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Removal of surface carbides from spark-machined molybdenum and tungsten

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When reactive metals such as molybdenum and tungsten are shaped by electrical discharge machining in the kerosene-based electrolytes generally employed for the process, they become covered with a thin, multiply-melted surface layer which contains carbide phases of variable composition. This surface layer is sometimes undesirable because its chemical and mechanical properties are different from the base metals. It has been demonstrated that the carbide can be removed by a high-temperature anneal in a reducing atmosphere. The anneal also removes surface cracks on molybdenum introduced by the machining, but the heat treatments employed here did not remove surface cracks on tungsten. The high-temperature anneal had the unfortunate side effect of inducing a significant degree of grain coarsening in the metals.

1. Introduction

Electrical discharge machining is employed for shaping a wide variety of metals when narrow cuts or complex contours are required. On those metals which form stable carbides, this machining produces carbide-containing surface layers when hydrocarbon electrolytes are employed. The carbide containing surface layers are generally much harder than the base metal, a circumstance which has motivated the development of various spark-processing techniques for improving the wear resistance of metals [1]. Although hardened surfaces are desirable for some applications, the altered surface properties are sometimes undesirable. Efforts in our laboratory to remove the altered surfaces by chemical means were only moderately successful because carbides are, on the whole, more resistant to chemical attack than are their parent metal. Attempts to remove the carbides by chemical dissolution are further complicated by the fact that they do not occur as discrete single-phase layers on the free surface, but are intimately mixed with unreacted base metal within the rapidly solidified melt puddles formed by the spark discharges [2]. Thermal treatments in a reducing atmosphere were found to be effective in removing the carbide phases at the free surface as well as those embedded within the spark discharge melted surface layer. The thermal treatments also removed copper impurities which derived from the copper-impregnated graphite electrodes used to machine the molybdenum and tungsten samples studied.

2. Experimental procedure

Samples of various geometries were spark machined in a commercial kerosene-based electrolyte using flat copper-impregnated graphite electrodes. The electrical discharge machining (EDM) apparatus had a square-wave output with 50% duty cycle. Machining was done with gap potentials between 50 and 75 V and peak currents near 8 A.

Chemical etching of spark-machined molybdenum was done in various concentrations of HF, an acid which is reported to dissolve MoC and Mo_2C, but not molybdenum [3]. As will be discussed, these experiments did not succeed in removing the Mo_2C, and no attempts were made to remove the carbide from spark-machined tungsten by etching. Efforts to remove the carbides by thermal treatments consisted of heat treating the samples for 1 h to $2000 \pm 10\,^{\circ}C$ in either argon or Ar–5% H_2. The heat treatments were done in an induction furnace equipped with a molybdenum susceptor, the furnace being flushed with the appropriate gas for 2 h prior to heating.

Samples were examined by scanning electron microscopy (SEM) after spark machining and after further processing. Topological images were obtained in either the secondary electron imaging mode or the back-scattered electron imaging mode. Energy-dispersive X-ray analysis was conducted at 10^4 V to ensure good resolution of the carbon K_{α_1} peak. X-ray diffractometry employing CuK_α radiation was conducted on the base metals and on processed samples. Identification of phases was done by matching of diffraction peaks with those given in standard data files.

3. Results

X-ray examination of spark-machined molybdenum samples showed peaks for molybdenum and Mo_2C, and tungsten samples exhibited tungsten and W_2C peaks. No peaks were found for MoC or WC, but on both metals peaks were found indicating the presence of copper. In both the as-received condition and after spark machining, the relative heights of the diffraction peaks from the base metals were inconsistent with published values, indicating that the starting materials were textured. For both metals in the EDM condition, the diffraction peaks of the carbide phase were weaker than those from the base metal. For example, the maximum intensity ratio of the Mo_2C peak relative to molybdenum was 0.09, and the corresponding ratio for tungsten was 0.02. This suggests that the carbide layers were relatively thin. The relative heights of the carbide diffraction peaks also differed somewhat from published values, indicating that the carbides probably solidified with a preferred orientation. No attempts were made to characterize the textures of either the base metals or the carbides. Further results from the X-ray studies are presented after consideration of the SEM observations. Results from studies of molybdenum will be presented first.

3.1. Microscopy of molybdenum samples

Scanning electron microscopy of the as-machined molybdenum surfaces showed morphologies typical of those produced by such processing. This is evident in Fig. 1, where the low-magnification view in (a) illustrates how the repeated electrical discharges create a

