JOURNAL OF MATERIALS SCIENCE 6 (1971) 981–988

Carbon Self-Diffusion in Tungsten Carbide

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Dense, hot pressed tungsten carbide specimens were used to study the self-diffusion of ^{14}C into WC in the temperature range 2238 to 2643°K. The necessity for extended diffusion anneal times was eliminated by using a submicron sectioning technique, and the diffusion penetration depth was determined by spectrophotometric W^V thiocyanate analysis of the sample sections. The existence of two clearly delineated diffusion mechanisms was demonstrated from the shape of the activity versus penetration curves. The first obeyed a bulk diffusion law, originated at the specimen surface, demonstrated anomalously low diffusion coefficients, dominated to a depth of about 0.5 μm, and could be represented by the expression:

$$D_{\text{vol}} = 1.90 \times 10^{-6} \exp - (88{,}000/RT) .$$

Autoradiography demonstrated that the second mechanism was grain-boundary diffusion which dominated at depths greater than 1 μm. The Fisher grain-boundary diffusion analysis and the Suzuoka analysis gave apparent grain-boundary diffusion activation energies of 74 Kcal/mole and 71 Kcal/mole respectively. By using an estimated value of the bulk diffusion coefficient, the Suzuoka analysis permitted direct calculation of the grain-boundary diffusion coefficient, and can be represented by:

$$D_{\text{g.b.}} = 4.57 \times 10^{2} \exp - (71{,}000/RT) .$$

1. Introduction

The present interest in very high temperature materials has intensified fundamental studies of transport properties in transition metal carbides. However, self-diffusion in these systems has not been treated extensively, largely due to the inherent experimental difficulties arising from applying sectioning techniques to extremely hard and brittle materials.

A technique frequently used to measure diffusion in carbides is the layer growth method. Here, the rate of growth of a carbide layer on a metal surface is measured. Several major assumptions are made which render the results of questionable relationship to tracer self-diffusion studies. It is assumed that the diffusivity is independent of the concentration, that the growth of the carbide phase is controlled by carbon transport only, and that a relatively simple (usually linear) concentration profile exists in the diffusion zone.

The assumption of concentration independence of carbon diffusivity has been tested experimentally [1] for NbC, and the diffusion coefficient was observed to decrease with increasing carbon content. Finally, the layer growth technique was compared directly with the tracer self-diffusion method for Nb_2C. The results showed that the experimental diffusion coefficients measured by the two techniques were essentially different. Arrhenius diagrams were linear for both techniques, and approximately parallel, however, the coefficient of diffusivity by layer growth was about 100 times greater than the tracer diffusion coefficient.

That there should exist a difference may well be explained by the fact that the tracer self-diffusion coefficient is described by the equation:

$$j = - D \frac{\partial c}{\partial x}$$

However, the analogous expression for the layer

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growth method is:

$$j = -D\left[\frac{\partial \ln a}{\partial \ln c}\right]\frac{\partial c}{\partial x} - \left[D\left(1 + \frac{\partial \ln \gamma}{\partial \ln c}\right)\right]\frac{\partial c}{\partial x}$$

where a is the activity and γ the coefficient of activity. The two experimental coefficients differ by the factor $[1 + (\partial \ln \gamma/\partial \ln c)]$. Therefore if the activity coefficient is concentration dependent, we may expect diffusion data from the tracer technique and from the layer growth method to differ.

Tracer self-diffusion studies have been reported by several authors [3-7] in transition metal carbide systems; however, the present study is concerned primarily with a submicron sectioning technique, and its application to studying the relative contributions of grain boundary and bulk carbon self-diffusion in polycrystalline WC.

An early solution to the grain-boundary diffusion problem was presented by Fisher [8] and can be applied to the work herein in the form:

$$\log A = [2^{1/2}(D_{\mathrm{v}}/D_{\mathrm{gb}}\,\theta)^{1/2} \log \mathrm{e}/(\pi\, D_{\mathrm{v}}t)^{1/4}]\,y + \text{const.} \qquad (1)$$

where A is activity of the specimen sectioned from between depths $y - (\delta\, y)/2$ and $y + \delta\, y/2$, θ is the grain-boundary thickness, y is the distance of tracer penetration, in time, t, D_{V} and D_{gb} are the volume and grain-boundary diffusion coefficients respectively.

