protected and this can be achieved in the usual two ways, either by the use of nozzles, trailing shields and backing bars, or by welding in a cabinet filled with inert gas. The choice of which to use must depend on circumstances, but where possible a properly designed cabinet is preferable, as this reduces the rise of contamination. If open air welding is necessary, machine welding is better than manual, because the higher speeds and greater steadiness of the torch mean less contamination. The flow of inert gas and the clamping and jigging arrangements both need careful adjustment to avoid the entrainment of air with consequent contamination. Contamination can still arise from impurities already present in the shielding gas or from the surfaces of the pieces being welded. Any oxide already present must be removed and also any dirt and grease. Thus extreme care is needed both in cleaning parts to be welded and in preventing any additional contaminants from being introduced into the shielding gas.

7.1.2. Electron-beam welding. The problem of contamination is avoided in electron-beam welding. In this process, a beam of electrons from an electron gun is focussed on the work to be welded; gun voltages range from 10 to 150 kV. There can be a health hazard with voltages higher than 20 kV as harmful X-rays are produced from the apparatus and shielding is necessary. By the nature of the process, it can only be carried out in high vacuum so that there can be no pick up of impurities from the atmosphere, although the requirements for cleaning are equally stringent. As compared with arc welding material of the same thickness, the weld pool and heat-affected zone are very much narrower, since the heat input is more concentrated. The actual ratio of depth to width of weld depends on the characteristics of the electron gun. The main problems of electron-beam welding are the very precise set-up of the work which is essential and spatter caused by gas liberated in the weld pool. There is also a limitation on the size of work which can be accepted, imposed by the size of the vacuum chamber.

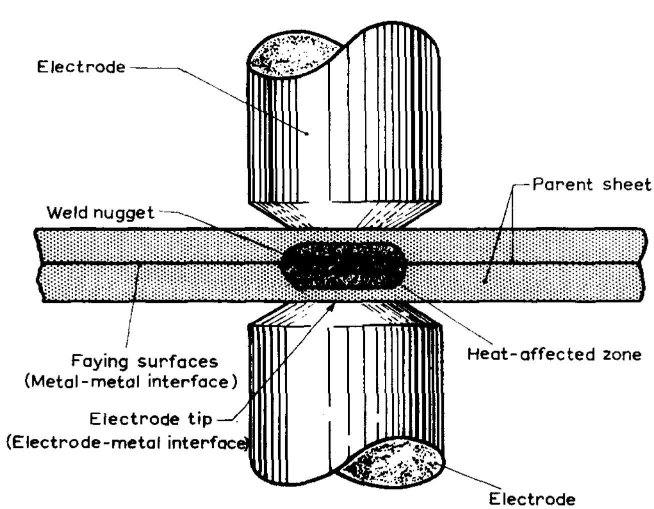


Fig. 7. Schematic diagram of a spot weld illustrating terms used in spot-welding.

It has been suggested that by welding at a slow speed and maintaining the pool molten for as long as possible, some purification of the weld metal might even be obtained[34]. However this would not affect the heat-affected zone. A more advantageous feature is that an immediate post weld heat treatment of the weld area alone is possible.

7.1.3. Resistance welding. As the name implies, heat is generated for welding by resistance to the passage of a low voltage high current pulse. This is normally produced in the single turn secondary of a transformer by passing an alternating current or discharging a condenser through the primary windings. A schematic diagram of a spot-weld illustrates the process (Fig. 7). The two sheets are pressed together by the electrodes which carry the current. Heat is generated at the three contact surfaces and in the body of the material. Owing to the high thermal conductivity of the electrodes heat becomes concentrated around the faying surfaces and a molten nugget is formed as shown. The molten nugget exerts a hydrostatic pressure and is contained by a shell of parent material which is also heated — the heat-affected zone. At the end of the current pulse, cooling is very rapid and stresses are set up owing to differential contraction. Overlapping welds are formed in the same way to give stitch and seam welds.

Surface preparation and cleanliness are important as the surface is incorporated in the weld nugget. Contamination by the atmosphere is however less since the molten nugget is not exposed. With high melting point materials (especially Mo and W which have high thermal conductivities) the temperatures reached at the electrode–metal interface will encourage electrode pick-up, sticking and wear. The weld nugget will have the properties of a cast material (with a possible redistribution of impurities already present in the sheet) and the heat affected zone, which most affects weld ductility, will be recrystallised. With alloys, of course, the effect of the temperature cycle in the heat affected zone will depend on alloy composition, but in all cases any improvement in properties produced by working will be nullified.

In projection welding, heat is localised by the configuration of the component. In butt welding, heat is generated at the rod or tube interface, and in flash welding by arcing and burn off of metal: in both cases the joint is made by forging the components together when they have been heated.

In projection, butt and flash welding fused metal is not normally present in the weld. However, the thermal cycles during welding will produce a heat affected zone with similar structures to that of a spot weld. Although the zone will be small in a projection weld it will be larger in a butt or flash weld. The short times used for projection welding could limit contamination but the longer times for butt and flash welding will necessitate some form of protective atmosphere to reduce surface contamination. With anisotropic material, *e.g.* worked rod, the upset in butt and flash welding will result in a change of orientation which could affect weld properties.

7.1.4. Pressure welding. Pressure welding relies on high applied load, with or without external heating, to form a bond. The state of the surface is critical, as thin films of oxides etc. can markedly affect bonding. As bonding is dependent partly on diffusion and partly on deformation, the time taken for bonding is longer and the deformation is much higher than in resistance welding. There is one commercial equipment available for pressure welding aluminium but experimental work is normally carried out with home-made rigs.

With refractory metals, it appears that applied heat will be necessary to assist bonding and reduce the extent of deformation. Protective atmospheres — helium, argon or vacuum — will be required, as well as extremely careful preparation. The advantages of low temperature welding are offset by the deformation required: the effect of this will be particularly marked with anisotropic material, *e.g.* rod, and weld strength will be reduced. The process is best suited to joining rod and it could only be useful for thin sheet material.

7.1.5. Ultrasonic welding. Energy is supplied by high frequency, low amplitude vibrations which disturb the surface and facilitate bonding. Pressure is applied during welding but the applied load is limited as it could reduce the vibrations. The results reported for ultrasonic welding of any material are conflicting and the process is only applicable to thin sheet material. No commercial equipment for ultrasonic welding is yet available in the United Kingdom. A British process which combines resistance heating and ultrasonic vibrations is being developed. Welding equipment specifically for the refractory metals is being developed in the U.S.A.[85].

Welding can be carried out at low temperatures, but high deformation is often required. Another problem which has not been completely solved is whether further welds weaken previous welds.

It appears that ultrasonic welding has a limited application and cannot necessarily be relied on when other welding techniques are unsuitable.

7.1.6. Friction welding. In friction welding heat is generated by rubbing the two components together by rotation of one or both so that a welding temperature is reached at the interface. At this temperature a high applied load forges the joint. The process is confined to parts which can easily be rotated, *e.g.* rod or tube and commercial equipment has only recently become available.

Joints can be made at relatively low temperatures with low deformation. The temperature gradients are gradual and for certain applications the process compares favourably with flash welding. Insufficient work has been done to delineate its range of usefulness, but joining rod and tube of both similar and dissimilar materials appears to be the main application at present.

7.1.7. Brazing. For certain applications, such as joining the refractory metals to other metals or for fabricating some types of structure, *e.g.* honeycombs, brazing can be considered. A brazing metal has to comply with certain requirements: (a) its liquidus must be below the solidus of the parent metals; (b) it must flow readily under capillary attraction; (c) it must wet the surfaces to be joined. A further condition is usually added, that it must not alloy readily with the parent metal. However, for high temperature as opposed to room temperature service, this condition does not apply; indeed alloying is probably necessary, although there must be an absence of low melting point eutectics or brittle intermetallic compounds. In general, if there is no alloying of braze metal and parent metal, the joint will be strong and ductile at low temperatures, but weak at high temperature. Intermediate phases usually produce joints that are both weak and brittle.

