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Solid-state diffusion bonding of tungsten-25 rhenium alloy

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Nickel has successfully been used as an interleaf material to join W-25Re between 900 and 1400° C. The bond strength was found to depend on the temperature and stress at which the bonding process was conducted. It was also found that nickel reacts with the parent metal and forms a Ni–W–Re ternary alloy. The formation of the alloy causes significant embrittlement in the parent material. The alloy first nucleates at the grain boundary and then grows into the grain. Quantitative studies of the growth kinetics of the ternary alloy and its effect on the bond strength are discussed. Joining of W–25Re by self-diffusion bonding has also been successfully demonstrated at temperatures above 1500° C. The effect of surface conditions will be correlated with the quality of the joint.

1. Introduction

Tungsten exhibits some interesting properties. It has the highest melting point of all metals, a high elastic modulus, excellent creep strength and high density. In fact, tungsten doped with potassium or thoria are well-known materials for lamp filaments and some heating elements. However, the material also has some deficiencies preventing it from wider structural application. The major one is its very high ductile-to-brittle transition temperature, particularly when the material is in a recrystallized state, which makes the material difficult to handle. In 1960, researchers ([1] pp. 114–25, [2]) found that the addition of rhenium can greatly ductilize group VIB metals, including tungsten. Although the exact mechanisms are still controversial, it is generally agreed that the addition of rhenium to tungsten can increase the recrystallization temperature, decrease the ductile-to-brittle transition temperature and also improve the creep strength. These improvements make the W–Re alloys attractive for some special structural applications, in spite of the high cost of rhenium. A satisfactory joining technique for the alloys still needs to be demonstrated in order to produce useful structures from the alloys.

Fusion welding and brazing of refractory metals are, in general, not desirable due to the recrystallized microstructure produced in the joint. In view of this it is preferred to reduce the bonding temperature by conducting solid-state diffusion bonding (SSDB) at a sufficiently low temperature to prevent recrystallization. This requirement to perform SSDB below the recrystallization temperature of the materials to be joined is fundamentally a problem. This is because a good metallurgical bond always requires migration of the initial interfaces. These interfaces become new grain boundaries as the two pieces of metal are joined together. However, two methods are, in principle, still applicable and avoid the recrystallization problem during SSDB. One is by applying an interleaf material to activate the bond interface, and the other is to greatly increase the recrystallization temperature of the bonding material by alloying.

Temperature and pressure are two important parameters during SSDB. Temperature has a dual function. First, it determines the rate at which atoms diffuse across the bond interface. Second, it promotes the surface deformation of the bonding samples by external pressure to ensure a proper interfacial contact. The second process is essentially a creep process. Therefore, temperature and pressure are actually two interdependent parameters during the course of diffusion bonding. Normally, the higher the temperature, the lower the necessary pressure and vice versa.

In the present study, experiments were conducted with wire specimens. One advantage of using wire specimens is elimination of the consideration of pressure requirement. Ideally, one always has an initial point contact which gives an extremely high contact pressure. However, the final pressure, as well as the contact area, will be determined by the creep of the wire. In the present paper, it is demonstrated that W–Re alloy can be successfully joined at temperature as low as 900° C by using nickel as the interleaf material. Self-diffusion bonding of W–Re is also demonstrated. The temperature (about 1500° C) that is required to produce a good bond is, however, much higher using self diffusion.

2. Experimental details

Tungsten–25% (atomic) rhenium filament of 0.13 mm diameter was obtained from Rhenium Alloys Inc. The as-received filaments were electrolytically etched in a 10% HF solution with 10 V a.c. and 2 A cm^{-2} current density to remove the surface contaminants. The result of this surface cleaning process will be discussed in the next section. Nickel coating was applied by

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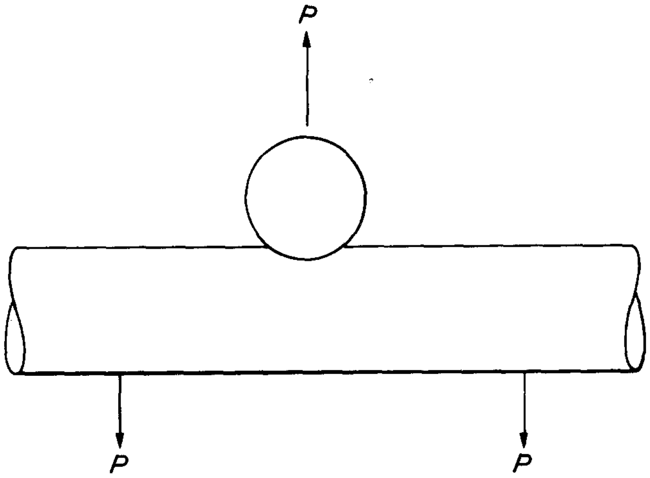

Figure 1 Schematic representation of the bond strength test.

plating from a $NiCl_2$–HCl strike bath, followed by deposition of about 5 μm nickel from a low-pH Ni-sulphamate bath [3, 4].

