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# Coarsening of hafnium carbide particles in tungsten

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The coarsening behaviour of finely dispersed HfC particles in a W–HfC alloy was investigated by monitoring the growth rate of the particles. An activation energy of 480 kJ mol$^{-1}$ was obtained for the process. Diffusion experiments of hafnium in tungsten were conducted at temperatures between 1773 and 2573 K using a secondary ion mass spectroscopy technique to determine the diffusion contribution to the coarsening process. The diffusion process at high temperature is controlled by lattice diffusion with an activation energy of 335 kJ mol$^{-1}$ whereas that at low temperature is governed by grain-boundary diffusion with an activation energy of 170 kJ mol$^{-1}$. It appears that the coarsening process is controlled by two energy barriers: one dictated by the diffusivity of hafnium and the other by the solubility limit as a function of temperature. The strain energy required to dissociate the carbide particles into individual species was also considered. The effects of the coarsening of HfC particles in a dispersion-strengthened W–0.4 mol % HfC alloy on recrystallization and creep deformation were illustrated using a concerted experimental modelling analysis. Results show that the strengthening effect of the HfC particles is significantly reduced at temperatures above 1800 K, due to particle coarsening.

## 1. Introduction

The high-temperature mechanical properties of metals can be significantly enhanced by the presence of finely dispersed particles in the matrix. These particles can restrict grain growth and dislocation motion, both of which lead to higher strength and lower creep rates of the materials [1]. However, these particles tend to coarsen at elevated temperatures resulting in a reduction in strength with prolonged high-temperature use. Refractory alloys are used extensively in energy systems due to their high-temperature properties. Tungsten, which has the highest melting temperature among elemental metals, does not possess sufficient creep resistance at temperatures above 1600 K. Different dispersion-strengthened tungsten alloys have been developed to extend the usefulness of tungsten to higher temperatures. One of these alloys, tungsten with 0.4 mol % finely dispersed HfC particles (W–HfC), has the optimum properties for high-temperature applications [2–6]. Hafnium carbide is used as the strengthening agent due to its high chemical stability and its compatibility with tungsten. The presence of HfC particles retards the rate of grain growth, as well as restricting dislocation motion, both of which are beneficial for creep resistance. The long-term behaviour of this alloy depends largely on the evolution of its microstructure which is governed by the diffusion of its constituents [7]. Data on the diffusion of carbon in tungsten [8, 9] and tungsten self-diffusion [9–11] are available, but no direct measurements have been made on the diffusion of hafnium in tungsten. The only diffusion data available were extrapolated from coarsening studies [3, 11] and are highly unreliable. In this study, the coarsening and diffusion behaviour of hafnium carbide particles in tungsten was correlated. Utilizing these data, the lifetime of W–HfC for high-temperature application was predicted.

## 2. Experimental procedure

Tungsten with 0.4 mol % hafnium carbide particles (W–HfC) was chosen as the material to be investigated for this HfC coarsening study. The alloy, in the form of a 15 mm diameter rod, was obtained from Westinghouse Corporation in Pittsburgh, PA. Optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to determine the microstructure of the materials. For TEM analysis, thin areas (in 3 mm diameter specimens) were produced by jet polishing with a solution containing HF, $HNO_3$, and $CH_3OH$ [12]. Diffusion of hafnium in pure tungsten and the W–HfC alloy was measured using 1 mm thick samples cut from the appropriate materials. The tungsten material was obtained from Johnson Matthey AESAR and was 99.9% pure. The samples were coated with a hafnium layer with a thickness of the order of 100 nm by means of electron-beam evaporation. These samples were processed under different conditions with the objective of isolating the effects of grain boundaries and hafnium carbide on the diffusion process. Three types of substrate materials were used: large grain size (100 μm) pure tungsten by preannealing the material at 2373 K for 1 h prior to diffusion annealing (denoted as

TABLE I Experimental conditions for SIMS analysis

| Sample substrate | Grain size (μm) | Diffusion annealing temperature (K) | Diffusion time (h) |
|---|---|---|---|
| W/Preanneal | 100 | 1773 | 8 |
| | | 1973 | 1 |
| | | 2123 | 1 |
| W | 10 | 1773 | 8 |
| | | 1923 | 1 |
| | | 1973 | 1 |
| | | 2123 | 1 |
| W-HfC | 10 | 1773 | 8 |
| | | 1973 | 1 |
| | | 2123 | 1 |
| | | 2273 | 1/3 |
| | | 2573 | 1 |