As compared with welding, brazing suffers from one serious disadvantage for high temperature use; this is the fact that the brazing metal has a lower melting point than the parent metals which in itself reduces the possible service temperature or, putting it the other way round, the intended service temperature imposes a lower limit on the liquidus of the brazing alloy. For the present review brazing alloys with liquidi less than 1000°C have been ignored, as possible service temperatures with such alloys seem too low to be of any interest. There may also be an upper limit on the melting point of the brazing alloy: if the parent metal depends on work-hardening to reach the required strength, the recrystallisation temperature must not be reached. Recrystallisation must of course also reduce the strength of a weld, but the affected area is usually smaller, whereas in furnace brazing for example, the whole work piece has to be brought up to brazing temperature.

An increase in service temperature could be obtained if the remelt temperature of the braze could be raised. For this to happen, the braze metal must diffuse into the parent metal and *vice-versa* at temperatures below the initial brazing temperature. The characteristics of the phase diagram between the braze and parent metals must be suitable, with a complete absence of eutectics of low melting point and of brittle intermetallic compounds. Fast diffusion rates would also be advantageous.

Protection from contamination is equally important in brazing the refractory metals, and this restricts possible brazing techniques. Oxyacetylene torch brazing is only possible at low temperatures (too low to be of any interest in the present report). Thus the techniques are restricted to furnace brazing (in vacuum, inert gas, or possibly for Mo and W only, hydrogen), induction brazing (with protection as for furnace brazing), torch brazing (with an inert-gas shielded tungsten arc) and resistance brazing in which heat is generated by the passage of current as in spot welding. Of these techniques furnace brazing is the only one suitable for large or complex structures, but the process cycle is slow: if recrystallisation is to be avoided, the permissible brazing temperature is reduced as compared with induction brazing. The latter is much quicker and also less demanding in terms of equipment, but it is restricted as to the size and more particularly the shape of work. Torch brazing has been little used, but should be the most suitable method for attachments, where it is undesirable to heat up the whole job. Resistance brazing has a range of application similar to that of spot welding.

In many cases it will not be possible to use a chemical flux, either because its subsequent removal would be impossible or because it would react undesirably with the brazing or parent metals. In any case, attempts to produce a suitable flux have not been successful. Therefore reliance must be placed on prior cleanliness or the self-fluxing ability of the brazing metal.

Jigging and fit-up are extremely important in brazing, more so than in welding, and there is also a difference in possible types of joint, *e.g.* for brazing thin sheet a lap joint is far superior to a butt.

The actual placement of the brazing alloy must depend on the geometry of the joint, but it will usually be in the form of wire or strip. However, in some cases where a pure metal is being used for brazing, it may be practicable to electroplate the parts to be joined.

7.2. Assessment of joint properties

Joints are usually assessed by their appearance, by radiography and by determination of the mechanical properties. Tests for the mechanical properties are different for fusion welds, resistance welds and brazed joints; these are considered in more detail below. In all mechanical tests the strain rate is important since the refractory metals are strain-rate-sensitive. In general low strain rates give more optimistic results.

7.2.1. Tests on fusion welds. The following remarks apply only to butt welds: there are no generally accepted methods for testing edge, lap, corner or fillet welds. The most common test is the transverse tensile test, which applies the same load to the parent metal, heat-affected zone and weld metal (the stress is not necessarily the same, depending on the presence or otherwise of a weld reinforcement). This test reveals the weakest zone and gives some information about its ductility but gives no information on the other regions. The longitudinal tensile test (although rarely used) gives a better comparison of the three regions. In this test the three zones are all at the same strain, and information is thus obtained as to which is the least ductile. Testing a specimen consisting of parent metal gives a strength comparison. In some cases an all-weld-metal specimen is desirable. The transverse and longitudinal tensile tests are complementary and both should be carried out.

Bend tests are also used for weld assessment, especially in the refractory metals field. Although more common than the longitudinal bend test, it is difficult to find much justification for the transverse bend test. The longitudinal bend test has the same virtue as the longitudinal tensile test; it strains all areas equally, although it gives no information on strength. Ideally bend tests should be carried out by pressing the specimen round the former with, for example, a lead pad. This technique avoids strain peaks. However, other types of bend test are also in use, *e.g.* the wrap-round test. Since the bend test can be carried out in stages more readily than a tensile test it is more useful for finding where cracks initiate.

Electron-beam welds can be assessed by the same tests as arc welds, although it would be difficult to produce all-weld-metal specimens.

In most cases tensile tests are confined to room temperature. But for design purposes tests should be made at service temperatures. Bend tests on refractory metal welds have been made over a range of temperature to try to follow the brittle–ductile transition.

7.2.2. Tests on resistance welds. Most strength tests are carried out on single spot welds; the two main tests are the shear test and the + tension test. For stitch and seam-welds (welds overlapping) the shear test and tension-peel test respectively are used.

The shear test gives weld strength but, particularly in seam welds, it does not necessarily reflect weld size and ductility: brittle welds often have a high shear strength. The + tension (or tension-peel) test loads the edge of the weld and the numerical values reflect heat affected zone and weld ductility, as well as weld size. The + tension test will give more information on spot welds in refractory metals where changes in mechanical properties are expected, and when heat treatments have to be evaluated. A face fracture indicates a brittle weld, a slug failure a more ductile weld.

Other routine tests include microsectioning, radiography (for internal flaw detection) and hardness surveys. Measurement of the weld diameter, indentation, sheet separation, and penetration are used to define the welds produced by a given set of welding conditions. Consistency tests are also carried out. Similar tests would be used with ultrasonic and pressure welds.

Butt welds (and friction welds) are tested by a tensile test, but weld strength does not reflect ductility. Some form of bend test (over 2 supports) is used to compare weld *versus* parent rod ductility.

7.2.3. Tests on brazed joints. Brazed joints are usually inspected visually for flow of the brazing alloy. Various specimens have been used for assessing the mechanical properties, including single-lap shear, double-lap shear and slotted-type shear specimens for sheet, and tensile specimens for rod. Of the shear type, the double-lap is probably best.

7.3. Niobium

The main facts about Nb to bear in mind when considering its weldability are that it reacts with air at a temperature as low as 200°C, that it also reacts with hydrogen, water vapour, carbon dioxide and carbon monoxide, that diffusion of interstitial impurities is rapid above red heat, and that the concentration of impurities markedly affects the strength and ductility[30]. Recrystallisation of worked metal reduces the strength but increases the ductility.

7.3.1. Arc welding. All reported work has been on the tungsten-arc process, usually d.c. with the electrode at negative polarity[19,21,22,27,30,35–40], but some work on a.c. has also been reported[40]. The purity of the shielding gas is clearly important but for pure Nb 99.98% argon is satisfactory[39].

The use of filler should be avoided where possible; where it cannot, mechanised feed is preferable, so that there is less risk of contaminating the filler outside the protective shield.

If the proper precautions are taken, the weld properties of pure Nb are good. The weld metal and heat affected zone are softer than work hardened parent sheet and of similar hardness to annealed parent sheet[38]. The weld tends to be slightly harder owing to some pick-up of impurities. Post-weld annealing may increase the hardness of the weld metal, because oxygen or nitrogen from the surface may diffuse in. Porosity is sometimes observed, possibly owing to carbon monoxide or dioxide, as a result of incomplete deoxidation[39].

The effect of a bad atmosphere is very well illustrated by some American work in which a flow-purged cabinet was used for bead-on-plate welds in vacuum-sintered Nb[35]. Even though the argon was purified, there was an increase of hardness from 125 VPN in the base metal to 188 VPN in the weld. Welds were also made under commercial purity argon, (giving 220 VPN in the weld) and nitrogen–argon and oxygen–argon mixtures. (1% nitrogen gave a weld hardness of 363 VPN.) Welds made in atmospheres containing nitrogen had no ductility and showed transgranular cracks with evidence of nitrogen contamination. The bend-test transition temperature was above 20°C for all welds.