Bonding experiments were conducted by laying four wires to form a quadruple cross pattern and then sandwiching the structure between two optically lapped alumina plates. A dead load was applied on the top plate during the course of diffusion bonding. The dead load was approximately 30 g per joint. All experiments were performed in a vacuum that was maintained at 10^{-3} Pa or better. Bond strength tests were also conducted with a specially designed fixture. This bond test is similar to a three-point bending test and is schematically represented in Fig. 1. The tests were conducted by applying incremental loading until failure occurred.

3. Results and discussion

3.1. Using nickel as interleaf

A micrograph is shown in Fig. 2 of a nickel-coated W–Re wire. The coating is uniform and is about 5 μm thick. It was noted that the as-received wires were cracked along their length, a feature that is commonly observed in drawn refractory metal or alloy wires [5]. The nickel plating not only coats the outer surface of the wire, but also tends to seal up cracks that intersect the surface.

Solid state diffusion bonding experiments were conducted using the nickel-coated W–Re wires over the temperature range 900 to 1400° C using different bonding times. It appeared that successful bonds can be produced at all the above temperatures within a reasonable period of time, normally less than 5 h. It was also found that the quality of the bond was not strongly affected by the bonding time. The bonding time seems to be a less effective parameter than either the applied load or the temperature. Usually, it is much easier to slightly raise the temperature or pressure than to increase the bonding time in order to achieve a good bond. This is because the processes involved in diffusion bonding, such as creep, interfacial migration and cavity sintering, are all diffusional. Therefore, it is expected that, temperature and pressure affect the degree of diffusion bonding either exponentially or by a power law, respectively. However, since steady-state creep, interfacial migration and cavity sintering rates are all relatively time independent it is expected that time is effective by no more than a linear term. In spite of the apparent bonding between the wires, it was also observed that the nickel coating reacted with the W–Re wire. This reaction increases as the bonding temperature increases. Fig. 3 shows a microstructure of the bond interface produced at 1200° C after 5 h. A good metallurgical bond is obviously well-established by the Ni–Ni joint. The reaction zone between the nickel and the W–Re wire

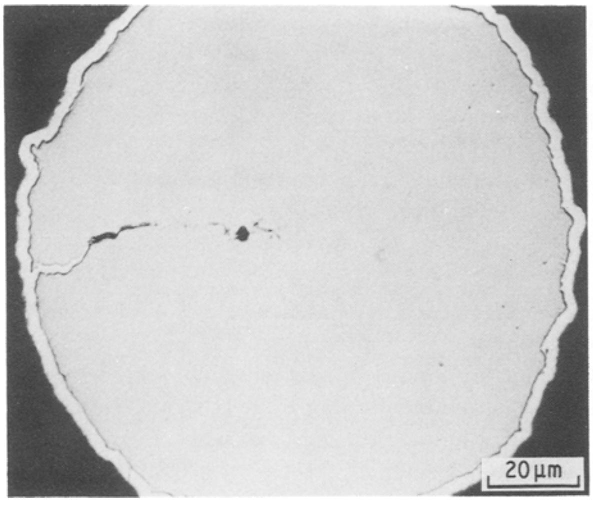

Figure 2 W–25 Re wire coated with 5 μm thick nickel.

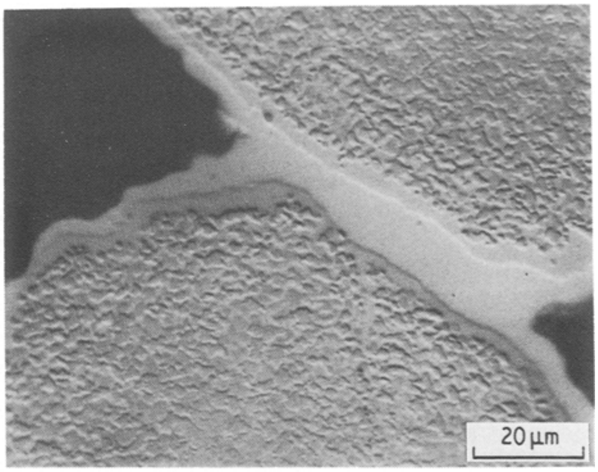

Figure 3 Micrograph showing the reaction between nickel and W–Re at 1200° C for 5 h.