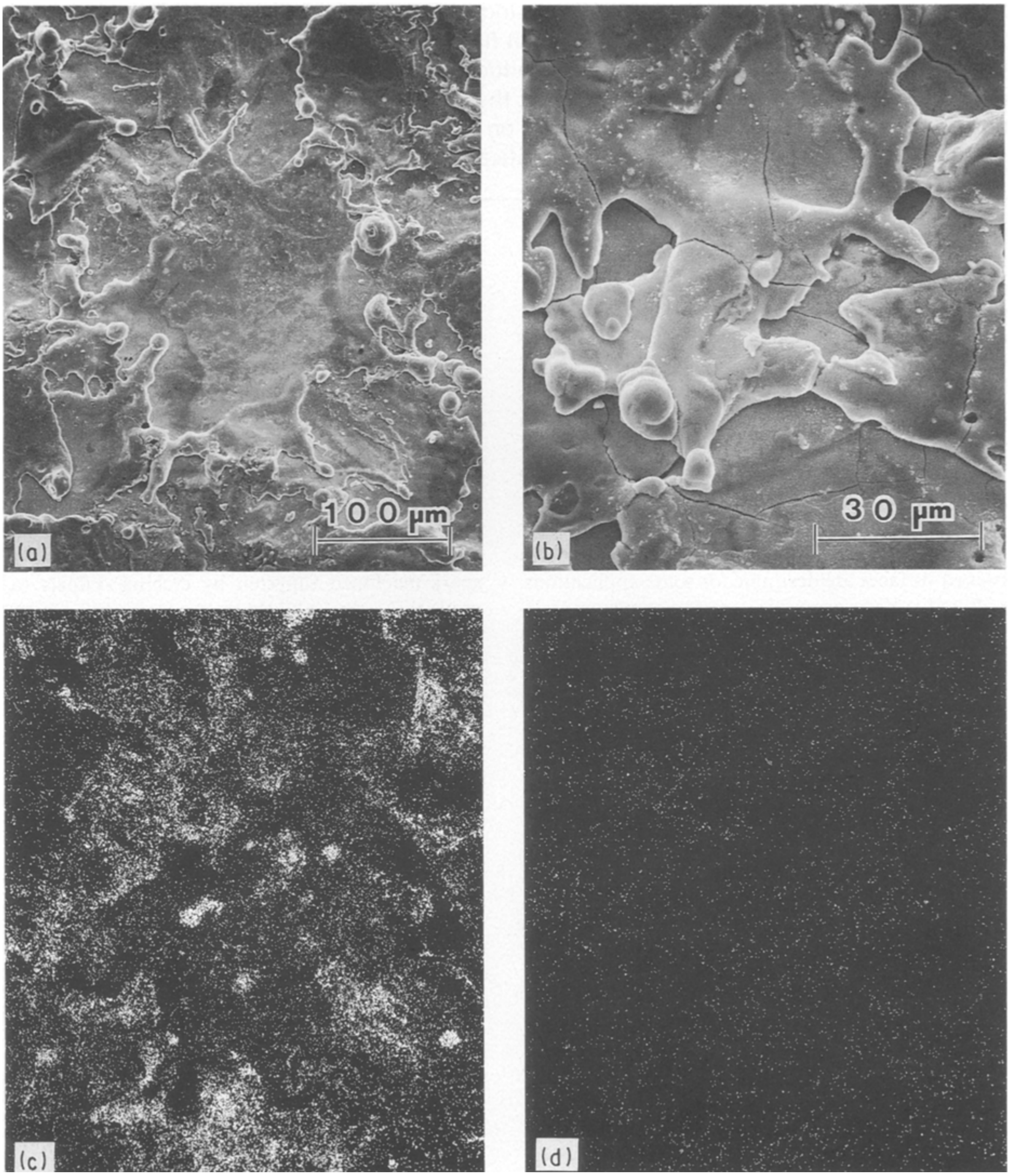

Figure 1 Surface of a molybdenum sample as-spark-machined. (a, b) SEM views from different regions. The EDX mappings of (c) copper and (d) carbon are from the area pictured in (a).

pattern of randomly positioned, often overlapping melt puddles. Associated with these puddles are splatters of displaced material. Fig. 1b, from a different area on the surface pictured in (a), shows some of the splatters in greater detail. It also shows fine cracks of the sort common to metals which produce hard surfaces upon spark machining [2]. The X-ray diffraction results make it clear that this surface is at least partially covered with Mo_2C, but it is not possible to differentiate it from molybdenum by its appearance in the SEM.

The surface pictured in Fig. 1a was examined by energy dispersive X-ray analysis (EDX). This examination revealed the widespread presence of copper, which resulted from erosion of the copper-containing tool used for the machining. The EDX map of copper shown in Fig. 1c was made in the same area represented in Fig. 1a. It demonstrates that the copper is non-uniformly distributed on the surface, and some correlation can be made with features evident in Fig. 1a. Because copper is completely immiscible with both liquid and solid molybdenum, it is likely that copper transferred to the workpiece as molten droplets displaced from the tool and that these droplets remained on the free surface as a discrete phase throughout the processing. Fig. 1d shows the carbon "map" of the surface shown in Fig. 1a. It shows that there is some carbon in the surface, but the regions of high and low intensity do not correspond with features evident in Fig. 1a. Copper and carbon peaks can also be seen in Fig. 2, which shows the EDX spectrum obtained from an area similar to that shown in Fig. 1. This figure, like Fig. 1c and d, suggests that the sample contained far more copper than carbon, but the X-ray studies showed much lower peak intensities for copper than for Mo_2C, making it clear that such was not the case. The patches of copper are very thin, but the copper is more evident in Figs 1 and 2 because of the higher atomic weight of copper and the fact that it is not alloyed into the base metal.

The sample pictured in Fig. 1 was sectioned with a diamond saw, mounted on edge in epoxy, polished, and etched in a solution made up of equal parts H_2O, 3% H_2O_2, and 30% ammonia water. Examination of the sectioned surface in the SEM revealed structures such as those shown in Fig. 3. The bulk of the sample showed the highly cold-worked structure evident on the left-hand side of Fig. 3a. The grains in this unheated portion of the sample were a few micrometres thick and highly elongated in the plane of the specimen. This figure also shows evidence of a heat-affected zone near the surface, in which the initial grain structure could not be observed. It was not clear from microscopic examination what caused the altered appearance in this zone, but it may simply represent the depth to which sufficient heat was supplied to permit recovery of the cold-worked starting structure. Fig. 3a also demonstrates the fact that in some areas thermal stress caused partial spallation of the hardened surface.

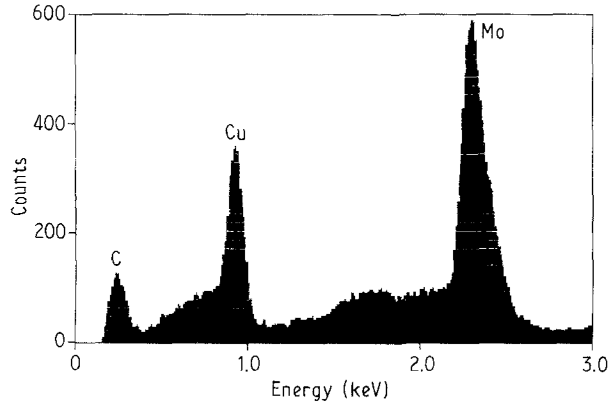

Figure 2 Results of energy dispersive X-ray analysis of spark-machined molybdenum surface.