In later work, a vacuum-purged cabinet was used with tank and purified helium as well as argon[29] (the tank helium was found to be purer than the purified). A Nb–0.6% zirconium alloy was welded and the hardness of the weld was lower than that of the parent sheet. The transition temperature was also low (−30°C) in bend tests. Pure Nb and a Nb–1% titanium alloy were also welded in helium, but the oxygen content of the parent sheet was high. The pure Nb weld had grain boundary films and inclusions, the titanium alloy weld containing precipitates in the grains and the boundaries.

In further work, arc melted alloys (rolled and annealed) were welded (bead-on-plate) in helium in a cabinet[36]. No cracking was observed but there was some porosity and the weld appearance was not very good. Two specimens of pure Nb were welded and the transition temperature increased from −150 to 75°C. Of the alloying additions zirconium (0.88–10.24%), vanadium (0.82–6.78%) and W (1.5–1.83%) all raised the transition temperature. Titanium (1–16%) first raised the transition temperature, then lowered it below −200°C. Hafnium (1%) also lowered the transition temperature. Measurements of the oxygen and nitrogen concentrations in the pure Nb were inconclusive, as were hardness measurements on the alloys. The metallographic features also were not clear.

Of the alloys more likely to be used commercially those containing 33% Ta–0.75% zirconium (FS82), 15% W–5% Mo–1% zirconium (F48) and 10% Mo–10% titanium (D31) have been studied[21,22,27,37]. FS82 was readily welded but the transition temperature (as determined in longitudinal bend tests) was raised from −195° for the parent sheet to 16°C[27].

There was a corresponding increase in strength and hardness due, it was suggested, to solution of a second phase. An increase in welding speed did not significantly alter the bend test transition temperature, but helium was better than argon. The transition temperature was also increased when D31 was welded, from −170° to over 316°C, and in this case cracking was also experienced (in one batch of material more at high speeds than low, in another *vice versa*). Preheat to 66–93°C did not prevent cracking. There was a dendritic precipitate in the weld zone which probab y reduced the ductility. Heat treatment at 1150°C for 24 or 72 h emphasised the dendritic pattern but reduced the transition temperature to 66–93°C, perhaps by an over-ageing process.

The F48 sheet was variable in quality, since the transition temperature varied from −128° to 38°C. As welded, it increased to 371° but was reduced to 204°C by heat treatment for 24 h at 1290°C; cracking was noted, but was eliminated by preheat to 66–93°C. When welded with Nb–1% zirconium filler and given a post weld heat treatment of 2 h at 1370°C F48 was ductile[21]. In the very little work which has been done on MIG welding of Nb, helium was found to give a slightly better shape to the weld bead than argon[21,22].

7.3.2. Electron-beam welding. Although electron-beam welding of Nb is practicable, there has been very little work reported. Vacuum sintered Nb is porous as electron-beam welded, owing to impurities[41]; therefore arc cast material should give sounder welds. It has been claimed that Nb–0.75% zirconium and D31 give slightly better results when welded by electron-beam than by the tungsten arc[22,42].

7.3.3. Resistance welding. There are only a few references to spot[22,27,30,43] and seam welding[30] Nb and none on flash, butt or projection welding. As with Mo (Section 7.5.3.) choice of welding conditions is influenced by the need to reduce oxidation, limit the extent of the recrystallised zone and reduce electrode wear. Short weld times and high currents are normally used, although FAULKNER[27] considers long times might be more advantageous.

Careful pre-weld treatment is advisable and metal surfaces should be clean. A nitric acid pickle[30] can be used to remove scale; FAULKNER[27] used a solution of 22% hydrofluoric, 8% nitric and 15% sulphuric acid to remove oxide. Seam welding conditions are given by COX[30] (Table VI), but no indication is given as to how they were selected and there are no strength values. He recommends water or carbon tetrachloride to improve cooling and possibly oxidation protection and mentions that a nitric acid pickle can be used to remove copper adhering to the Nb sheet. Welds in pure Nb are ductile as they pull a slug[44]. FAULKNER[27] describes attempts to

TABLE VI

SEAM WELDING CONDITIONS FOR Nb[30]

Sheet thickness (in.)	Tip load (lb.)	Electrode wheel face (in.)	Wheel speed (in./min)	Weld time cycles		Weld current (A)
				On	Off	
0.020	50	1/8	36	3	2	4,000
0.010	50	1/8	36	3	2	3,300
0.005	25	1/8	36	3	2	1,100

TABLE VII

SELECTION OF SPOT WELDING CONDITIONS USED ON Nb ALLOYS

Alloy	Ref.	Sheet thickness (in.)	Electrode		Weld force (lb.)	Time cycles				Current (A)		Shear strength (lb.)	Mode of failure
			Alloy	Tip. diam. (in.)		Pre-heat	Up-slope	Weld	Down-slope	Pre-heat	Weld		
FS82	22	0.025	M28	3/32	2200	—	2	4	0	—	25,500	900–1000	Slug
		0.070	M100	1/4	2200	—	2	6	2	—	27,100	2,700	Slug
FS82	27	0.020	Copper	8*	850	—	—	3	—	—	Not given	470–530	Slug
		0.060	Copper	24*	1580	—	—	15	—	—	Not given	2,100–2,700	Shear/Slug
D31	27	0.020	Copper	8*	910	—	—	6	—	—	Not given	660–740	Slug
		0.060	Copper	24*	1420	—	—	12	—	—	Not given	1,240–1,390 with titanium foil	Shear/crack
F48	22	0.020	—	—	650/1500	60	—	2	60	3,500	17,500	500–900	Shear
		0.040	—	—	650/1500	60	—	2	60	3,500	17,500	300–1,080	Shear

* Radius of dome-shaped electrodes.

reduce pick-up and wear but the best electrodes require changing after only 10 welds.

Recent information is available on spot welding three Nb alloys, FS82[22,27,43], D31[27] and F48[22,43]: a summary of welding conditions and weld strengths is given in Table VII. FS82 welds have adequate strength and are ductile, but D31 and F48 welds are brittle. This is reflected in the low strengths for the thicker sheets and in microsections which showed internal cracks. Post-weld heat treatment of F48[22] restores weld ductility but does not improve weld strength. The engineering and possible mechanical advantages of spot welds made without fusion (similar to a "stuck" weld) are mentioned[22,27] but the close control of welding conditions required for this type of weld makes it impracticable.

The use of inserts, brazing compounds or Nb fibre mats has been reported[27,43] and the strength of titanium insert welds are given in Table VII. There are no details as to their strength at elevated temperatures, but their behaviour would be similar to that of a brazed joint. The effects of possible contamination by a fibre mat have not been reported.

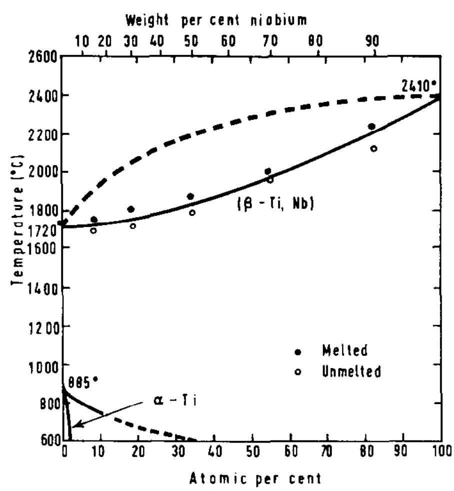


Fig. 8. Phase diagram for niobium–titanium.