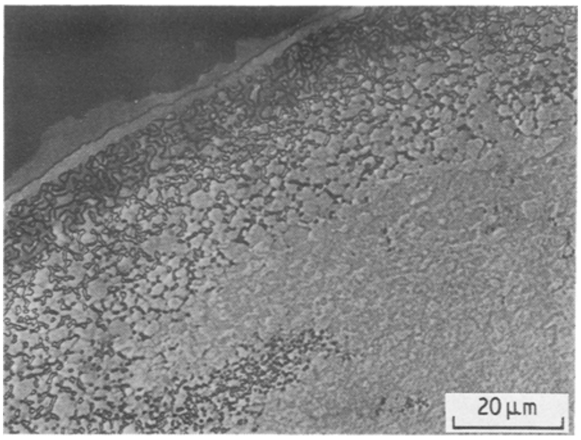

Figure 4 Reaction between nickel and W–25 Re at 1300° C for 1 h. Four zones are shown in the microstructure; they are nickel coating, W–Re–Ni ternary phase, W–Re and W–Re–Ni two-phase mixture and W–Re core.

is also readily observed. The reaction characteristics between nickel and W–Re wires are interesting and need further discussion.

A cross-section of a coated wire which has been reacted at 1300° C for 1 h is shown in Fig. 4. The microstructure consists of several zones: nickel, reactant layer, two-phase mixture, grain-boundary decorated W–Re and W–Re core. The micrograph suggests that the reaction took place by (1) inward diffusion of nickel along the grain boundaries of W–Re, (2) nucleation of a new phase at the grain boundary, particularly at the triple point, and (3) growth of the new phase toward the grain interior. The reactant layer and the two-phase mixture zones represent a completion and incompletion of the growth of the new phase, respectively. The zone of nickel-decorated grain boundary represents the completion of nucleation or the early stage of growth of the new phase. A similar, but not identical, phenomenon has been reported in Ni–W binary system, in which it was observed [6] that nickel strongly reacts with grain boundaries of tungsten because of the low solid solubility of nickel in tungsten. In the case of Ni/W–Re, in addition to the grain-boundary activity of nickel, because of the high mutual solid solubilities between nickel and rhenium [7], nickel was dissolved in the W–Re matrix and formed a new ternary phase. Special efforts were made to identify the new phase by long-time annealing of the nickel-coated W–Re specimens. Both EDAX and EMP analyses indicated the coexistence of tungsten, rhenium and nickel in the new phase. The chemical composition in the new phase was found to be uniform indicating that the new phase is either a stoichiometric compound or equilibrated solid solution. Some attempts were made by using X-ray diffraction techniques to identify the new phase. The tests were conducted with powdered samples prepared from heat-treated wires. However, the test results failed to show the existence of any intermetallic compound. The diffraction pattern obtained from the powdered samples was similar to that from a W–Re sample. Therefore, the new phase can only be tentatively identified as a ternary solid solution.

Quantitative determination of the reaction kinetics was made by measuring the thickness of the reactant as a function of time and temperature and the results are shown in Fig. 5. In the figure, the data were plotted as the square of thickness/time against the reciprocal

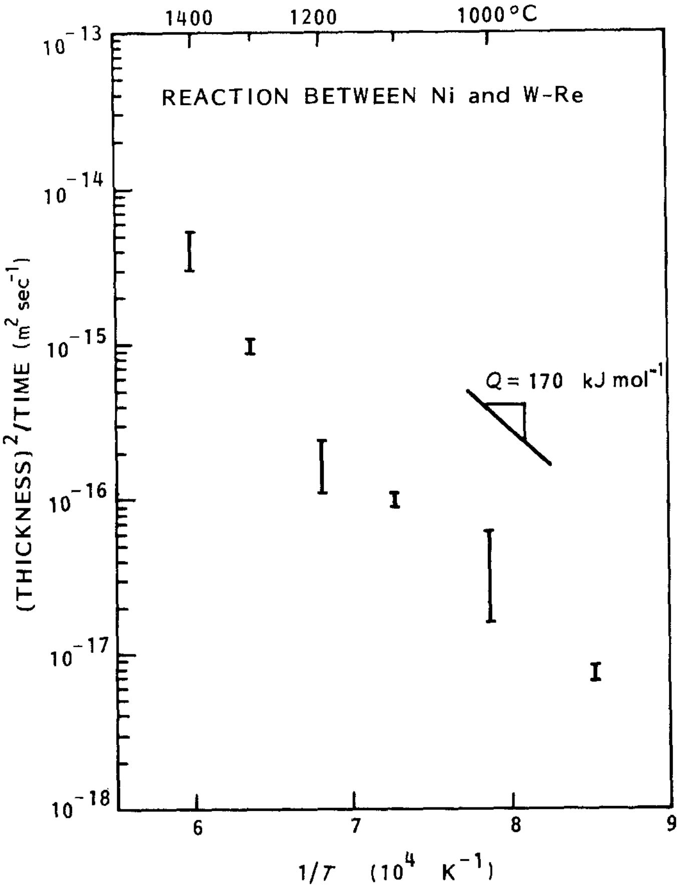

Figure 5 Reactant layer thickness as a function of temperature and time. The linear relationship in the plot shows the reaction is a diffusion-controlled process.