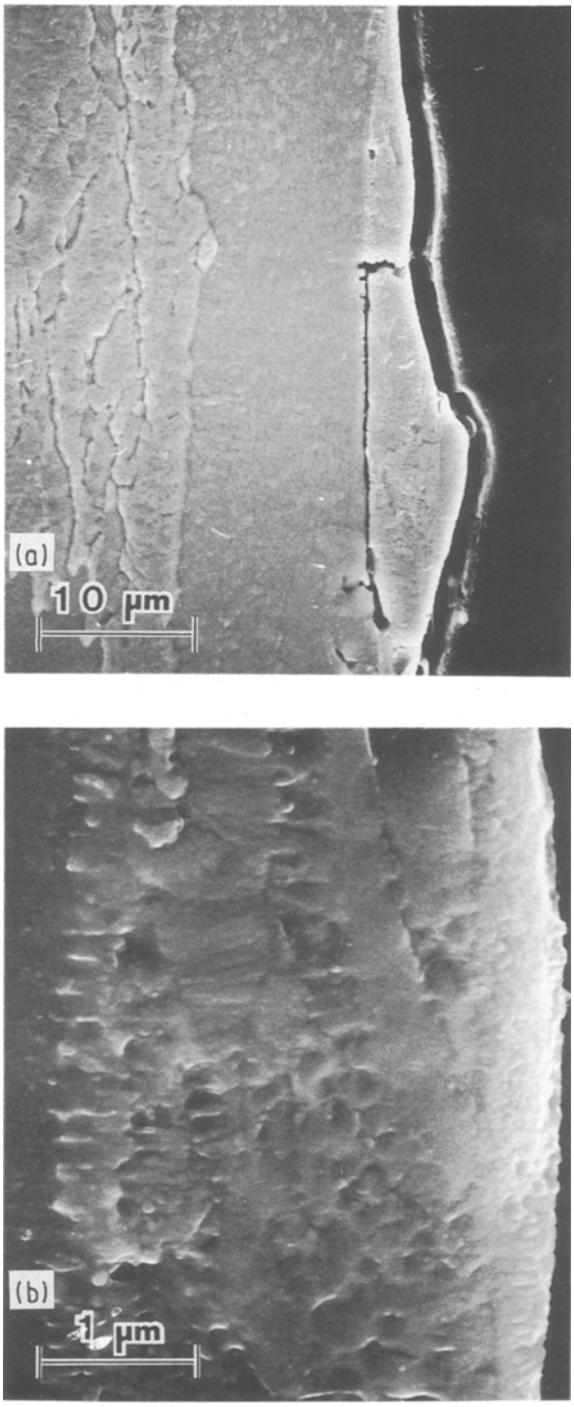

Figure 3 Cross-sectional view of the sample pictured in Fig. 1. (b) High-magnification view showing a portion of carbide-containing surface layer.

The high magnification view in Fig. 3b shows a small portion of the surface zone depicted in Fig. 3a. This image demonstrates that the surface was melted repeatedly during the spark machining, with the deepest melt depth in this region being about 3 μm. As can be seen in Fig. 3a, some areas had thicker surface layers, up to 6 μm, but some regions appeared not to have been melted to depths greater than about 2 μm. The etchant employed did not discriminate sharply between molybdenum and Mo_2C, but the surface zone shown in Fig. 3b appears to consist of an intimate mixture of metal and carbide. This interpretation is consistent with observations made on similar surfaces in titanium and zirconium [2], and is supported by X-ray results which will be presented later.

Heat treating produced dramatic changes in the structures observed both on the free surfaces and in sectional views. Differences on the free surfaces can be seen by comparing Figs 4 and 5 with Fig. 1. These figures show the surfaces after heat treatment for 1 h at 2000 °C in argon (Fig. 4) and in Ar–5% H_2 (Fig. 5). These images show that the surfaces were smoothed by diffusion during the anneals, and they, as well as other areas examined, show no evidence of the fine cracks which were evident before the anneals. The cracks were apparently eliminated by diffusion, thereby lowering the surface area of the samples. Figs 4 and 5 also show that the grain sizes after the anneals were of the order of 50 μm. Similar grain sizes were found on the back surfaces of the heat-treated samples. Prior to the anneals the grain sizes were only a few micrometres, as can be seen in Fig. 3a.

The high-temperature heat treatments in both argon and Ar–5% H_2 were found to be effective in removing copper and carbon from the molybdenum surfaces. This is demonstrated by Fig. 6, which shows an EDX energy spectrum obtained from a spark-machined molybdenum sample which was heated in argon at 2000 °C for 1 h. This spectrum shows virtually no copper and a carbon concentration indistinguishable from that observed on unprocessed molybdenum. Very similar results were obtained from a molybdenum sample which was annealed in Ar–5% H_2. The relative peak heights for copper and carbon in these samples and in the other molybdenum samples investigated are shown in Table I. The table also includes results from a study of commercially prepared Mo_2C and molybdenum powders. All values in the table represent the average of two independent determinations. In no instance did the individual peak heights differ by more than 20% from the averages. In all samples except the as-machined one, the copper peak height ratios in Table I actually represent a

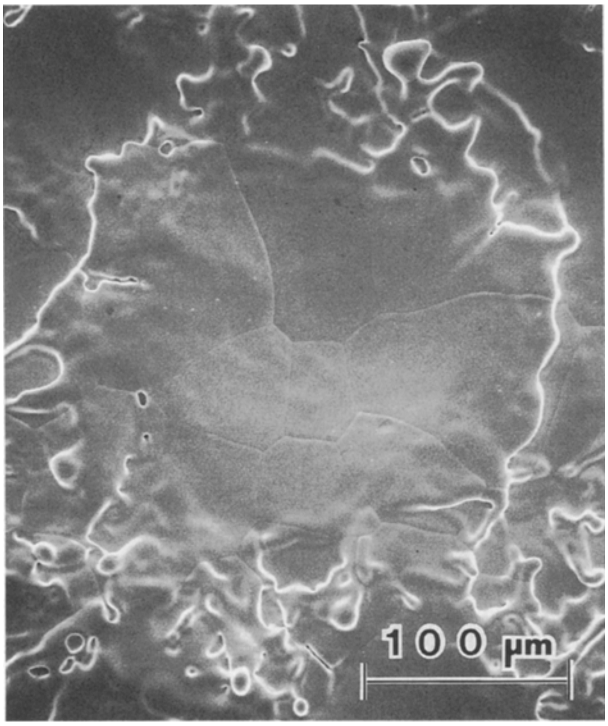

Figure 4 SEM view of a molybdenum sample after it was heat treated in argon at 2000 °C for 1 h.