7.3.4. Brazing. There is very little published information on the brazing of Nb, perhaps because welding is relatively easy. The oxide on the surface is sufficiently refractory to make brazing difficult; the technique of plating with copper or nickel, followed by a high temperature (1200°C) diffusion treatment *in vacuo* will give a surface which is more suitable for brazing[38]. However, since copper does not alloy with Nb and there is a eutectic at 1175°C with nickel, this does not seem suitable for high service temperatures, although the remelt temperature of a nickel braze might be raised by diffusion. From the existing phase diagrams, titanium would appear to be a suitable brazing filler: the phase diagram (Fig. 8) shows complete solid solubility except for low concentrations of Nb and no difficulty should be experienced. Some limited experimental work supports this view[45]: in this work palladium, platinum, platinum–10% iridium and platinum–10% rhodium were also used. The first three produced brittle joints, the last also severely eroded the base metal and was quite unsuitable.

In the case of Nb alloys, there may be a limiting temperature above which embrittlement will occur but otherwise there seems no reason why brazing temperatures of up to 1750°C should not be used[43].

7.4. *Tantalum*

The problems involved in welding Ta are exactly similar to those in welding Nb, except that reaction with air does not start until 400°C and Ta has a rather higher tolerance for impurities[31]. The high density may cause trouble with drop-through of the weld pool in fusion welding.

7.4.1. Arc welding. Provided proper precautions are observed and the base metal is sufficiently pure, Ta is readily weldable. Although the use of a.c. is not impossible, d.c. electrode negative is greatly to be preferred, both because the weld bead is narrower and deeper and because in open-air welding, air is less likely to be entrained. The hardness of weld metal should be similar to that of the annealed parent sheet[31]. Machine welding is preferable to manual and if a filler must be used mechanised feed is less risky. However, the very little systematic work carried out on the welding of Ta has not really provided a clear picture[31,46–49].

In the United States where there is a choice between helium and argon, the use of helium has been recommended for thicker sheets, because of the higher arc voltage, and argon for thin sheets because of the lower striking current[46]. A simple investigation of the effects of the initial vacuum level in a vacuum purged cabinet and of the effect of chilling has also been carried out[47]. With a slow cooling jig, an initial vacuum of 1 torr was necessary to allow a knife edge bend in the weld whereas, with a rapid cooling jig, an initial vacuum of only 10 torr allowed such a bend. An attempt was made in another investigation to correlate the carbon and oxygen contents of various batches with their weldability[48]. The results of the investigation were inconclusive: most of the unweldable batches contained inclusions but not all; some batches containing more than 100 p.p.m. of oxygen were weldable, others with less were not; some sound weld metals contained more oxygen than some of the unweldable batches. However, there was some evidence that an increase in carbon improved the weldability. The mechanical properties were also reduced by the coarse grain size of the weld metals: some grains extended right through the thickness of the sheet (0.02–0.03 in.).

Some work has also been carried out in the U.S.S.R.[49]. The effects of the purity of the shielding argon were studied: as the concentration of nitrogen rose, porosity was found and also some cracking. The best results were obtained with argon–0.1% nitrogen–0.1% oxygen.

There have been no reported experiments on the MIG process and only one mention of the welding of alloys, according to which the 10% tungsten alloy is weldable[50].

Submerged arc welding under water or carbon tetrachloride is still sometimes recommended[51]. This technique chills the weld very quickly but there is some risk of contamination, particularly with carbon if carbon tetrachloride is being used, and there is also a health hazard from carbonylchloride (phosgene). The method has little to offer as compared with the TIG process.

7.4.2. Electron-beam welding. There is very little published information on the electron-beam welding of Ta[52]. However, it certainly can be welded in this way, and the properties would be expected to be good.

7.4.3. Resistance welding. Ta wire and sheet has been used in the construction of electronic valves and condenser cans for many years. SPRARAGEN[2] summarises work to 1941 and the techniques are also described by NEGRE[53]. Very short weld times (1–2 cycles) and the use of flood water-cooling, alcohol, or carbon tetrachloride are recommended to reduce surface heating and increase cooling. NEGRE also suggests the use of large tip diameters to produce small diameter welds and says that the surface round the electrode tips should not reach red-heat. Welds are weak (but not as weak as W); this is attributed to the recrystallised zone round the weld, but the strength is adequate for this type of joint.

Work on specific thicknesses of Ta sheet is limited[31,54,55]. Pre-weld cleaning is advised by VAGI[55] who used a 55% sulphuric, 25% nitric and 20% hydrofluoric acid pickle and COX[31] who used a mixture of sulphuric and chromic acids. Both followed pickling by cleaning with acetone. Pick-up from the electrode occurs[31,55] and COX[31] suggests a nitric acid pickle to remove copper on the weld. Possible methods of reducing pick-up include a Mo foil insert[2], tungsten or tungsten faced electrodes[31] and the formation of solid phase welds[55]. These welds, made with no apparent melting, are described[55,56] and give a slug type failure. There is no indication of the range of welding conditions which give the solid-phase weld (similar to a "stuck" weld) but it is probably small. For this reason this type of weld should be carefully investigated before recommending its use. Reported seam welding conditions[2,31] are given in Table VIII.

No information is available on butt or flash welding Ta.

TABLE VIII

SEAM WELDING DATA FOR Ta

Ref. no.	*Thickness (in.)*	*Track width (in.)*	*Force*		*Wheel speed (in./min)*	*Weld times (cycles)*		*Weld current (10^3 A)*
			(lb.)	*estimated (lb./in.^{2}*)*		*on*	*off*	
31	0.020	0.10	50	10,000	36	2	2	4.5
	0.015	0.10	50	—	36	2	2	3.4
	0.010	0.10	50	—	36	2	2	2.8
	0.005	0.10	25	—	36	2	2	2.5
2	0.020	0.187	200	21,000	90	3	1	5.5
	0.050	0.187	500	—	36	3	1	7.2

* Based on assumed length of wheel contact of 0.050 in.

7.4.4. Brazing. The remarks made about Nb also apply to Ta, except that even less work has been done. The lowest melting point in the nickel system is higher, at 1360°C, but intermetallic compounds still exist. However, diffusion brazing might be successful. Titanium would again appear to be the most promising brazing metal. Except that the melting point is very high, Nb would also be suitable.

7.5. Molybdenum

There are many accounts in the literature of attempts to weld Mo, and in nearly all of these the result was the same: a joint was obtained which might be sound but was certainly brittle[16,23,24,33,38,53,57-61,71]. The basic reason for this was that the Mo used was insufficiently pure.

Mo is even more easily contaminated than Nb (except by hydrogen) and an even lower concentration of impurities reduces the ductility to an unacceptable level. Commercial Mo is only ductile when cold worked, recrystallisation reduces the ductility, usually to zero. The bend-test transition temperature is also affected: it normally ranges from −45°C to 40°C, but can be much higher for a weld.

7.5.1. Arc welding. More work has been reported on the arc welding of Mo than on the three other refractory metals. A theme common to all the early reports was that the quality of the parent sheet varied considerably, that if recrystallised it was brittle, and that welds were both weak and brittle, usually failing in the weld bead or recrystallised zone. Cracking and porosity were frequently encountered. Various techniques were employed in an attempt to prevent these defects, such as pre-heat, purification of the shielding gas etc., but without very much success. It was quickly realised that metal produced by arc casting gave better results than that produced by vacuum sintering, owing to its lower interstitial content.

The problem has been attacked in two ways and for ease of discussion it is convenient to consider them in turn. They are: study of the effect of impurities in the welding atmosphere, together with attempts to purify the shielding gas, and study of the effects of alloying additions. However, it must be remembered that these are both basically a study of the effect that interstitial impurities have, and of the means by which such effects can be reduced.

Some workers have, in effect, studied the relationship between interstitial concentration and weldability, by comparing material produced by different methods[16,18,24]. Besides the inert gas shielded process, the atomic hydrogen process has been tried, but without success[61].