A more recent analysis of grain-boundary diffusion is that of Suzuoka [9] who adopted an instantaneous source model wherein the concentration of the surface source is time dependent. The grain-boundary diffusion coefficient, D_{gb}, is determined from the slope:

$$\gamma = -\frac{\partial \log A}{\partial\, y^{6/5}} \qquad (2)$$

and the relation:

$$0.973 \log(\Delta - 1) = 6.567 - 1.644 \log \gamma - \log (D_{\mathrm{v}}t)^{1/2} \qquad (3)$$

where $\Delta = D_{\mathrm{gb}}/D_{\mathrm{v}}$.

The solution to the fundamental differential equation for diffusion in an isotropic medium used in this work is given by [10]:

$$A = \frac{M}{(\pi D_{\mathrm{v}}t)^{1/2}} \exp(-y^2/4D_{\mathrm{v}}t) \qquad (4)$$

where M is the total amount of diffusing species per unit area, and other symbols correspond to those in equation (1).

2. Experimental Procedure

The tungsten carbide powder (A. D. Mackay Co, N.Y.) used for all sample preparation was 99.99% purity level, having an average particle size of about 3 μm, and 0.03% uncombined carbon. For the free carbon analysis, the WC sample was dissolved in a mixture of nitric and hydrofluoric acids leaving the free carbon unattacked. The suspension was filtered through a filtering crucible lined with ignited asbestos, dried and ignited in an induction furnace. The carbon dioxide formed during ignition was absorbed in Ascarite (Arthur Thomas Co, Phila. Pa.) and weighed.

Since the particular composition of binary compounds is often influential in diffusion experiments, the stoichiometry of the WC sample was verified on the powdered WC by comparison of the a_0 and c_0 lattice parameters of the hexagonal WC used with accepted literature data. Using an X-ray method of successive approximations [11], a_0 and c_0 were calculated to be 2.900 ± 1 Å respectively and compared favourably with Metcalfe's values for $\mathrm{WC}_{1.0}$ of 2.906 and 2.837 Å for a_0 and c_0 respectively [12].

The WC powder was fabricated into cylindrical samples 19.05 mm diameter by 6.35 mm in height by means of hot pressing techniques using a high strength graphite die. The pressing was performed in a single action, induction heated press with a graphite susceptor tube surrounding the die and maintained in a helium atmosphere. Pressures of 668 Kg/sq cm, and temperatures of 1500°C for 20 min were employed to achieve 99%, or better, theoretical density. Comparison of X-ray diffraction patterns for the free powder WC and the hot pressed pieces indicated only a small amount of preferred orientation of the (001) planes.

There was some concern regarding the oxygen content of the hot pressed WC samples, particularly since such an impurity would most likely tend to segregate at grain-boundaries, thereby obscuring the value of grain-boundary diffusion measurements. A vacuum fusion technique* was employed wherein the diffused, annealed samples of WC were dropped into a graphite crucible containing molten iron, and the CO formed by reaction of the oxygen in the sample with the crucible was oxidised to CO_2 and analysed volumetrically. Oxygen levels of about 0.03% were found and judged to be unobjectionable.

In order to avoid grain growth and strain

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*The analyses were performed by courtesy of the Carborundum Co, Niagara Falls, New York.