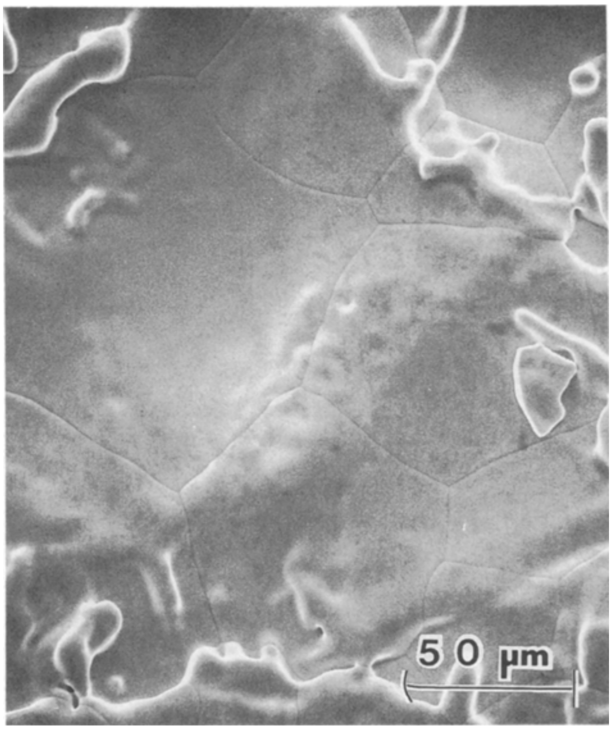

Figure 5 SEM view of a molybdenum sample after it was heat treated in an Ar–5% H_2 gas mixture at 2000 °C for 1 h.

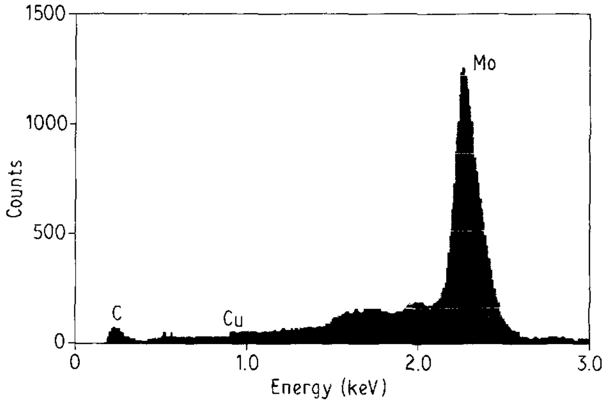

Figure 6 Results of energy dispersive X-ray analysis of spark-machined molybdenum surface after it was heat treated in argon at 2000 °C for 1 h.

TABLE I EDX peak ratios from molybdenum samples

Sample condition	C:Mo peak height	Cu:Mo peak height
As-machined	0.144	0.444
Heated in Ar	0.042	0.045
Heated in Ar–5% H_2	0.053	0.043
Back-surface averages	0.032	0.033
Mo_2C standard	0.085	0.052
Mo powder	0.050	0.045

background level because no discernable peaks were actually present. The data in the table demonstrate that the carbon contents of the heat-treated specimens are well below that for Mo_2C, but that the carbon concentration of the as-machined surface is higher. Because the only way the sample could contain higher carbon levels than Mo_2C would be if the surface were rich in MoC, and the X-ray results show this phase was not present, we conclude that the high initial carbon values must have arisen from carbonaceous wastes left from the spark machining. Such wastes were thick enough to be imaged in the SEM on poorly cleaned samples and have been observed previously on powders made by spark machining [2].

When the heat-treated molybdenum samples were examined in cross-section, little evidence could be seen of carbides near the spark-machined surface. This point is illustrated by Fig. 7, which shows a section through the surface of a sample heat treated in argon, and in Fig. 8, which shows a sample heat treated in Ar–5% H_2. These photos show that the surfaces are still rough, and that they have some residual porosity, but the prominent carbide phase seen in Fig. 3 is missing. There are some small precipitates, which may be carbides, along the grain boundaries in Fig. 7, but, as Fig. 8 demonstrates, the sample heat treated in Ar–5% H_2 shows no second phase at all. The porosity evident near the surface in Fig. 8 is probably a residual porosity from subsurface cracks of the sort evident in Fig. 3.

3.2. Microscopy of tungsten samples

The tungsten samples were examined in the same ways as the molybdenum samples just described. When examined in the SEM, the spark-machined surfaces were similar to those of the molybdenum, but comparison of Fig. 9, which is from as-machined tungsten, with the analogous molybdenum surface shown in Fig. 1, reveals that the tungsten surface is somewhat rougher. The tungsten surfaces also appear to exhibit more cracks. As with the molybdenum samples, there was no way to discern in the surface views which phases might be present. Elemental mapping of carbon and copper by EDX showed distributions similar to those observed with molybdenum. As with molybdenum, the EDX peaks for both carbon and copper became much less pronounced when the samples were heat treated for 1 h at 2000 °C in either argon or Ar–5% H_2.

Heat treatment of the EDM samples of tungsten in argon and Ar–5% H_2 produced less pronounced changes in the appearance of the machined surfaces than did the same processing on molybdenum samples. This is illustrated by the presence of cracks in Figs 10 and 11, which show surfaces after the two heat treatments. Thermal grooving at grain boundaries was also less pronounced, so the grain structure was less conspicuous in tungsten. There was still significant grain growth, as is demonstrated in Fig. 12. This

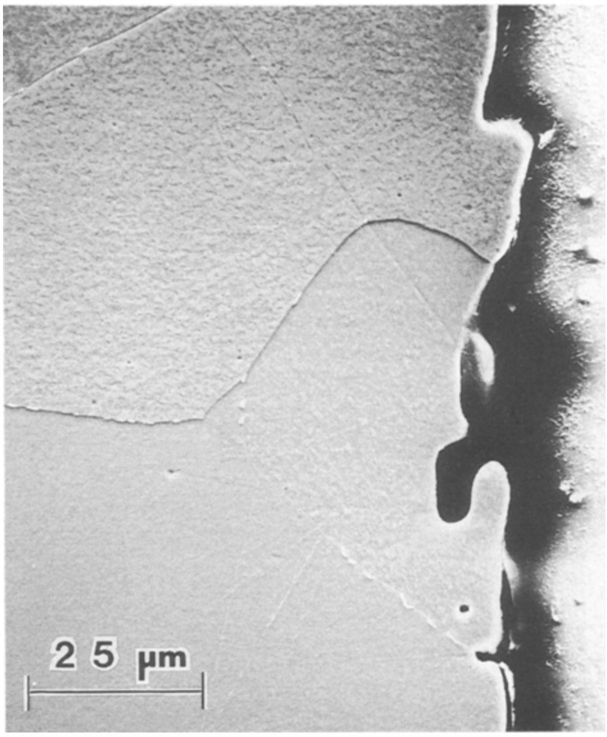

Figure 7 Cross-sectional view of a molybdenum sample after it was heat treated in argon at 2000 °C for 1 h.