Only one investigator has studied the effect produced by adding interstitial elements to the shielding gas[13,62]. In this work, oxygen or nitrogen were mixed with argon and then passed into a welding cabinet. Bead-on-plate welds were made in 0.06 in. thick sheet of carbon deoxidised arc cast Mo (tungsten arc, electrode negative), and specimens bend tested over a range of temperature. The analysis of the parent sheet was 18 p.p.m. oxygen, 30 p.p.m. nitrogen, and 600 p.p.m. carbon. As the concentration of oxygen in the argon increased from 0.02% to 0.4% centre bead and crater cracking was noted[13]. A graph was obtained relating the oxygen content of the weld bead to that of the atmosphere (Fig. 9). In the transverse bend tests, the as-rolled parent sheet gave a full bend at −100°C, the annealed (1200°C for 1 h) parent sheet at −30°C. Welding raised this temperature to 100°C even in pure (99.95%) argon, while the addition of 0.2–0.3% oxygen raised it to over 300°C. The temperature of brittle failure followed a similar pattern. It was suggested that these effects were caused by grain boundary oxide films. The type of fracture was also analysed and it was found that nearly all fractures had initiated intergranularly. Once started, propagation could be either inter- or trans-granular, usually the latter, especially as the test temperature increased.

The work on nitrogen was carried out in a similar way (but the oxygen concentrations were not measured)[62]. The effects produced by nitrogen were similar to, but less severe than, those due to oxygen. The temperatures for a full bend and for brittle

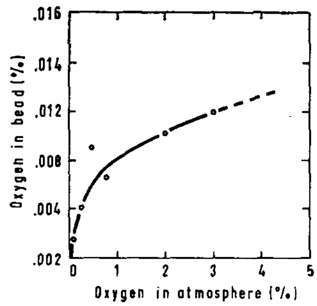


Fig. 9. Oxygen picked up during welding as a function of oxygen in the welding atmosphere[13].

failure increased as the nitrogen content increased, up to 0.07% in the bead. At this level continuous grain boundary films were observed and any further increase had no effect on the properties (unlike oxygen where the properties continued to fall). A graph was obtained of the take up of nitrogen into the weld metal compared with the concentration in the atmosphere (Fig. 10)[62]. Again most bead specimens began to fail intergranularly.

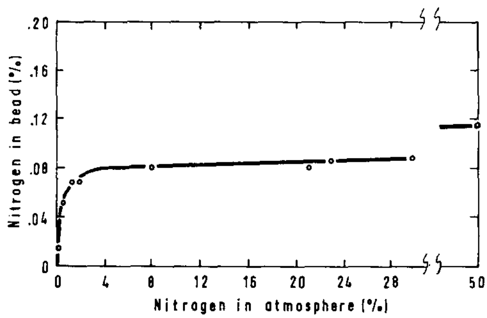


Fig. 10. Nitrogen picked up during welding as a function of nitrogen in the welding atmosphere[62].

Purification of the welding gas had been attempted in two ways, either by passing the gas through purifying columns and cold traps or by gettering the gas by arcing on titanium and zirconium. In the former case, phosphorus pentoxide and liquid air or dry ice traps have been used to remove water vapour, and hot calcium, magnesium or zirconium chips to remove nitrogen or oxygen. Of the two methods, that of arcing on scrap titanium can only be used in a cabinet , but has the advantage of simplicity and also of purifying the atmosphere immediately before welding.

In no case has any startling improvement in weld properties resulted. The improvement in ductility has been small compared with that attainable by the addition of some alloying elements, even where the oxygen and nitrogen concentrations were not increased over those of the parent plate[17].

The effects of alloying additions have already been considered in Section 2.2.1. above. The most common additions for deoxidation are titanium and carbon. However, there are contradictory reports as to their effects: for instance the optimum titanium concentration has been set at 0.46% by one worker[17], but at 0.70% by others, who found 0.46% gave no advantage over pure Mo[16]. There is a similar disagreement as to where the optimum carbon concentration occurs[15,16]. There is one report that the titanium alloy was both less ductile and less easy to weld than pure Mo[63,64]. The most reasonable explanation for these disagreements is batch to batch variation: differences in the level of interstitial impurities and even in the exact method of fabrication can give rise to very large differences in behaviour.

One attempt has been made to introduce a deoxidant into the weld pool by melting in titanium or Ta foil[24]. The parent metal was sintered and of poor quality: the addition of titanium allowed welds to be made without cracking but the ductility was low and in any event such a technique can do nothing for the heat-affected zone. A Mo–35% rhenium alloy has also been used as a filler with some success (an 82° bend as against 4° without the filler) but again the heat affected zone was less ductile[65]. The use of a rhenium-rich filler from which rhenium is diffused into the heat affected zone by heat treatment has been suggested[65], but the practicability in all but a few cases is open to question.

There has been one investigation of the consumable-electrode welding of Mo[66]. Considerable difficulty was experienced with arc stability and metal transfer, while poor weld bead contour, cracking and porosity were also observed. The current density, polarity of the electrode wire, the shielding gas and the use of an emissive compound were the variables. The optimum conditions were d.c. electrode negative in helium, the electrode wire being coated with cesium chloride to improve electronic emission: these conditions improved the arc stability and metal transfer to the greatest extent and also produced the best weld bead contour and reduced cracking and porosity. An attempt was made to compare MIG and TIG welds in $^1/_8$ in. plate. The grain size was similar in both welds although it had been hoped that the former would give a finer grain size; however, the chilling was different in the two cases, the TIG weld being more heavily chilled. Transverse bend tests indicated that there was no difference in ductility; both were poor, so was the parent sheet in comparison with some earlier material[16]. However, in this case, the conditions of testing were not identical. TIG welds in the two materials also differed in ductility, but neither the welding nor the test conditions were the same, so that comparison is difficult.

Submerged arc welding has not been studied recently. In the only investigation reported, there was difficulty in choosing a flux: those recommended for steel were not very good but some specially designed ones were even worse, while the weld appearance was poor and there was a lot of porosity[59]. Weld properties were not reported, but bearing in mind the early date of the work, were probably poor.

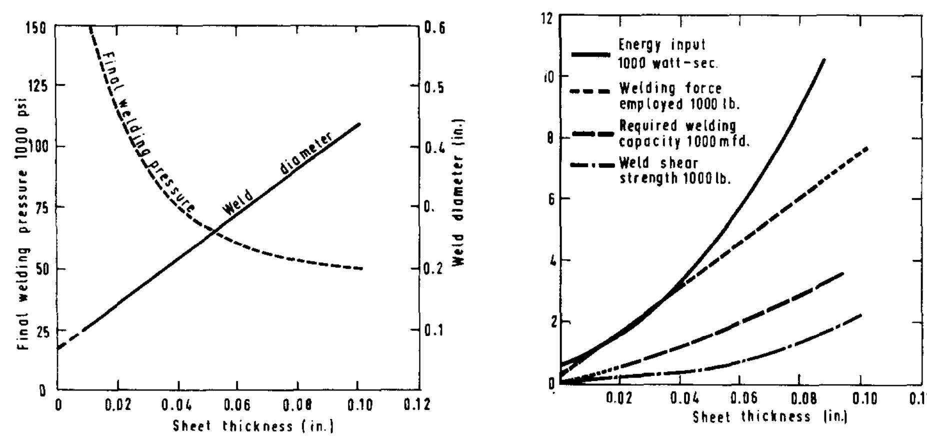
7.5.2. *Electron-beam welding*. The electron-beam welding of both pure Mo and Mo–0.5% titanium has been studied[41,67–69]. In general, the welds had better properties than arc welds, there was less porosity and cracking (and no preheat was necessary to prevent cracking), the heat affected zone and weld bead were narrower and the grain size in the weld smaller. The ductility varied but in one weld a 90° longitudinal bend at room temperature was possible[67]. Up to the recrystallisation temperature of the parent sheet, the weld metal was weaker but above this point the strengths were the same[69].