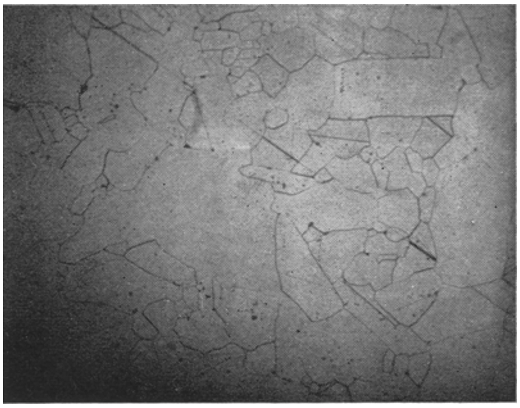

Figure 1 Photomicrograph of tungsten carbide structure prior to diffusion anneal (× 200).

release during the diffusion runs, all samples were pre-annealed at temperatures higher than the diffusion temperature and for a time equal to the run time. The hot pressed specimens were lathe-ground to ensure an accurate circular face, and then polished optically flat on the diffusion surface. The average grain size was calculated using the method of Fullman [13], and in all cases the average grain size of the annealed specimens ranged from 21 to 26 μm. A typical resultant microstructure is shown in fig. 1.

The carbon diffusion runs were performed in an induction heated unit under a small positive pressure of purified helium.

Carbon-14 was obtained from New England Nuclear Corporation in the form of amorphous carbon powder, having an activity of 5 μc/gm. This was dispersed mechanically and ultrasonically in Aquadag, a commercially available concentrated colloidal dispersion of pure graphite in water obtained from Acheson Colloids Co, Port Huron, Michigan. A drop of the radioactive slurry (about 95% Aquadag) was placed on the sample surface, the water vehicle subsequently evaporated and the specimen baked in a vacuum at 300°C for 1 h to develop an adherent ^{14}C coating of about 10^5 cpm activity, and about 0.5μm thickness. The uniformity of the ^{14}C dispersion was determined by autoradiography to be satisfactory only after ultrasonic dispersing techniques.

In order to employ the sectioning technique for the determination of such small diffusion coefficients as were anticipated in the WC system without resorting to extremely long diffusion anneals, it was necessary to design an apparatus for removing submicron layers from the diffused sample surface [14]. This was essentially a lapping technique wherein the removed layer could be retained and transferred quantitatively for counting and thickness measurement. After each layer removal the optical flatness of the sample was checked interferometrically under a 5876 Å helium lamp. This system was tested for accuracy by comparing spectrophotometric and weight loss data and found to be satisfactory within experimental limits.

In order to determine the section activity, the section was transferred to a modified Tracer-Lab fine precipitate apparatus and deposited on a filter* under vacuum. Thus, the sample sections were counted on the filter under uniform and consistent geometry using a shielded windowless gas-flow counter.

Knowing the sample density, geometry and stoichiometry, it was possible to determine section thickness by tungsten analysis of the removed section. After counting each section, the filter and sample was transferred to a platinum crucible and the cellulose filter completely digested with fuming H_2SO_4. After the acid was evaporated the remaining WC section was fused with Na_2CO_3 at about 850°C in order to transform the tungsten into a water soluble W^{VI} form. This was then reduced quantitatively to W^V by Sn^{++} solution in 10M HCl and a spectrophotometric determination of the tungsten thiocyanate complex formed in spectroscopically pure acetone was performed [15]. Standard curves were obtained using a Zeiss spectrophotometer and the absorption peak was observed at 398nm. For the individual section removed, a similar analysis was performed and the section thickness determined from the standard curve and the sample geometry.

The temperature measurement during diffusion runs was made with a Pyrometer Co optical pyrometer, which was previously calibrated against a W(3% Re)-W(25% Re) thermocouple purchased from Engelhard Industries. Corrections for heat up and cool down time were made to determine the effective time, t_{eff}, at run temperature [16]. Temperature measurements were obtained from the surface of a thin graphite wafer resting on the sample.† The measured run temperature was maintained

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*The radioactive assay filters were obtained from the Millipore Filter Co, Boston, Mass.

†Periodic checks of the graphite disc showed no detectable ^{14}C diffusion from the sample surface into the disc.

constant within ± 0.5%, while the uncertainty in the absolute value of the temperature was that normally associated with calibrated optical systems.