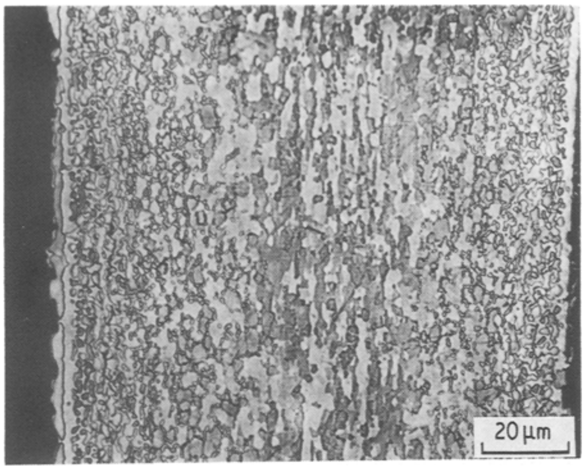

Figure 6 Cross section of reacted Ni/W–25 Re wire at 1300° C for 1 h, showing the acceleration of recrystallization in W–Re by nickel.

TABLE I Bond test results for Ni/W–Re joints

Bonding conditions*		Test results†
Temperature (° C)	Time (min)	
900	120	> 200 g
1000	150	> 200 g
1100	600	< 200 g, but > 100 g
1200	300	50 g broke wire
1300	60	< 100 g, but > 50 g
1400	60	< 100 g, but > 50 g
1500	60	50 g broke wire

*Bond produced with a 30 g per joint dead load.

†All test samples failed in the wire, except the one produced at 900° C.

of the absolute temperature. In spite of some scatter in the thickness measurements, the near linearity of the data, particularly at temperatures lower than 1200° C, confirms the reaction to be diffusional in nature. The activation energy for the reaction was measured to be about $170\,\mathrm{kJ\,mol^{-1}}$. The physical meaning of this activation energy is uncertain. The whole reaction process, as mentioned earlier, involves inward diffusion of nickel along the grain boundaries of W–Re, nucleation of the new phase, followed by the growth of the new phase. The slowest step of this sequential process would be expected to control the reaction rate. The activation energy for grain-boundary diffusion of nickel in tungsten was estimated to be $358\,\mathrm{kJ\,mol^{-1}}$ [6], which is nearly twice that of the activation energy for the reaction between nickel and W–Re. The result suggests, at least, that grain-boundary diffusion of nickel in W–Re is much faster than that in tungsten. Apparently the presence of rhenium in tungsten promotes the diffusion rate of nickel.

The reaction between nickel and W–Re results in several effects. First, it reduces the recrystallization temperature of W–Re. The evidence is presented in Fig. 6 in which is shown the longitudinal cross section of a nickel-coated W–Re wire annealed at 1300° C for 1 h. It is readily observed that although the core region still retains a wrought structure, the region near the wire surface has already fully recrystallized. A similar result was also observed in the Ni–W system [4, 8, 9], in which nickel was found to accelerate the recrystallization process in tungsten. The second effect, and the more important one, is that the reaction causes significant embrittlement to the W–Re wire as discussed below.

Bond strength tests were conducted using the method described in Section 2. The results are summarized in Table I. Since the joints were produced by solid state diffusion processes, it is expected that better bond strengths would be obtained after higher temperature diffusion bonding due to greater interdiffusion at the bond interface. However, the observed general trend is that the higher the bonding temperature, the lower the bond strength, as long as the bonding time is held constant. These results are therefore somewhat confusing. As also noted in the table, all test samples, except the one produced at 900° C, failed at the wire itself and not in the bond joint. Additional evidence indicates that the W–Re was severely embrittled because of the Ni/W–Re reaction mentioned above.

The fracture surface of a tested sample prepared at 1200° C for 5 h is shown in Fig. 7. The sample obviously failed intergranularly with no sign of plastic deformation in the wire. In contrast, some plasticity can easily be observed on the fracture surface of a fully recrystallized W–Re, as shown in Fig. 8. The embrittlement phenomenon observed in Ni/W–Re may not be solely attributed to the intrinsic cracks in the original W–Re, as mentioned earlier, since the cracks appeared in both materials. The embrittlement that occurs in the W–Ni system has been clearly identified [6] to be due to the decohesion of grain boundaries in tungsten by nickel segregation. In the present case, it is not clear if the embrittlement is due to a possible intrinsic brittleness of the new W–Re–Ni ternary phase or due to a weak interface between W–Re and W–Re–Ni. Microhardness measurements were conducted with the wire heat treated at 1300° C. Hardness values of 700 and $593\,\mathrm{kg\,mm^{-2}}$ were obtained from the outer region and the core, respectively. Since the outer region represents a mixture of W–Re and W–Re–Ni, as shown in Fig. 5, and the core represents W–Re, it is, therefore, reasonable to assume that the ternary phase is harder than the binary W–Re.