W/100 μm); fine grain size (10 μm) pure tungsten (denoted as W/10 μm); and fine grain size (10 μm) tungsten with 0.4 mol% HfC (denoted as W–HfC/10 μm). Diffusion anneals were conducted in an ultra-high vacuum (ion-pumped) system with a base vacuum of $10^{-7}$ Pa. Sample heating was achieved by electron-beam heating and the temperature was monitored by thermocouples and an optical pyrometer. The durations of the annealing are given in Table I and they were chosen to provide similar diffusion lengths. The diffusion annealing temperature for tungsten was limited to 2123 K due to significant grain growth at higher temperatures. Hafnium profiles in tungsten and the alloy were directly measured by secondary ion mass spectroscopy (SIMS) using a 12 keV oxygen ion beam as the probe. A quadrupole SIMS unit manufactured by Atomika Technische Physik GmbH was used. A mass of 177 was used for detecting hafnium and 184 for tungsten. The sputtering rate was not measured in the SIMS but rather determined by measuring the depth of the crater created by the scan using a profilometer (Alpha-Step 200 by Tencor Instruments) after the SIMS analysis. Step height determinations were also made by tilting the sample in a scanning electron microscope and correlating the angle with crater wall displacement.

## 3. Results

Coarsening experiments were conducted for the W–HfC alloy at temperatures between 2073 and 2523 K for durations of 1 h. Fig. 1 shows the microstructure, as revealed by TEM, of the HfC particles in the sample after annealing for 1 h at 2373 K. Ardell [7] suggested a general equation for coarsening as

$$r^3 - r_0^3 = Kt \qquad (1)$$

and

$$K = 8\gamma D C_e V_m^2 / 9RT \qquad (2)$$

where $r$ and $r_0$ are the average particle radius at time $t$ and at the onset of coarsening respectively, $\gamma$ is the interfacial free energy of the particle–matrix interface, $D$ and $C_e$ are the diffusion coefficient and the concentration of the rate-limiting solute in the matrix in equilibrium with a particle of infinite size, respectively, $V_m$ is the molar volume of the particle, $R$ is the gas constant, and $T$ is the absolute temperature. The parameter $K$ is commonly referred to as the coarsening rate. The HfC particle size is difficult to determine because of limited statistics and inhomogeneous particle distribution. In this study, using areas with reasonable particle density, coarsening rates for HfC were estimated and they were found to depend on temperature in the following manner

$$KT(\mathrm{m^3\,K\,s^{-1}}) = 1.3 \times 10^{-12} \exp(-Q_{\mathrm{coarsen}}/RT) \qquad (3)$$

where the observed activation energy for coarsening, $Q_{\mathrm{coarsen}}$, was found to be 480 kJ mol$^{-1}$. Fig. 2 shows the dependence of $KT$ on temperature plotted in the Arrhenius manner.

In order to elucidate the role of atomic diffusion on the coarsening process, the diffusivity of hafnium in tungsten and W–HfC was measured using a SIMS method. Fig. 3 shows the SIMS profile measured from a preannealed tungsten sample diffusion annealed at 2123 K for 1 h. Results from the analysis show a hafnium layer on the surface indicating that

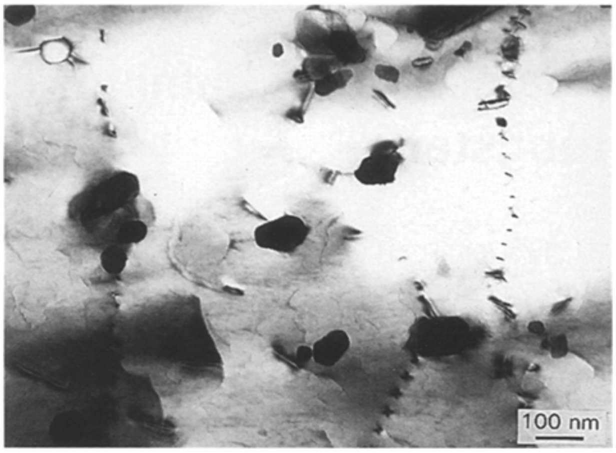

*Figure 1* Microstructure of HfC particles after annealing at 2373 K for 1 h.