In one of the few reports by workers in the United Kingdom, the transition temperature of carbon deoxidised pure Mo was measured by bend tests over a range of temperatures[68]. The transition temperature (in longitudinal bend tests) was raised by welding, from just below room temperature to just above, while the load necessary to produce failure (or a full 180° bend) was halved. Heat treatment at 1200°C for one hour, which recrystallised the parent sheet, further increased the transition temperature to about 40°C. Heat treatment at 1600°C for half an hour followed by water quenching was even more harmful: the transition temperature for the weld metal reached 100°C, for the parent sheet 150°C. In transverse bend tests, the transition temperature as welded was about 80°C.

7.5.3. Resistance welding.

Spot welding. The process has been in use in the electronics industry for many years and NEGRE[53] describes the practice in detail. He recommends high currents and short welding times with strict control to prevent overheating the outer surface of the metal in order to avoid oxidation. Distilled water, alcohol or Vaseline are also suggested as protective media to reduce oxidation. Pick-up from the electrode occurs and should be removed from the surface of the weld. The welds are brittle and heating for 20 min in hydrogen at 1,000°C improves the mechanical strength. Weld strengths are not given since most welds are not stressed. Several examples of welded joints including dissimilar metals are given by BAER[70].

Cross-wire welding techniques used in the electronics industry are described by GOODMAN[71]. The high strength and ductility of the wire produced by drawing is removed by the welding operation. He recommends short weld times ($\frac{1}{2}$ cycle) for



(a) (b)

Fig. 11. Conditions used for and results obtained from spot welding molybdenum. (a) Weld diameter and final welding pressure. (b) Energy input, welding force, required welding capacity, and weld shear strength[72].

consistency and to reduce oxidation, but the short weld times mean high heating rates and rapid electrode wear. The use of platinum and nickel inserts to reduce the weld current and the extent of the recrystallised zone is also mentioned.

Work which gives recommended welding conditions is rare. HEUSCHKEL[72] gives conditions for condenser discharge welding of up to 0.100 in. powder metallurgy sheet (Fig. 11a and b). Weld diameters appear to be 80% of electrode tip diameter, although no dimensions are given. The microstructure of a spot weld shows an extensive recrystallised zone. JOHNSTON *et al.*[5] made spot welds in 1/16 in. thick sintered sheet which was recrystallised and coldworked. The investigation was not comprehensive. The use of carbon tetrachloride appeared slightly benefical and weld failure occurred in the heat affected zone.

The use of Ta inserts is mentioned by NEGRE[53] who states the weld is always weak. JOHNSTON *et al.*[5] tried 0.001 in. nickel foil and a brittle intermetallic compound was formed. FASTE[73] recommends zirconium as a suitable insert. MOSS[74] in his work on pressure welding (see below) recommends the use of inserts which form extensive solid solutions with Mo, *i.e.* chromium, W, and Ta. Resistance spot brazing using normal brazing compounds is also used[75].

Pick-up on the electrode and contamination of the work piece from the electrode also occur. HEUSCHKEL[72] found the problem worse for thinner sheet materials and recorded an electrode life of 3 to 4 welds between electrode dressing. He suggests welding under water and the use of short weld times. JOHNSTON *et al.*[5], COX[38] and CLIMAX MOLYBDENUM CO.[75] used a variety of electrode materials including copper, 49W–1Ni–50Cu, W, Mo and other refractory metal faced electrodes. JOHNSTON[5] used an unusual technique of coating the electrodes with lead foil before each weld but this would be impracticable for production use. None of the materials tried has been satisfactory.

Techniques which localise the heating between the two sheets are also recommended as a means of reducing electrode wear. Grit-blasting[72], sandblasting[75], and projection welding[75] have been suggested but experimental details are rarely given.

Ultrasonic welding of 0.015 in. Mo–0.5% Ti sheet is described by WEARE *et al.*[76]. Poor quality welds with high interior deformation were made, which were cracked and very weak.

Butt-welding. The welding of rod prepared by a number of methods has been done by KEARNS[23] and JOHNSTON *et al.*[5]. It appears that careful end-preparation with fine emery paper just before welding[74] is adequate although KEARNS[23] included both rough polishing on a cloth-wheel and electropolishing in Coon's solution (150 ml methyl alcohol, 50 ml hydrochloric acid, 20 ml sulphuric acid) as well. Two test methods were used for evaluating welds — the bend test[23] and the normal tensile test[5]. The bend test in which the specimen is bent between two supports, gives a clearer distinction between brittle and ductile welds. In both cases welded specimens were machined to remove upset before testing and JOHNSTON[5] also removed the original surface of the rod. Welding conditions are given and these illustrate the effect of heating time. Times shorter and longer than a given value give brittle welds. A protective atmosphere is essential and it was found that helium[23], argon[5] and dried hydrogen[23,5] give brittle welds. High vacuum (10^{-4} torr), carbon tetrachloride or water gave welds with some ductility[5]. KEARNS[23] found that whereas triple vacuum-melted or solid state purified rod gave ductile welds *in vacuo*, arc-cast and powder metallurgy rod did not. In contrast JOHNSTON[5] claims some ductility for welds made in carbon tetrachloride or water, stating that arc-cast rod gave better welds than powder metallugy rod. The difference in opinion is probably explained by the type of test used to assess ductility. KEARNS[23] attempted to improve ductility by heating at 1130°C for 2 min and found this improved rod but not weld ductility.

Flash welding. The main work has been done by NIPPES *et al.* in two reports[77,78]. The first covers temperature measurements to determine the effect of welding variables and the second gives the determination of welding conditions. THOMPSON *et al.*[79]

carried out a limited investigation on Mo–0.5% titanium based on the work by NIPPES[77,78].

NIPPES[77] found that for ½ in. powder metallurgy rod the parabolic flashing cycle was in two stages. During the first the instantaneous temperature increased with burn-off until a second stage was reached at which a stabilised temperature distribution existed. In order to keep the recrystallised zone to a minimum a short clamping distance and high platen acceleration are required.

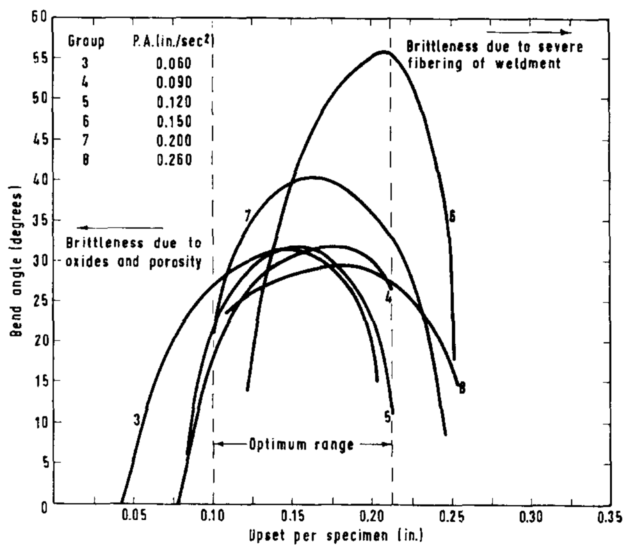


Fig. 12. Summary curves showing effect of upsetting conditions on bend angle of arc-cast molybdenum flash welds (all welds made in air)[78].

The second report[78] covers work with ½ in. x ¼ in. × 2.6 in. long specimens in both arc-cast and powder metallurgy rod. Bend tests on machined specimens were used to evaluate the welds and showed considerable scatter. High platen acceleration with certain values of upset gave the greatest ductility. The results are summarised in Fig. 12. Brittleness occurred at low upsets owing to oxides and porosity and again at high upsets as a result of distortion of the fibres in the parent metal. It was also found that using an atmosphere of argon or hydrogen gave less ductile welds. This is difficult to explain but as they found heavier carbide precipitation in these atmospheres it was suggested that this loss of ductility was due to a lower rate of oxidation and carbide removal.

Some work[78] with powder metallurgy rod showed that flash welds in air, argon and hydrogen had similar ductilities. The best conditions are not defined but are not the same as for arc-cast metal.