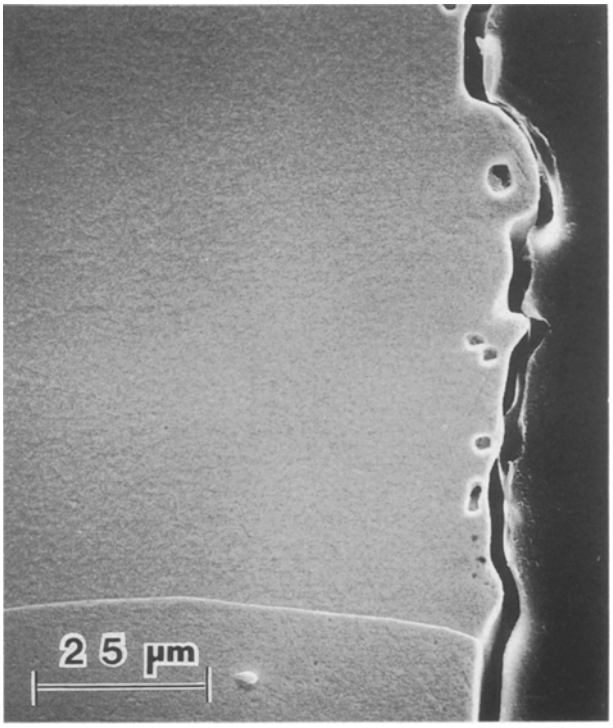

Figure 8 Cross-sectional view of a molybdenum sample after heat treatment in an Ar–5% H_2 gas mixture at 2000 °C for 1 h.

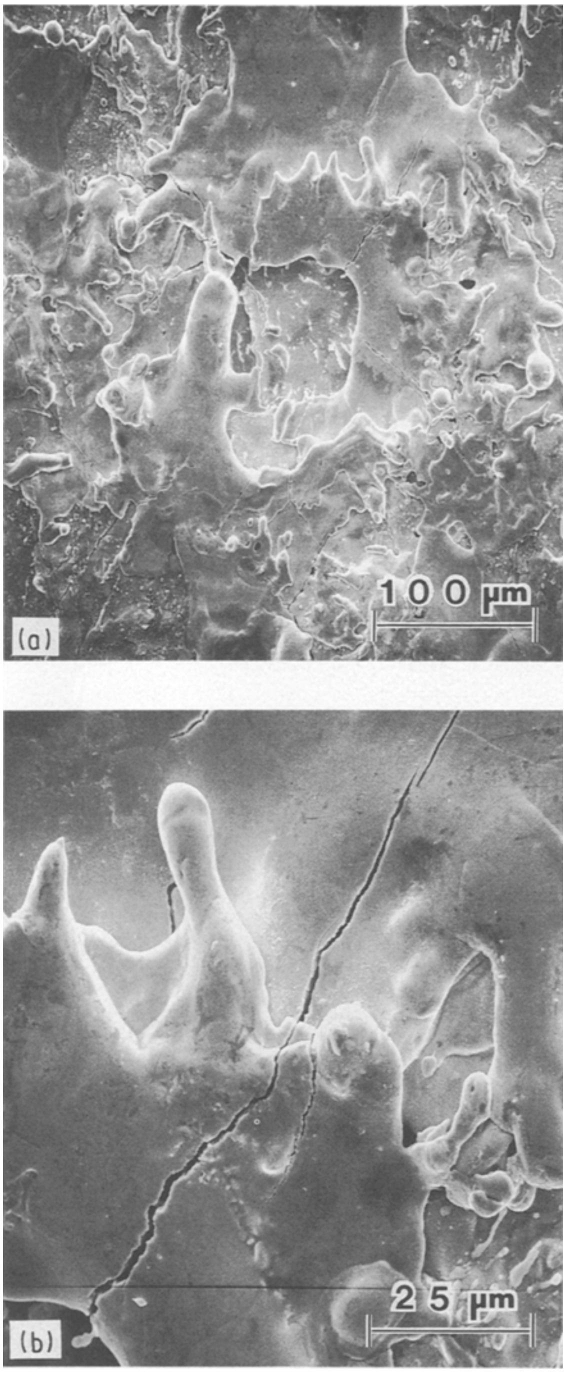

Figure 9 (a) Surface of a tungsten sample as-spark-machined. (b) High magnification view showing thermally induced cracking.

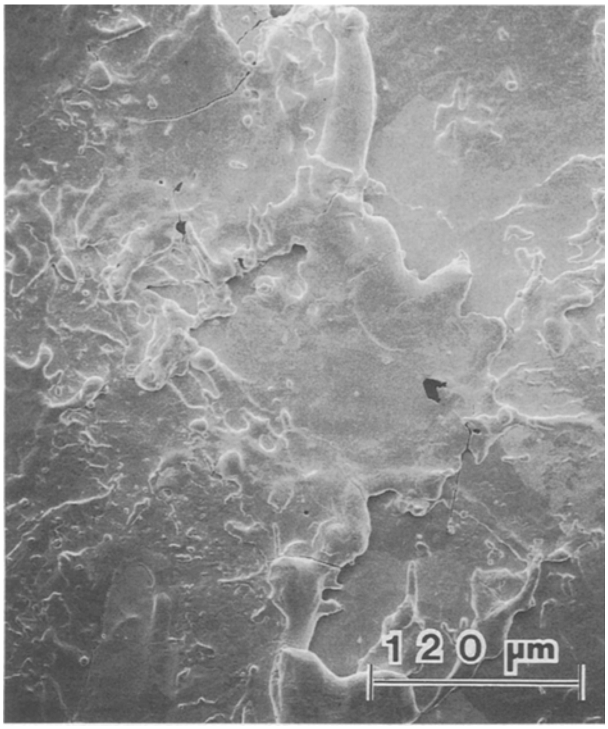

Figure 10 SEM view of a tungsten sample after it was heat treated in argon at 2000 °C for 1 h.