There are a number of systematic errors introduced into the measurement of a tracer diffusion coefficient. The experimental uncertainty in section thickness was determined by a statistical error treatment [17] and the standard deviation in radioactive counting was obtained according to conventional counting statistics [18]. The finite section thickness can contribute some uncertainty in assigning an activity to a point in the diffusion zone. Using the error treatment of Shirn [19] modified to apply to the solution of the diffusion equation used in this work, the true D is seen to deviate negligibly from the measured value due to the typically small value (0.08μm) of the section thickness. After each section removal the sample surface was examined interferometrically to determine the extent of surface contouring. Such crowning was kept to a minimum by constant resurfacing of the Al_2O_3 lapping plate.

3. Experimental Results and Discussion

After diffusion anneals of from 6 to 12 h the samples were mounted in a lathe and about 25 μm were removed from the perimeter of each to ensure precise sample geometry and to eliminate any confusing contribution from surface diffusion along the sample sides. Then sections were removed on the submicron sectioning apparatus, and analysed to determine section activity and thickness. Since it has been demonstrated that the error introduced by the small, finite size of the section thickness was negligible; therefore the data on the radio-activity of each section was treated as point information at y, the depth of the section below the diffusion interface. Penetration depth was determined by summing contiguous section thicknesses. A typical experimental plot of activity versus penetration distance is shown in fig. 2. See Appendix 1 for error treatment.

Inspection of fig. 2 shows the existence of two clearly delineated diffusion processes taking place. The first process starts at the specimen-tracer interface and dominates to a penetration depth which is not temperature dependent. When the data for this first diffusion process are plotted according to equation 4 (see fig. 3) a linear figure results defining isotropic, bulk diffusion in the dense, polycrystalline system.

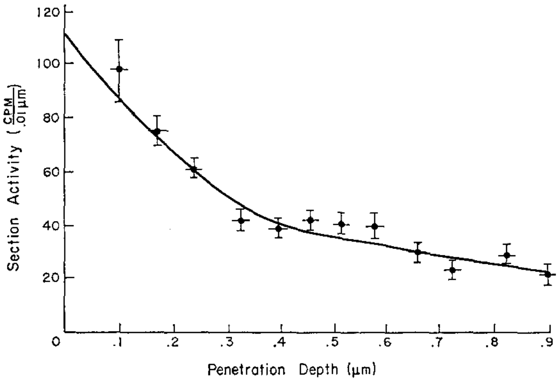

Figure 2 Radioactivity of ^{14}C as a function of diffusion penetration – temperature 2343° K, t_{eff} of 3.98 × 10^4 sec.

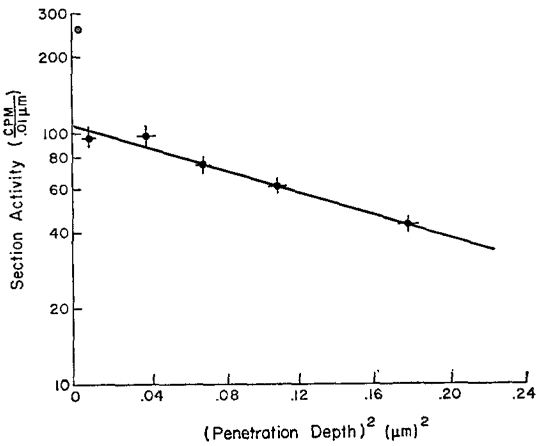

Figure 3 Bulk diffusion plot according to equation 4 – temperature 2343° K, t_{eff} of 3.98 × 10^4 sec.

The bulk diffusion coefficients were calculated from the slope of the above curves and an Arrhenius plot of this data is shown in fig. 4. An apparent activation energy of 88 Kcal/mole was obtained from the slope, $-Ea/R$.

In contrast to the diffusion coefficients shown in fig. 4, available literature data on similar systems [3, 6, 7] indicate that volume self-diffusion coefficients of 10^{-6} to 10^{-7} cm^2/sec would be expected in the temperature range of interest. However, the availability of a submicron sectioning technique in the present investigation may well have permitted detection of a "surface-layer" effect not representative of the bulk of the sample. However, this layer still demonstrated volume diffusion behaviour.