The fracture mode of a bond test sample depends on the bonding temperature. At intermediate bonding temperature, around 1000 to 1100° C, the fracture surfaces show mixtures of ductile and brittle regions. The two distinct regions are simply manifestations of the reacted and unreacted zones. As mentioned earlier, bond tests of the joined sample produced at 900° C showed fracture at the bond interface, not within the wire, as shown in Fig. 9. A reactant layer was, nevertheless, observed and measured to be roughly 0.2 μm thick. The results seem to suggest that there is a critical amount of reactant which is necessary to cause mechanical degradation in the wire. Similar results have also been reported in the Al–B system. Ochiai *et al.* [10, 11], in their study of thermal compatibility between aluminium and boron filaments, have found there is a critical thickness of reaction layer, below which there arises no degradation of mechanical strength of the filament. In the present

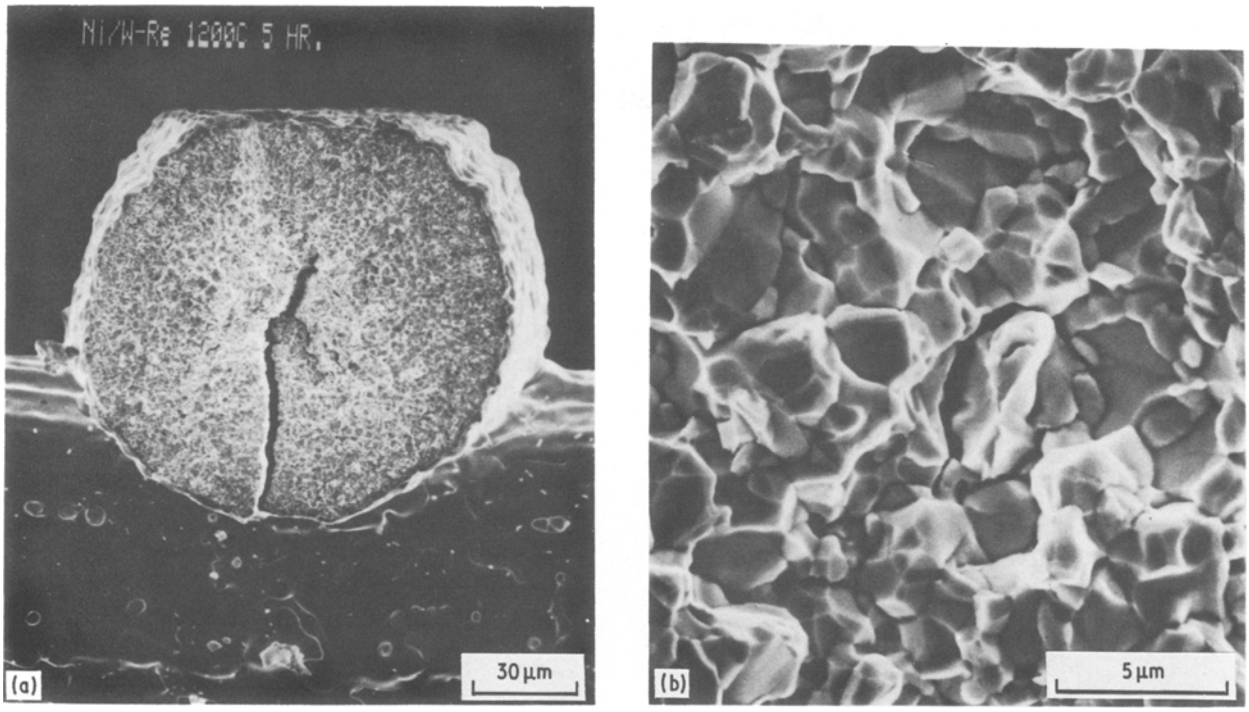

Figure 7 Fracture surface of Ni/W–Re wire exposed to 1200° C for 5 h.

case, the thickness is certainly below 0.2 μm. For practical purposes, Fig. 4 can be used to estimate the time and temperature regimes in which no embrittlement would take place. It is interesting to note that one can also estimate the bond strength. By assuming a square contact at the joint with the linear dimension of the contact no more than the diameter of the original wire, i.e. 0.13 mm, calculation shows that a 200 g load corresponds to a joint strength of over 120 MPa.