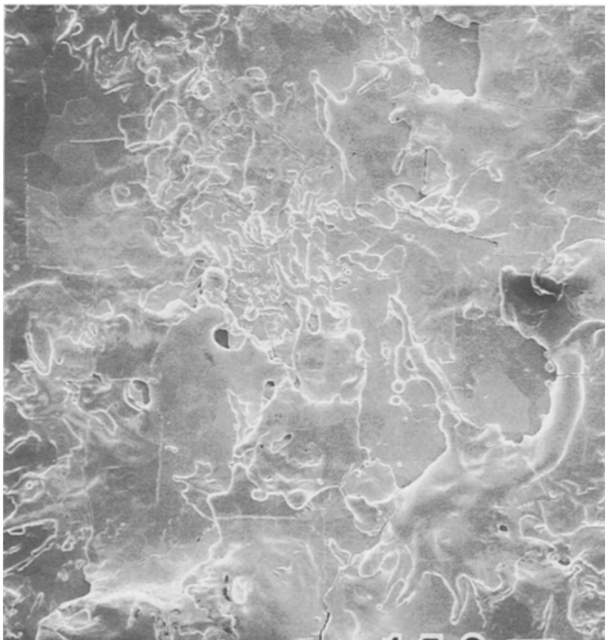

Figure 11 SEM view of a tungsten sample after heat treatment in an Ar–5% H_2 gas mixture at 2000 °C for 1 h.

SEM image, from the back surface of the sample pictured in Fig. 10, employed crystallographic contrast to emphasize the grain structure. It shows that the grains grew to an average size of approximately 50 µm, which is similar to the grain size of molybdenum treated in the same way. Prior to heat treating, the grains were pancake shaped, only about 1 µm thick and many micrometres long. This shape is evident in Fig. 13a, which is a sectional view of the as-machined tungsten sample. This photo also shows that thermal stresses produced by the spark machining caused some delamination of the hardened surface. The higher magnification view shown in Fig. 13b illustrates that the hardened surface contained a fine dispersion of the carbide in tungsten, the carbide having been attacked somewhat less than the metal by the etchant. This effect is more evident in Fig. 14, in which can be seen a band of carbide overlain by a tapered band of metal that is in turn overlain by a metal/carbide mixture. The submerged carbide was obviously produced at the bottom of a melt puddle which was later filled in by action of the repeated electrical discharges.

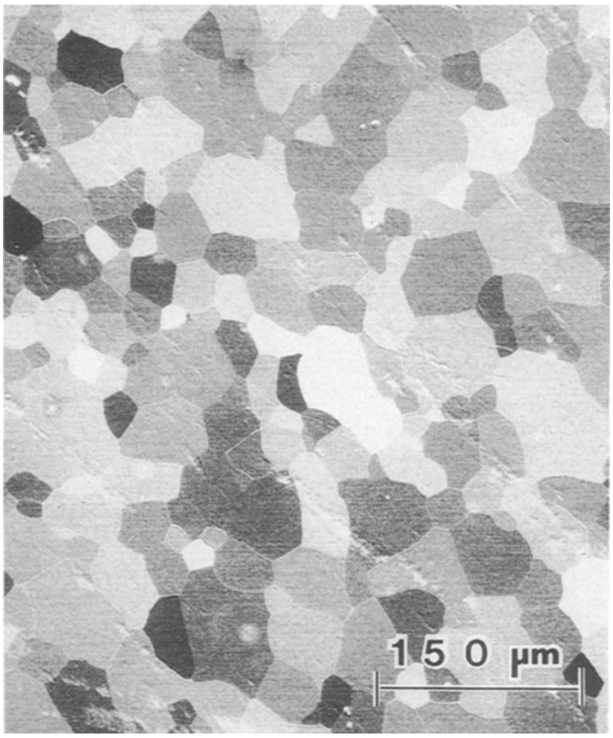

Figure 12 Back surface of a tungsten sample after it was heat treated in argon at 2000 °C for 1 h. SEM imaging employed crystallographic contrast to emphasize the structure.

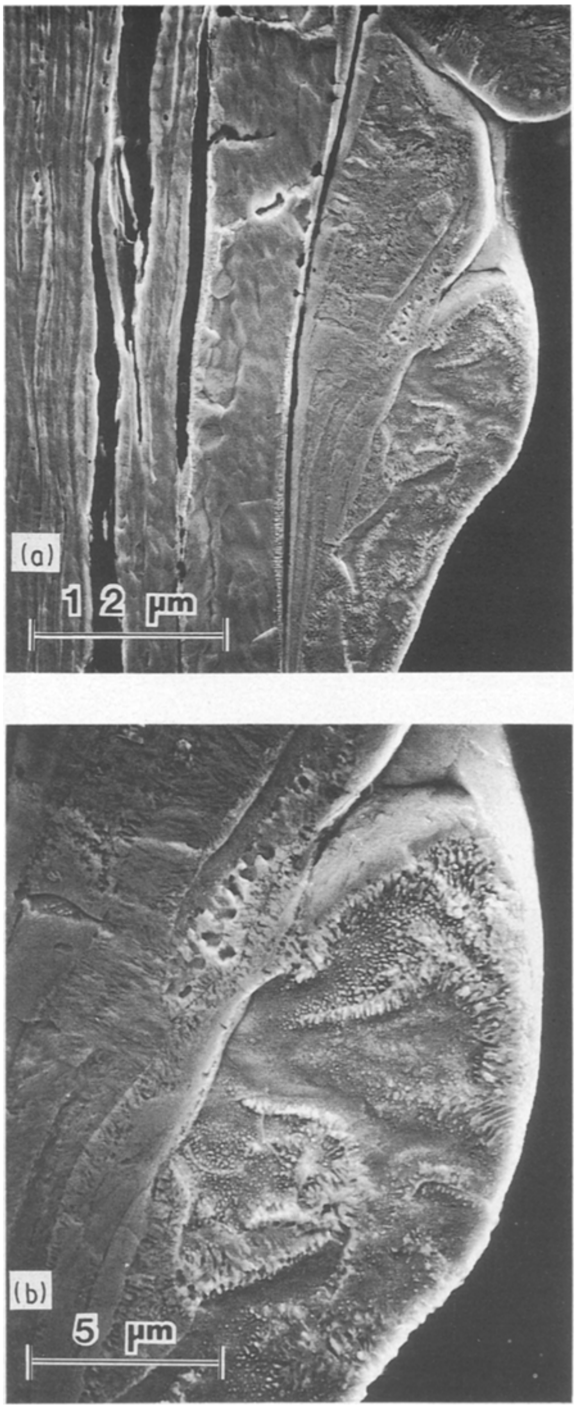

Figure 13 (a) Cross-sectional view of the sample pictured in Fig. 9. (b) High-magnification view showing the mixture of metal and carbide phases.