Previous investigators have reported this same effect for diffusion systems lending themselves to convenient submicron sectioning techniques.

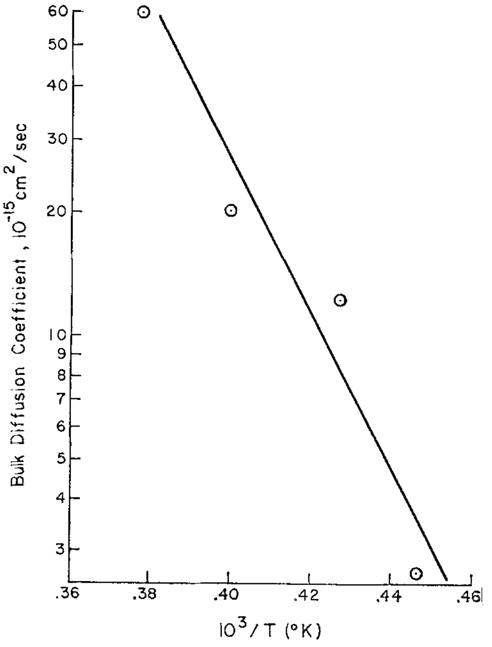

Figure 4 Arrhenius plot for the bulk diffusion process from which was calculated an apparent activation energy of 88 Kcal/mole.

Styris and Tomizuka [20] studied ^{65}Zn diffusion in copper single crystals using a chemical sectioning technique permitting the removal of sections less than 0.2 μm thick. These authors observed a bulk diffusion coefficient 3 × 10^3 smaller than that found by a lathe sectioning technique for a penetration distance up to about 1 μm. Pawel and Lundy [21] used a sectioning technique based on the removal of anodically formed oxide to study the diffusion of ^{95}Nb into Ta. They found apparent volume diffusion coefficients at a penetration distance less than 1 μm which were 10^2 times smaller than diffusion coefficients determined on the sample interior. Similar results were found for C in ZrC[7]. In the latter case, a chemical sectioning technique produced sections comparable in thickness to those obtained in this work and found carbon diffusion through the surface layer proceeding about 10^6 times slower than the interior.

It is concluded, therefore, that the anomalous lattice-type diffusion data observed in the specimen "surface-layer" probably represents diffusion through an oxide layer or a region strongly distorted from the normal WC structure.

As seen in fig. 2 there is another operating mechanism for ^{14}C diffusion beginning where the first stops. A clear picture can be seen only after the break in the above curves, since in the region of gradual curvature there exists a superposition of at least two diffusional processes. For two runs autoradiographs* were taken of a specimen surface prior to, and immediately after, this curve break. Typical autoradiographs after an average of seven days exposure in a desiccated light-tight box are shown in fig. 5.