3.2. Self-diffusion bonding

One of the most important parameters during a diffusion bonding process is the surface condition. Surface contaminants, particularly oxides, are well known to have an adverse effect on diffusion bonding of metals. Special efforts were made to characterize the surface of the W–Re wire by using Auger electron spectroscopy (AES). A general survey from the surface of the as-received wire indicates the presence of tungsten, rhenium, carbon and oxygen. AES depth profiles for those elements are shown in Fig. 10. It is readily seen that the carbon peak falls immediately after argon ion sputtering, suggesting carbon is not present as a carbide but rather as an environment absorbant. In contrast, the oxygen peak extends over 20 nm thick into the wire. Since both tungsten [7] and rhenium ([1] pp. 29–31) have very limited solid solubilities for oxygen, it is reasonable to assume that

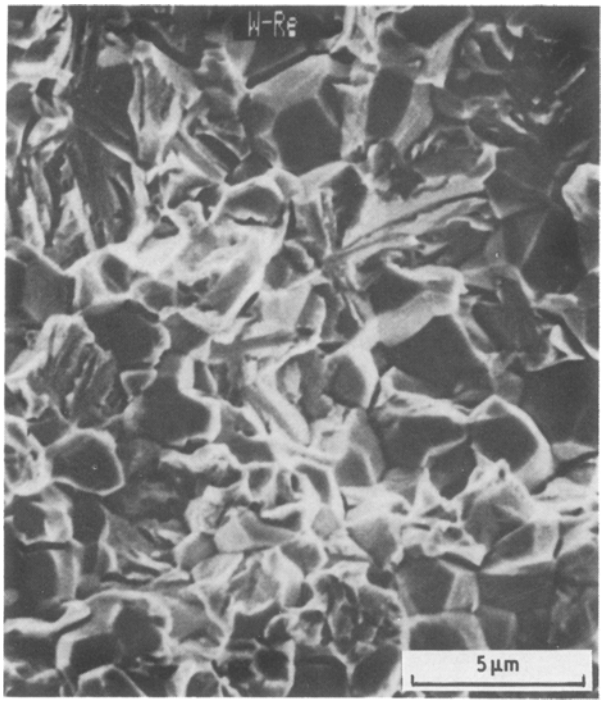

Figure 8 Fracture surface of a fully recrystallized W–Re wire.

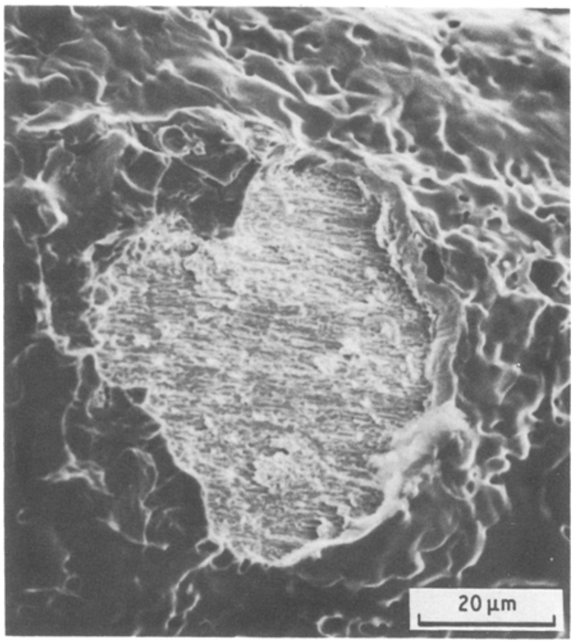

Figure 9 Interfacial separation of Ni/W–Re wires bonded at 900° C.

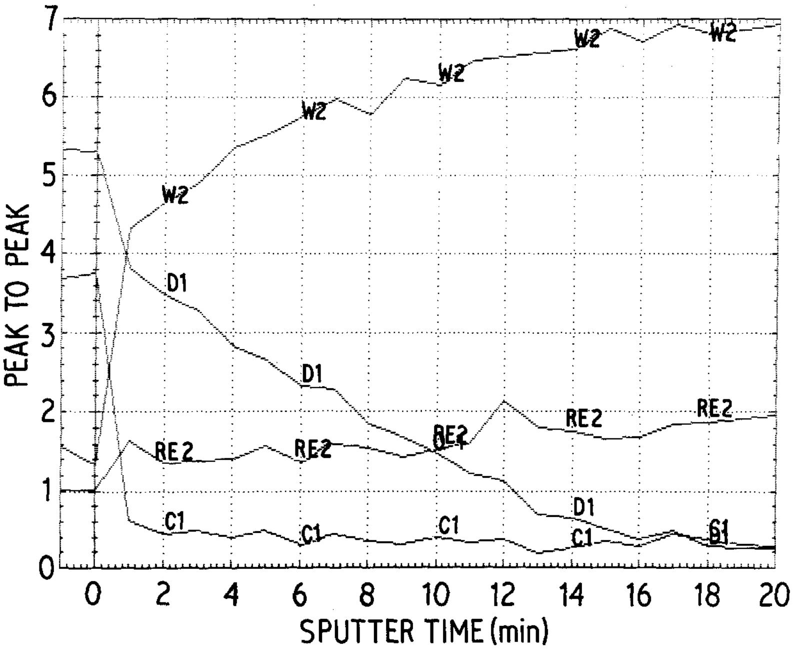

Figure 10 AES depth profile of an as-received W–Re wire. The oxide layer is approximately 20 nm thick.

the layer represents an oxide. The surface oxide was removed by electrolytically etching the wires in a 10% HF solution at 10 V a.c. and a 2 A cm^{-2} current density. An AES depth profile from a deoxidized wire is shown in Fig. 11. It is noted that both carbon and oxygen disappear within a minute after sputtering. As the measurements were conducted at 1 min intervals, the actual thickness of both elements was definitely less than 2 nm. And, it is almost certain that their presence is due to environmental absorption.