While the microscopic examination of molybdenum samples showed little evidence that addition of hydrogen to the heat-treating atmosphere made any difference, microscopic study of sectioned samples made it clear that hydrogen helps to remove the carbide from tungsten. This difference is illustrated in Figs 15 and 16, which show views of the samples treated in argon and Ar–5% H_2, respectively. The sample treated in argon has a clearly evident single-phase surface layer (shown in the next section to be W_2C), but the sample treated in Ar–5% H_2 showed only a few isolated grain-boundary precipitates (not illustrated) which may be carbides. The carbide layer completely covered the region shown in Fig. 15, but some areas were found to be free of this phase. It was not evident from the microstructures if these areas were free of carbide prior to heat treatment or if the heat treatment in argon was able to remove modest amounts of carbide through diffusive dissolution into the bulk material, or, perhaps, through decarburization via residual oxygen in the heat-treating atmosphere.

The region shown in Fig. 16 demonstrates that with tungsten, as with molybdenum, even when the carbides were removed by heat treatment in Ar–5% H_2, some porosity remained. Some porosity also remained in the sample treated in argon. Samples of tungsten treated in both argon and Ar–5% H_2 still showed evidence in some areas of the delamination illustrated in Fig. 13a, but the crack tips were blunted through diffusion processes.

Somewhat surprisingly, mapping of carbon radiation emission by EDX failed to show any higher carbon concentration in the carbide layer evident in Fig. 15 than could be seen in the base metal. This was also true of the other surfaces observed in cross-section. Apparently, absorption of the carbon radiation by the molybdenum and tungsten is so strong that the difference in detected intensity is too little to be discerned. It is for this reason that no carbon maps are shown other than that in Fig. 1d.

3.3. X-ray diffraction

As mentioned at the beginning of Section 3, X-ray diffraction of the spark-machined surfaces of both metals showed peaks for the metal plus either Mo_2C or W_2C. In most instances the diffraction peaks from

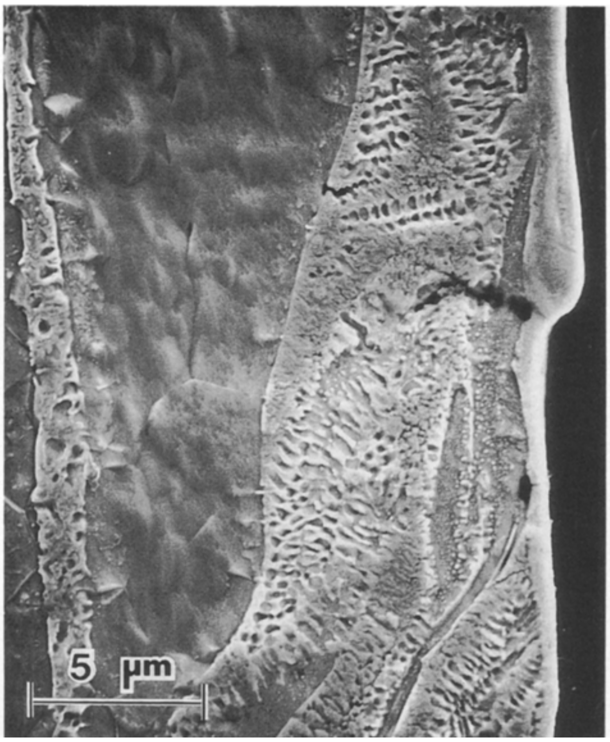

Figure 14 Cross-sectional view of the same sample pictured in Fig. 13. The view illustrates layering of carbide and metal produced by multiple melting.

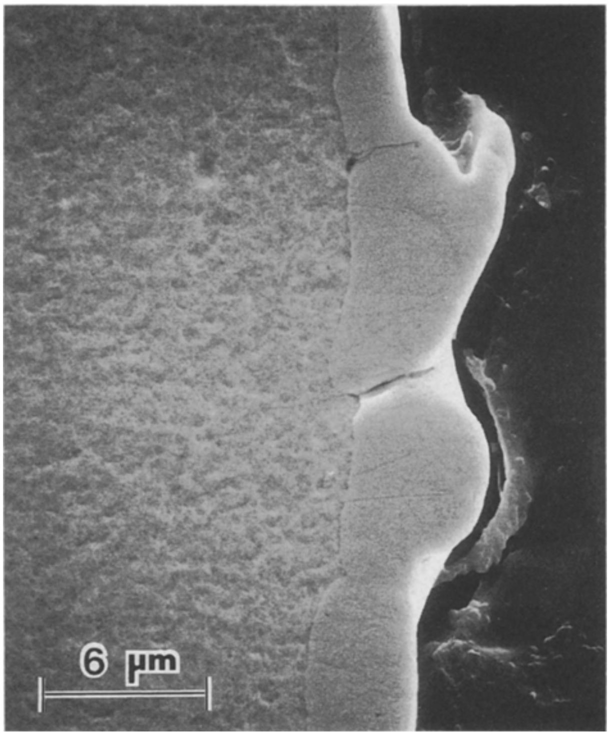

Figure 15 Cross-sectional view of a tungsten sample after it was heat treated in argon at 2000 °C for 1 h.

the carbide phases were weaker than those of the base metals, a result which is consistent with the microscopic observation that the carbide layers were only a few micrometres thick. Relative intensities of different diffraction peaks within both the metal and carbide phases differed from published values, so no quantitative study was possible of the amount of carbide present. Qualitative comparisons were, however, possible. These showed that the strongest diffraction peaks of the carbide were weaker than peaks for the base metal on both molybdenum and tungsten spark-machined samples. After heat treatment in both argon and Ar–5% H_2, molybdenum samples showed diminished carbide peak heights. The carbide peaks from the molybdenum sample heated in argon had about one-third of their intensity prior to treatment, and they were entirely missing from the sample heated in Ar–5% H_2. The weak carbide peaks in the argon-treated sample support the earlier suggestion that the small grain-boundary precipitates evident in Fig. 7 are Mo_2C, but it is surprising that such small precipitates would give detectable diffraction peaks. Diffraction results from the tungsten sample heat treated in Ar–5% H_2, were similar to those achieved with molybdenum, for barely perceptible carbide peaks were present in the diffractometer traces. Results from heating in argon only were strikingly different than those for molybdenum. On the sample studied, four of the W_2C diffraction peaks had higher intensities than did the strongest peak from tungsten. This result, found before the SEM results pictured in Figs 13–15, was at first quite surprising. It is, however, completely compatible with the microstructural results, for absorption calculations show that penetration depth of CuK_α radiation in W is comparable to the observed carbide thickness, with the beam intensity falling to one-half its initial value after penetrating only 2.1 μm of tungsten. This is less than the carbide layer thickness of 5 μm shown in Fig. 15, and because the carbide covered most of the surface, it is reasonable that the carbide peaks should be stronger than those from the metal.