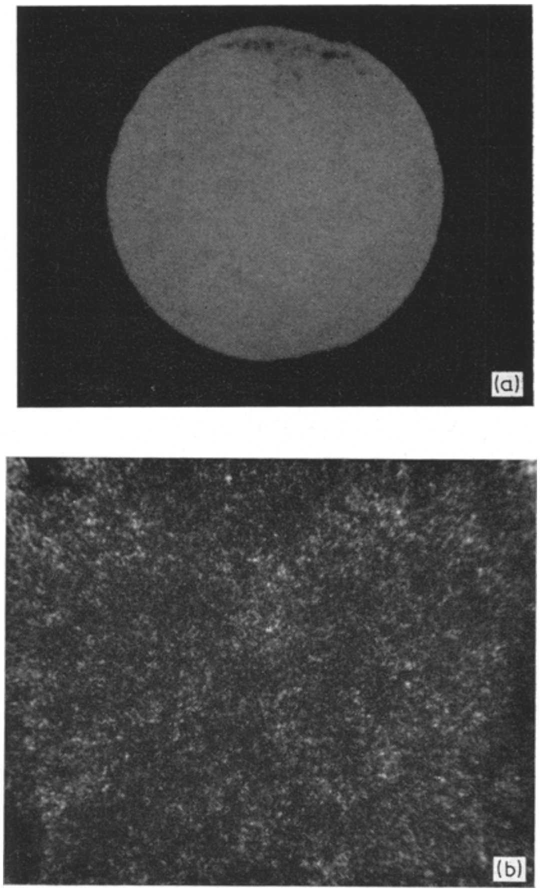

Figure 5 Autoradiograph of the WC sample surface. (a) Before diffusion anneal (× 5), (b) After onset of grain-boundary diffusion, exposure time of seven days (× 100). Diffusion temperature 2326°K, diffusion depth 0.6 μm.

Fig. 5a shows the surface prior to diffusion anneal and fig. 5b shows the surface after the curve break. Microscopic examination of the magnified negative shows the presence of interconnected grain boundaries evidenced by areas of heavier exposure, separated by largely under-

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*All autoradiography was done with no-screen X-ray film from Eastman Kodak Co, Rochester, New York.

developed regions interpreted as WC grains. Thus, it was concluded that the diffusional process responsible for the second segment of the activity-penetration curves was grain-boundary diffusion. The anomalous bulk-type diffusion zone terminated between 0.35 and 0.45 μm in all runs except the highest temperature run (2643° K) where the anomalous zone extended to a depth of about 0.7 μm.

The Fisher solution for grain-boundary diffusion was applied to the second diffusion process observed. A typical straight line plot of log A versus penetration distance is shown in fig. 6. In order to obtain D_{gb} from the slopes of these graphs it is necessary to know the diffusion coefficient for carbon in bulk WC, and the grain-boundary width. Since the data presented herein represent an anomalous bulk process and tracer self-diffusion, data for C in WC were not available from the literature, the value of D_V was estimated as follows.

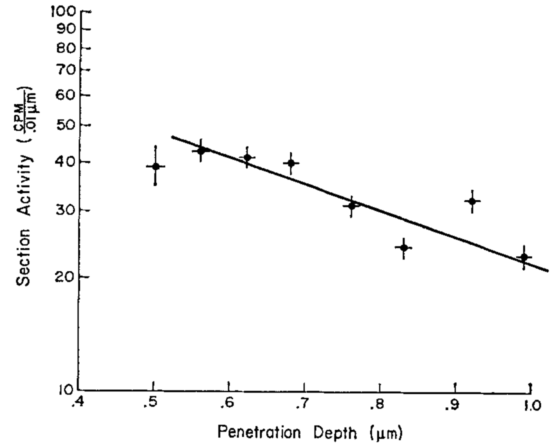

Figure 6 **Fisher plot of grain-boundary diffusion process according to equation 1. Temperature 2343°K t_{eff} of 3.98 × 10^4 sec.**