Diffusion bonding experiments on as-received and deoxidized wires were conducted at temperatures of 1300 to 1650° C. Successful results were produced with the deoxidized wires at temperature above 1500° C. Below this temperature, either it is difficult entirely to seal the interfacial voids or porosities within a reasonable period of time, or the bond strength is too low, due to insufficient interfacial contact area at the joint.

A photomicrograph of a joint produced at 1600° C for 1 h is shown in Fig. 12. As one can readily observe in the figure, it is almost impossible to locate the original wire interfaces and a good metallurgical bond has been well established. Also, the wires were fully recrystallized and resulted in equiaxed grain structure. It is interesting to notice that the recrystallized wires can be bent 90° (this corresponds to 7% plastic strain in the outer fibre) without showing any grain boundary or surface cracking. This is understandably due to the ductilizing effect of rhenium. While successful bonds can be produced with deoxidized W–Re wires, bonding between as-received wires was unsatisfactory even at temperature of as high as 1650° C and this is attributed to the thick oxide film on the wire surface. Fig. 13 is a typical photomicrograph of the bond interface produced at 1650° C for 5 h. In the figure, an initial surface contact between wires during the course of bonding is seen, as evidenced by the perfect mating surface contour of the wires at the site of separation. However, interdiffusion has never actually taken place at this particular site because of the thick oxide layer which acted as a barrier for diffusion. Separation of wires was simply a result of spring back

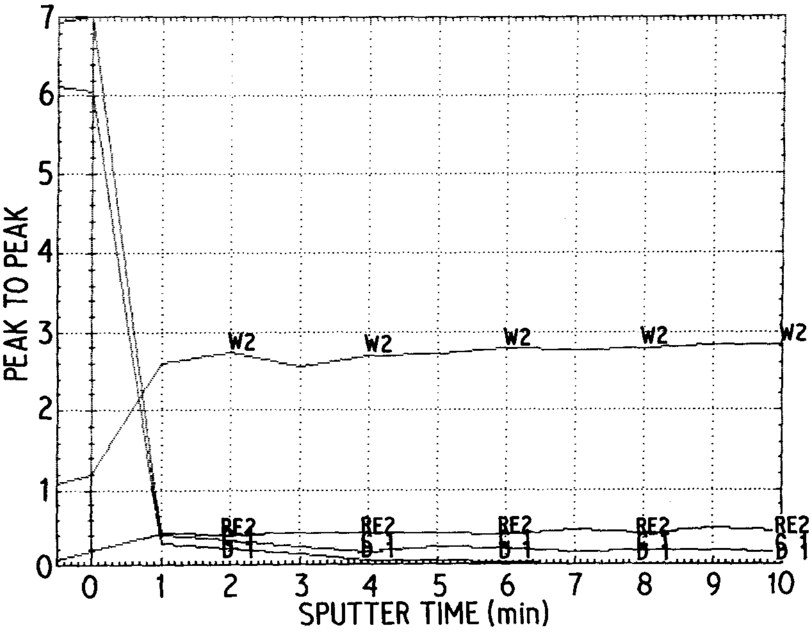

Figure 11 AES depth profile of a deoxidized W–Re wire.