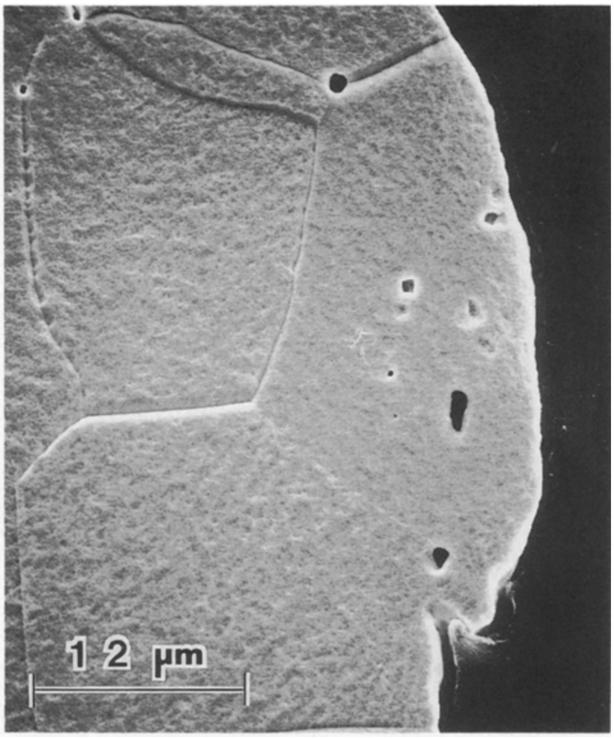

Figure 16 Cross-sectional view of a tungsten sample after it was heat treated in an Ar–5% H_2 gas mixture at 2000 °C for 1 h.

Perhaps, in retrospect, the most surprising result should be that the carbide peaks from the spark-machined tungsten were weaker than those of the metal. Prominence of diffraction peaks from EDM surfaces in both molybdenum and tungsten make it clear that surface layers evident in Figs 3, 13, and 14 must contain more metal than they do carbide, at least to the depth probed by copper X-rays. In molybdenum, the CuK_α radiation penetration depth is greater by nearly a factor of two than that in tungsten, so some of the X-ray intensity contained within the diffraction peaks of the metallic phase may have originated in the unmelted base metal, but most of the diffraction must have occurred within the carbon-enriched surface layer. Such results are consistent with the conclusion drawn from microstructural studies that the surface layers on both molybdenum and tungsten must consist of intimate mixtures of metal and carbide.

4. Discussion

The results presented make it clear that carbon contamination in the form of carbides can be removed from EDM surfaces of both molybdenum and tungsten by heat treating them in an atmosphere of argon with 5% H_2. Other reducing atmospheres could surely work also, the advantage of the gas mixture employed being that it is commercially available and safe to work with. Kinetic effects have not been investigated, but the 1 h heat treatment at 2000 °C used here removed nearly all carbides from the surfaces of the samples studied. The only detrimental effect observed was growth of the metal grains to a mean size near 50 μm. This grain growth would certainly be undesirable in any material which should undergo further cold working, but would likely make little difference with components which would not be highly stressed or which would subsequently be exposed to high temperatures.

The principal mechanism of carbon removal in flowing Ar–5% H_2 is believed to be by reaction of carbon at the surface with the hydrogen to form CH_4. This mechanism is not available in commercial purity argon, so it came as no surprise that argon was less effective in removing carbides. In fact, the decrease in carbide fraction at the surface of EDM molybdenum was greater than expected. It is not clear if some of the carbon was lost to the atmosphere or if all the excess diffused into the molybdenum matrix. The small precipitates observed along grain boundaries suggest that this latter mechanism may have been operative. An attempt was made to resolve the question of whether the excess carbon may have been absorbed into the molybdenum matrix by employing lattice parameter measurements. This effort was inconclusive because lattice parameter values obtained for the molybdenum from the EDM surfaces both before and after heat treatment were consistently within 0.00005 nm of 0.31482 nm, while values from the back surfaces of the same samples were consistently about 0.0001 nm larger. If the carbon were in solution, it would be expected to expand the lattice, not contract it. If any substantial amount of carbon was in solution at the high temperature, then it must have precipitated out during cooling, and if this occurred in the molybdenum sample heated in argon, then the carbon must have diffused to considerable depths to leave the surface so free of carbide. Diffusion rates for carbon in molybdenum are apparently not available at the temperatures employed. Diffusivities are available in the temperature range 1200–1600 °C [4], and at the upper end of this temperature interval the diffusivity is $3 \times 10^{-7}\ \mathrm{cm^2\,s^{-1}}$. In 1 h at this temperature, carbon would diffuse into the molybdenum to a depth of about 0.3 mm, so, at the higher temperature employed in this study, carbon could easily diffuse through the full 1.2 mm sample thickness. At 1600 °C, the diffusion rate of carbon in tungsten is approximately one order of magnitude lower than in molybdenum [4], and it is probably lower at the higher temperature employed here also. Assuming this to be true, the carbon was less able to dissolve away into the tungsten matrix, and so remained near the original surface when the spark-machined tungsten sample was heat treated in argon. The diffusion rate was, however, sufficient to permit the phase separation of metal and carbide shown by Figs 14 and 15.

The EDX measurements showed that heat treatment of both molybdenum and tungsten in either argon or Ar–5% H_2 removed the copper contamination produced by spark machining. Because copper has a substantial vapour pressure at 2000 °C, it was probably removed by evaporation. The heat treatment employed is not viewed as a reasonable method for removing such contamination, because chemical methods would be more practical. Heat treatment in Ar–H_2 atmospheres does, however, appear to be an effective and reasonable method for removing the carbides formed on molybdenum and tungsten by spark machining. The method should be equally effective on other metals which form carbides upon spark machining.

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