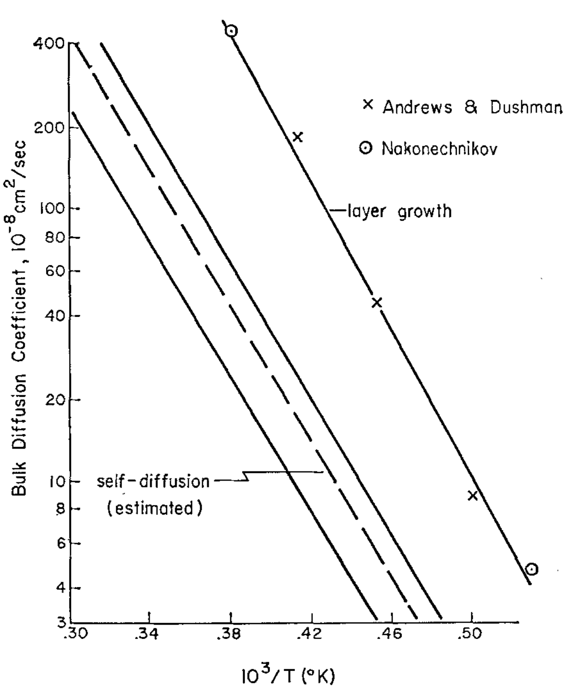

Figure 7 **Carbon self-diffusion in tungsten carbide.**

Comparison of available literature data for carbon diffusion in metallic carbides having interstitial structural similarity to WC (namely vanadium carbide, zirconium carbide and niobium carbide) showed that Arrhenius plots for carbon self-diffusion and carbon layer-growth diffusion were parallel in the 2000°C range. The former technique yielded a diffusion coefficient about an order of magnitude smaller than the layer growth technique in all cases. The layer growth data of Andrews and Dushman [22] and Nakonechnikov [23] in tungsten carbide are shown in fig. 7. The two workers are in remarkably good agreement. It is reasonable to assume that diffusion in the WC system will behave in a manner similar to the other interstitial carbide systems. Therefore by analogy to the VC, ZrC and NbC systems, the ratio (D layer growth/$D_{\text{self-diffusion }2273^\circ\text{K}}$) is formed for the WC system and the self-diffusion coefficient for carbon into WC is thereby estimated resulting in the lower curve in fig. 7.

Application of the Fisher and Suzuoka analyses to the second diffusional process observed in the penetration curves is shown in fig. 8 for a typical determination. An Arrhenius plot, derived from Fisher analyses, is shown in fig. 9, and its slope gives an apparent activation energy for carbon grain-boundary diffusion in WC of 74 Kcal/mole. The value of θ, the grain-boundary width, is not determinable.

From application of the more recent Suzuoka grain-boundary diffusion analysis an Arrhenius plot was generated and is shown also in fig. 9. In this analysis, no knowledge of the grain-boundary width is necessary, and the magnitude of the grain-boundary diffusion coefficients is reasonable. An apparent activation energy of 71 Kcal/mole was obtained for the grain-boundary diffusion of C into WC, which compares favourably with the result from the Fisher analysis. A

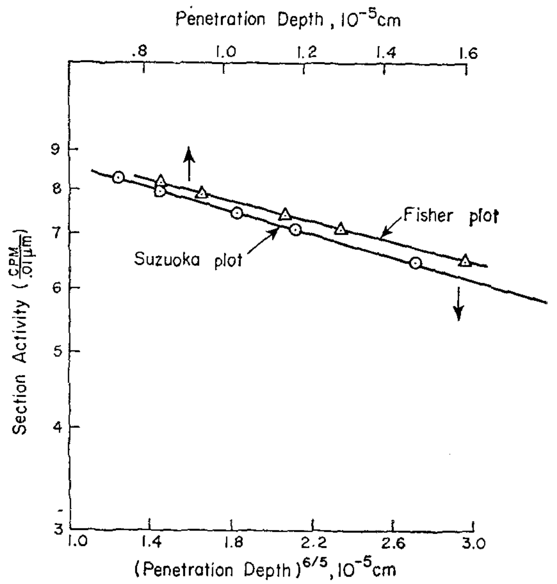

Figure 8 Grain-boundary diffusion curves as treated by the Fisher and Suzuoka analyses.

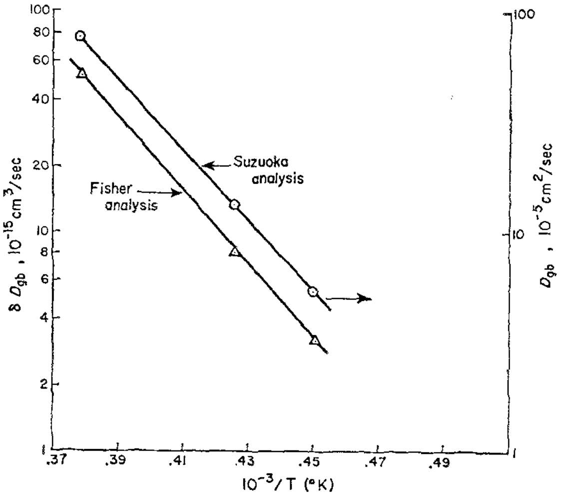

Figure 9 Arrhenius plot for grain-boundary diffusion according to the Fisher and Suzuoka analyses.

summary of the diffusion data is presented in table I.