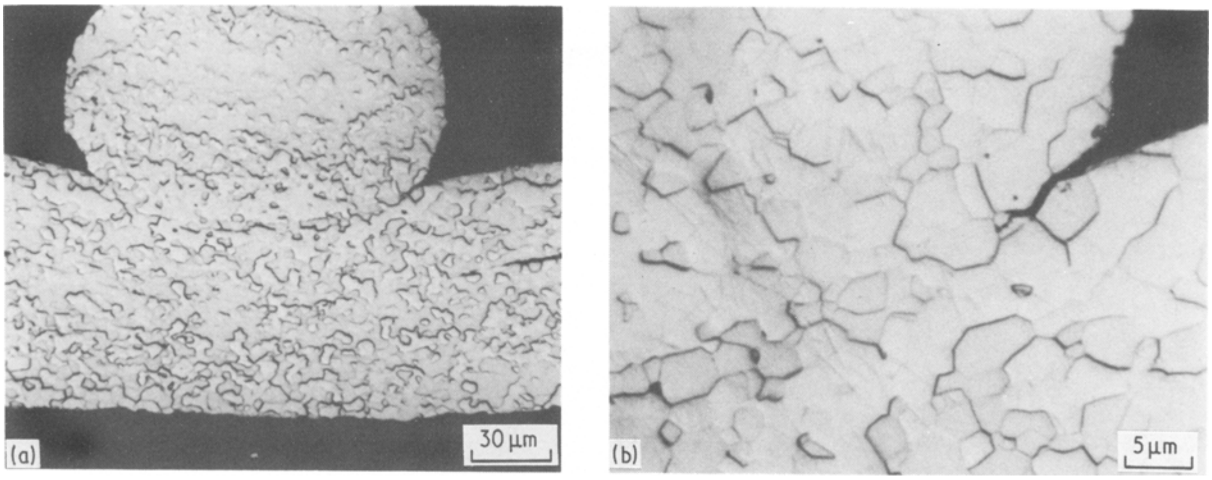

Figure 12 Microstructure of deoxidzed W–Re wires diffusion bonded at 1600° C for 1 h. A good metallurgical bond is readily observed.

on unloading. In contrast, the occasional bonds in the figure represent areas where the oxide film was ruptured during bonding. Interdiffusion only took place in those regions.

It is worth commenting further on the effect of an oxide layer on solid state diffusion bonding. One of the prerequisites for producing a good diffusion bond is an immediate metal–metal contact, which relies on either surface cleaning prior to bonding or the application of excessive loading to rupture the oxide film. However, the oxide layer is less of a problem in some metals which have a high solid solubility for oxygen, as long as the oxide layer is not too thick. This is because the high solubility of oxygen in the parent metal provides a high thermodynamic driving force to reduce the oxide *in situ* during the bonding process. As mentioned earlier, neither tungsten nor rhenium has a significant solubility for oxygen. Since it is impossible to reduce the surface oxide by the alloy, precleaning to remove the surface oxide is necessary to ensure a metal–metal contact during bonding. Otherwise, interdiffusion between the wires will not occur.

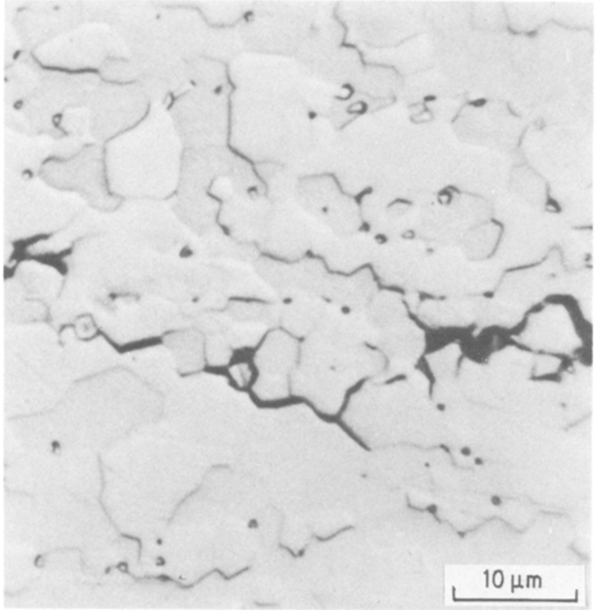

Figure 13 Microstructure of as-received W–Re wires diffusion bonded at 1650° C for 5 h. Some voids or pores are still present.

Bond strength tests were also performed using the same technique as that used for Ni/W–Re. The results are tabulated in Table II. Tests conducted with samples prepared at temperatures above 1500° C were difficult, bcause the wires underwent severe deflection or deformation during the test and, yet, there was no sign of bond joint breakage. This indicates an excellent joint between the wires.

In a structural application, self-diffusion bonding of W–Re is much more advantageous than using the nickel coating as a bond aid. This is because the former is essentially a monolithic material which can be used in service at a much higher temperature than the latter can and, meanwhile, there is no concern about the embrittlement effect on the parent material.

4. Conclusions

Solid state diffusion bonding of W–Re has been successfully demonstrated either by using nickel as a bonding aid or by direct contact of the material at a relatively high temperature. The former technique can be done at temperatures at as low as 900° C; the latter is possible only at temperatures above 1500° C. In spite of the advantage of bonding at low temperature by using nickel as an interleaf material, it has been found that nickel attacked the grain boundaries of W–Re and caused embrittlement. This limits the service temperature of such a joint. In contrast, W–Re joints produced by self-diffusion bonding, even though the bonding temperature is 1500° C or higher, can be used at temperature without concern of mechanical degradation. However, it has also been demonstrated that an oxide-free surface is crucial to produce

TABLE II Bond test results for DB W–Re joints

Bonding conditions*		Test results
Temperature (° C)	Time (min)	
1650†	300	200 g broke the joint
1600	60	> 200 g
1500	60	> 200 g
1400	240	200 g broke the joint
1300	2400	100 g broke the joint

*Bond produced with a 30 g per joint dead load.
†As-received wires.

such a good joint and this necessitates a preclean of the material prior to bonding.

Acknowledgements

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