The work by THOMPSON *et al.*[79] on Mo–0.5% titanium used similar techniques to those described above. The results again showed considerable scatter but higher upsets gave increased ductility. The welding conditions were chosen from the preliminary work. The welds were evaluated in an original manner. Four flash-welds were hot-rolled in an unconventional way parallel to the weld from 0.230 × 0.935 × 12 in. long bar to 0.040 × 4 × 6 in. sheet. Although edge splits occurred dye penetrant testing showed the welds to be free of defects. The sheet was cut and machined into test-pieces across the weld and coated for oxidation protection. Weld tests over a range of temperatures produced brittle failures below 1200° C and more ductile failures away from the weld, at higher temperatures.

7.5.4. Pressure welding. Moss[74] used 0.020 in. powder metallurgy sheet and welded in a special chamber using impact loading. Both argon and hydrogen were used as

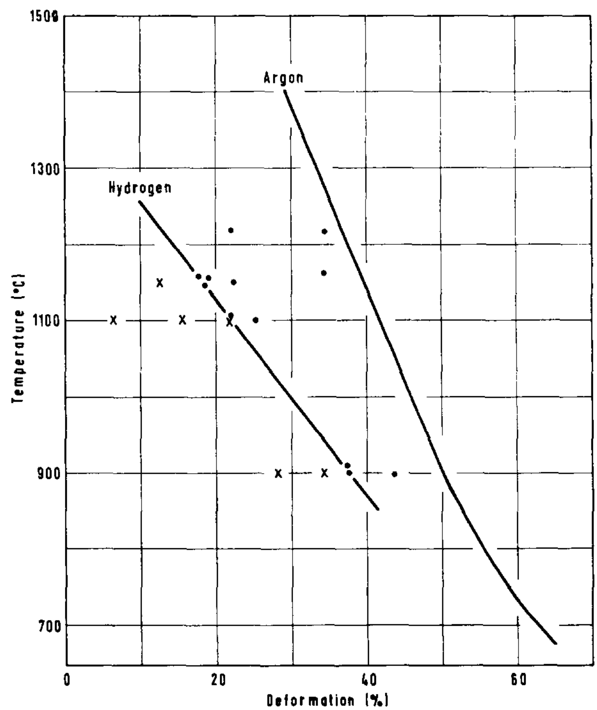


Fig. 13. Boundary conditions of temperature and of deformation necessary to pressure-weld molybdenum sheet in hydrogen and in argon[74].

TABLE IX

PRESSURE WELDING OF 0.020 in. POWDER METALLURGY Mo SHEET (AFTER MOSS[74])

Combination	*Atmosphere*	*Temperature (°C)*	*Deformation*	*Remarks*
Sheet				
Mo–Mo	Argon	1,000	45	Welding commenced
	Argon	1,200	36	Welding commenced
Mo–Ta–Mo	Argon	1,000	22	Welded
Mo–Ti–Mo	Argon	1,000	5	Welded
Mo–Pt–Rh–Mo	Argon	1,000	8	Welded
Mo–Ni–Mo	Argon	1,000	17	Welded
Mo–Co–Mo	Argon	1,000	10	Welded
Mo–Cr–Mo	Argon	1,200	3	Welded
Mo–Al–Mo	Argon	1,200	50	No weld

protective atmospheres, and it was found that hydrogen permits welding at lower temperatures and deformation. Unfortunately no strength tests were carried out on these welds but it was thought that welding could be done below the recrystallisation temperature. The results are illustrated in Fig. 13.

Moss also tried inserts of iron, stainless steel, Nb, Ta and chromium, and a micrograph indicated bonding. He suggests that inserts which form compounds with Mo (iron, cobalt or nickel) would be unsuitable, whereas inserts of metals which form solid solutions with Mo (chromium, W or Ta) should produce ductile joints. Table IX lists a selection of results obtained.

7.5.5. *Brazing.* Mo has no refractory oxide coating and is therefore more amenable to brazing than Nb or Ta[38]. A very large number of metals and alloys have been used to braze Mo[5,26,64,80,81], but there is little information as to the properties of brazed joints. Of the pure metals, copper wets Mo very well but does not alloy with it, so that its high temperature use is doubtful. There is a eutectic with nickel at 1315°C and also some intermetallic compounds. The technique of diffusion brazing has been studied in this case, with promising results[82]. The joint was held at 1350°C for some hours and it was found that most of the nickel was dissolved in the Mo (the solid solubility being of the order of 1%). At 1350°C, there are no stable intermetallic compounds, although these might form in service between about 800° and 1350°C. The effect of holding time was shown by loading two specimens, one of which had been held at the brazing temperature for 5 min and the other for 5 h, and increasing the temperature. The first specimen failed at about 1400°C, the second had not failed when 2000°C was reached: the time taken to raise the temperature would obviously affect the results but this was not reported. The disadvantages of this method are the high temperature and long times required: the latter especially would not suit a production process, while the former means that the parent metal will be recrystallised.

Titanium again appears to be a suitable metal for brazing although the brazing temperature is above the recrystallisation temperature. In this case also, the remelt temperature could probably be raised by diffusion, but there is some evidence from fusion welding that diffusion is slow[83]. Of the various alloys suggested for brazing Mo, there is insufficient evidence to allow conclusions to be drawn. Nickel, iron, cobalt and palladium base alloys have all been put forward and some sorting out seems highly desirable. For high temperature service, Nb–titanium alloys could probably be used.

In the case of pure Mo and its dilute alloys (*i.e.* those containing less than 10% of alloying addition), brazing does not seem particularly attractive. The gap between the required service temperature and the recrystallisation temperature is narrow and these alloys do depend for their strength on work hardening. The recrystallisation temperature of pure Mo is about 1175°C[26], of Mo–0.5% titanium 1345°C[26] and of Mo–0.5% Ti–0.08% Zr 1480°C[43]; yet for service at 1100°C, a brazing temperature of at least 1300°C is necessary. There is also the loss of low temperature ductility to be considered. In work carried out some years ago, brazed joints nearly always failed in the recrystallised zone at room temperature[80]: in this case the parent sheet was probably too low in purity, as some was fabricated from powder compacts. There have been no reports on the brazing of high purity Mo, where the loss in ductility might be less marked.

7.6. Tungsten

Of the four refractory metals, W is by far the most intractable. It has all the ease of contamination that characterises these metals, coupled with an even greater lack of ductility. At best, a heavily worked structure has only very limited ductility in one direction and this is reduced to zero on recrystallisation. The transition temperature is well above room temperature, ranging from 175° to 455°C[9]. The very high density could give rise to drop-through troubles with the weld pool during fusion welding.

7.6.1. Arc welding. There has been almost no work on the arc welding of W[50,84]. There are considerable difficulties: even a thoriated W electrode cannot be expected to survive for long the high temperatures involved. With the quality of material at present available, porosity and an absence of ductility are inevitable[50]. The transition temperature is also raised by welding, and cracking is common. The welding of W alloys has not been investigated but with the possible exception of the W–30% rhenium alloy there is no reason to suppose they will be any more weldable. The use of this rhenium alloy as a filler has been recommended[65]. This may improve the properties of the weld metal but cannot improve those of the heat affected zone.

7.6.2. Electron-beam welding. W has been electron-beam welded with some success [41,43,50]. As with Mo, the grain size of the weld is smaller than in an arc weld[41] but the joint is still brittle and its transition temperature increased *e.g.* the transition temperature of the base metal was 260°–315°C, of the weld 370°C[43,50]. Also the recrystallised zone is weak. The weld may show porosity if the base metal has been vacuum sintered[41]. Arc melted or electron-beam melted material should certainly be superior in respect of porosity and possibly in ductility and transition temperature.

7.6.3. Resistance welding. W has been used for many years in electronic[53] applications and in electrical contacts, but the joints are usually brittle and no strength values or welding conditions have been reported. Cross-wire welding is comprehensively described by GOODMAN[71] who recommends short times and high forces similar to those used for Mo. A micrograph of a cross-wire weld shows the extensive recı ystallised zone obtained.