An interesting point for comparison of the work reported herein and previous workers is the value of the ratio $(D_{gb}/D_V)_T$. Selecting a value for $1000/T(°K)$ of 0.42, this ratio becomes:

$$\frac{D_{gb}}{D_V} = 10^3$$

for C in WC based on the estimated value of D_V. In metallic systems [24, 25] this ratio has been approximated at 10^4 to 10^6 while in oxides, [26] it has been estimated to be about equal to unity. The value obtained places this value for carbides intermediate between pure oxides and pure metals.

4. Conclusions

Using a submicron sectioning technique to study the self-diffusion of ^{14}C into dense, polycrystalline, hot pressed WC, two distinct diffusion mechanisms were observed, separated graphically and treated mathematically. A bulk diffusion mode was observed to predominate in a surface layer which extended about 1 μm into the interior of the WC sample. Analysis of an Arrhenius plot for the bulk diffusion gave an apparent activation energy of 88 Kcal/mole; however, this diffusion proceeded at an anomalously slow rate having a diffusion coefficient about 10^6 times smaller than expected by comparison with existing data on similar systems. Other investigators have observed a similar effect using various submicron sectioning techniques. The exact nature of this surface layer is not known, but can conceivably be attributed to surface oxidation during normal atmosphere exposure, or in the present case, to a disruption or distortion of a surface layer during mechanical preparation of the specimen surface.

The second diffusion zone begins beneath the surface layer, and autoradiographic evidence indicated that this was a grain-boundary diffusion region. Using a correlation developed from available literature data on carbon self-

TABLE I Summary of diffusion data.

Temperature (°K)	Time (effective) (sec)	Anomalous volume diffusion coefficient (cm^2/sec)	Suzuoka grain-boundary diffusion coefficient (cm^2/sec)
2238	2.78×10^4	2.56×10^{-15}	5.10×10^{-5}
2343	3.98×10^4	1.20×10^{-14}	1.25×10^{-4}
2493	1.98×10^4	1.96×10^{-14}	*
2643	2.18×10^4	5.88×10^{-14}	7.05×10^{-4}

*Insufficient radioactivity in grain boundary penetration curve.

diffusion in transition metal carbides, the bulk diffusion coefficient for carbon in WC was estimated and used to obtain a Fisher and a Suzuoka analysis of this section of the ^{14}C penetration curve. The Fisher analysis gave an apparent activation energy for carbon grain-boundary diffusion of 74 Kcal/mole, while the Suzuoka analysis gave 71 Kcal/mole.

Appendix 1

Error Treatment – Section Thickness

As a general case, if $z = f(x, y, - - -)$, then the probable error in z is:

$$P_z = [(P_x \partial z/\partial x)^2 + (P_y \partial z/\partial y)^2 + - - -]^{1/2}$$

If one lets g be the section weight in gms, ρ the section density in gms/cc, and r the section radius, the section thickness is given by:

$$d = \frac{g}{\rho \pi r^2}$$

and from the general error equation above:

$$P_d = [(\sigma_g/\rho\pi r^2)^2 + (-\ g\sigma_\rho/\pi r^2 \rho^2)^2 + (-\ 2g\sigma_r/\rho\pi r^3)^2]^{1/2}$$

where σ's are the uncertainties in the various experimental measurements, where $\sigma_g = \pm 6 \times 10^{-6}$ gm, $\sigma_\rho = \pm 0.02$ gm/cc, $\sigma_r = \pm 5 \times 10^{-4}$ cm. The uncertainty in g was estimated from the spectrophotometric data. The maxinum uncertainty in d was found to be $\pm 0.02\ \mu$.

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Received 14 January in revised form and accepted 15 March 1971