NEGRE[53] described the welding of W to steel using high currents, short times and low forces to produce acceptable welds. Both NEGRE and GOODMAN[71] recommend the use of inserts of iron, nickel or platinum which require lower currents and reduce the extent of the recrystallised zone whilst improving weld strength.

Electrode sticking[84] is again a problem but high forces, short times and/or the use of inserts are said to reduce sticking.

7.6.4. Brazing. The remarks made about Mo apply in the main to W also. However, the problem is slightly eased by the fact that the recrystallisation temperature is higher and thus there is a wider range of possible alloys. For high temperature service, the other three refractory metals, or alloys of them, could all be used: titanium is not quite as attractive by itself since a eutectoid is formed. However, it could still be used as a component in brazing alloys.

8. CONCLUSIONS

8.1. Material quality

(a) At present the purity and method of fabrication of any refractory metal or alloy are the two most important influences on weld quality. In many cases comparison between results obtained with different batches of the same material is rendered difficult by variations in processing. Metal produced by arc casting or electron beam melting should be purer than metal produced by sintering.

(b) In the case of Mo the effects of interstitial impurities can be ameliorated, in at least some cases, by high temperature vacuum heat treatment. It is not known whether similar results are obtainable with W.

(c) The addition of titanium to Mo as a deoxidant appears to have beneficial effects and an alloy containing 0.5% titanium is commercially available. However, for welding it has been suggested that 0.5% is not necessarily the optimum addition.

8.2. Welding technique

The various techniques have not been adequately investigated and it is impossible to choose welding conditions with any certainty. Nevertheless, certain conclusions can be drawn:

(a) Scrupulous cleanliness of the work and care in handling must be observed.

(b) In arc-welding the shielding gas must be kept as pure as possible.

(c) As electron-beam welding is done under a high vacuum, contamination is very unlikely and it is possible to produce a narrow weld bead and heat-affected zone.

(d) With resistance welding several protective media have been used but it is not known if they are necessary.

(e) Pick-up of electrode material is a serious problem in resistance welding.

(f) There is little information on the effect of welding on the redistribution of impurities already present in the metal.

8.3. Weld properties

(a) Ductile welds can usually be produced in commercial Nb and Ta, rarely in Mo and never in W. Reported weld strengths and ductilities vary widely and correlation with parent sheet properties is practically non-existent. There is far too little known about the tensile properties of welds, especially at their likely service temperatures. Most work on fusion welds has been confined to bend tests and only the shear test has been used for spot welds.

(b) From the limited evidence electron-beam welds have better properties than arc welds.

(c) Very little work has been done on post weld heat treatment.

(d) No work has been reported on the fatigue properties of welds.

8.4. Alloys

(a) Although a number of higher strength alloys are being developed there is little information on their weldability.

(b) Welding trials on alloys have only been carried out at a late stage in alloy development. The weldability has not normally been considered when alloy composition is being chosen.

8.5. Brazing

(a) Although a large number of metals and alloys have been recommended for brazing the refractory metals, there is almost no information as to which are the most suitable either for a given parent metal or for a given service application.

While two different brazes may be equally satisfactory in service at room temperature, there can be marked differences at higher temperatures.

(b) Brazing seems more attractive for joining Nb and Ta than for Mo and W. In the case of dilute alloys of Mo, it is difficult to see much use for brazing for high temperature service.

(c) There is insufficient information as to the mechanical properties of brazed joints. What little information exists is confined to tensile or stress-rupture tests: there is no information on fatigue.

RECOMMENDATIONS FOR RESEARCH

It is obvious that there is insufficient knowledge and experience of most aspects of the welding of the refractory metals. Most reported work has been carried out in the United States: there appears to be little work in progress in the United Kingdom. The following aspects of each process should be investigated in any programme covering the welding of the refractory metals. (Some of this proposed work must already be in progress in the United States, but no information is available on current work.)

1. Electron-beam welding

(a) An investigation of the technique and the effect of the welding parameters on the resultant welds.

(b) The process should be used to produce welds with minimum contamination to act as a standard for other processes.

(c) Metallurgical effects due to welding should be investigated in both pure metals and alloys.

(d) The benefits to be obtained by various post-weld heat treatments, both on the weld bead alone and also on the heat affected zone should be assessed.

(e) The possibility of welding different types of joint (including complete assemblies) should be studied.

2. Arc welding

(a) A study of the welding of different batches of pure Nb, Ta, Mo and W, should be made in order to assess batch variations. Welds should be made under the best possible conditions by the inert-gas shielded tungsten-arc process in a cabinet.

(b) The tensile properties of the welds should be measured over a range of temperature. Room temperature tests will, of necessity, be carried out during the work involved under (a) but it also seems important to extend these tests up to any foreseeable service temperature. It may be desirable to carry out tests at low temperatures in order to follow ductile-to-brittle transitions. Bearing in mind the importance of strain rate in such work, it may be necessary to test at two or three different strain rates.

(c) The benefits to be obtained by vacuum heat treatment require investigation. Such treatments would have two objectives, to improve the properties of parent sheet whose mechanical properties were otherwise below standard, and to improve the properties of welds.

(d) The feasibility of open-air welding, as opposed to cabinet welding, requires investigation.

(e) The permissible level of contaminants in argon (and possibly helium) should be determined.

(f) The consumable electrode welding of these metals should be investigated.

(g) Much of the work on pure metals should be repeated on alloys. It is not yet clear, however, which alloys are likely to be of interest. This is especially so in the United Kingdom where there has been little work on alloy development. However, the Mo–titanium alloys do seem worthy of early investigation, if only to clarify the position as to what is the optimum addition of titanium. Provided that a supply of rhenium can be arranged, the alloys of Mo and W with rhenium should also be singled out, in view of their particularly attractive mechanical properties.

(h) If it is intended to develop alloys in this country the weldability of such alloys should be considered and investigated *ab initio*. This would require welding trials (including measurement of mechanical properties and metallographic examination) of a wide range of alloys, even though the number of possible alloying additions is restricted.

3. *Resistance welding*

(a) Existing electrode materials should be assessed to compare their performance. Electrodes of differing composition and plated electrodes should be investigated for their resistance to pick-up, wear and alloying.

(b) Spot welding (and later seam welding) conditions for pure Nb, Ta, Mo and W should be determined. Strength tests and microsections would be used to assess weld quality.

(c) The strengths of welds should also be measured over a range of temperatures up to the service temperature.

(d) The effects of post-weld heat treatment should be investigated including the possibility of heat treatment in the welding machine.

(e) Methods of reducing heating at the electrode–metal interface, including inserts, projections, fibre mats and variations in surface resistance, should be tried.

(f) Spot welding in various protective atmospheres—high vacuum (10^{-4} torr), argon, dried hydrogen and carbon tetrachloride—should be investigated.

(g) Spot brazing should be investigated in conjunction with other methods of brazing.

4. *Friction welding*

Friction welding has a limited application as at least one of the two components is normally rotated. However the metallurgical advantages of a weld made without fusion make this process attractive.

(a) The joining of rod in various metals and alloys should be investigated and an assessment made of the joint by strength tests and metallurgical examination.

(b) Dissimilar metal joints for specific applications should be investigated.

5. *Brazing*

(a) An assessment should be made of the various brazing metals and alloys for Nb and Ta and their alloys to determine which are the most suitable for brazing at given temperatures. Induction brazing in either vacuum or inert-gas appears to be the simplest technique for this purpose.

(b) The mechanical properties of brazed joints must be determined, both at room and elevated temperatures. Tensile, stress-rupture and fatigue tests should be carried out.

(c) If design considerations warrant it, a similar assessment should be made of Mo and W.

6. *Analysis*

It is essential that determinations of the level of interstitial impurities should be made, both in parent sheet and weld metal. Such direct determination would reduce the number of mechanical tests required, particularly in assessing different joint configurations.

7. *Fatigue*

At a later stage, the fatigue properties of welds at room and service temperatures will have to be determined.

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