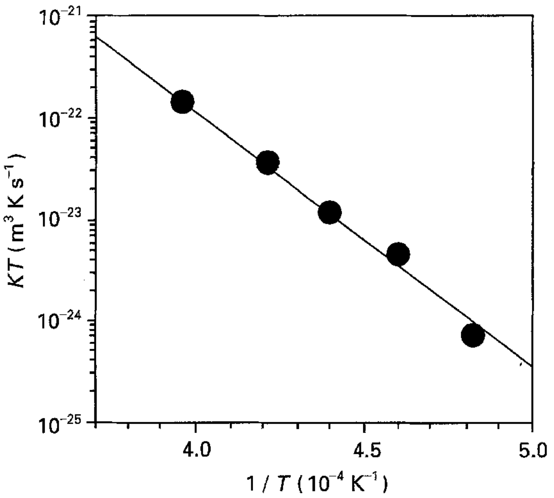

*Figure 2* Dependence of coarsening rate (expressed in $KT$) as a function of inverse absolute temperature. The activation energy for coarsening is 480 kJ mol$^{-1}$.

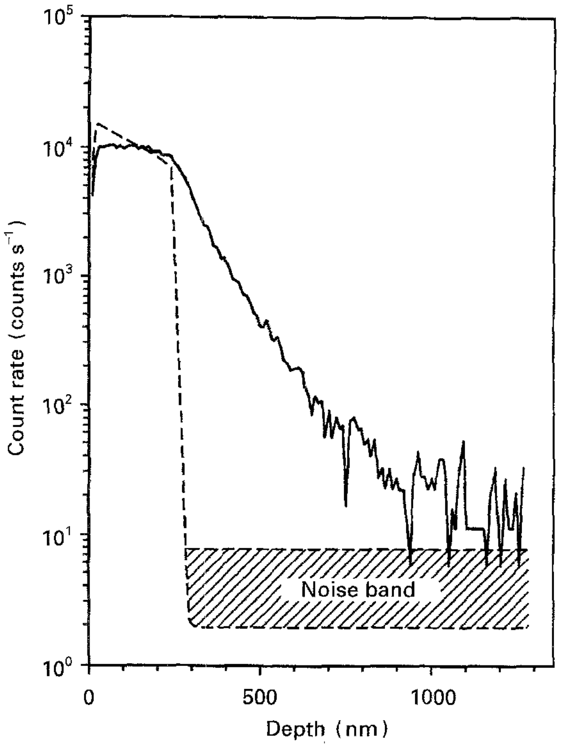

*Figure 3* Depth distribution, measured by SIMS, of hafnium in a tungsten sample preannealed at 2373 K for 1 h and then diffusion annealed at 2123 K for 1 h (———). The isotopes analysed were $^{177}Hf$ and $^{184}W$. Also included is the profile obtained from a similar sample but without diffusion annealing (– – –).

the condition resembles that of an infinite source. The diffusion profiles were fitted to the equation

$$C_x = C_s - (C_s - C_0)\ \mathrm{erf}[x/(4Dt)^{1/2}] \qquad (4)$$

where erf is the error function, $C_x$ is the concentration at position $x$ and time $t$, $C_s$ is the surface concentration, $C_0$ is the initial concentration, and $D$ is the diffusion coefficient. The diffusion coefficients obtained as a function of temperature for the three groups of substrate materials examined are plotted in Figs 4–6. In the case of the preannealed tungsten (Fig. 4), the grain size was about 100 μm and was found to remain constant even after annealing at 2123 K for 1 h. Because the size of the scan gate of SIMS was 30 μm (smaller than the grain size) and an effort was made to ensure that the scan area was within one grain area, the diffusion coefficients obtained using this substrate correspond to the lattice diffusion process. From the analysis, the equation of hafnium lattice diffusion coefficient into pure tungsten was found to be

$$D\ (\mathrm{m^2\,s^{-1}}) = 10^{-10} \exp(-Q_{\mathrm{lattice}}/RT) \qquad (5)$$

with a $Q_{\mathrm{lattice}}$ value of 310 kJ mol$^{-1}$.

One of the problems associated with SIMS analysis is the uncertainty regarding the effects of the analysing beam. It is possible that part of the diffusion profile is due to ion-beam effects, such as cascade mixing and radiation-induced segregation, and not thermal diffusion. A control experiment was conducted using a sample that has not undergone any diffusion treatment. The result from this control experiment is shown in Fig. 3. A comparison of the two profiles

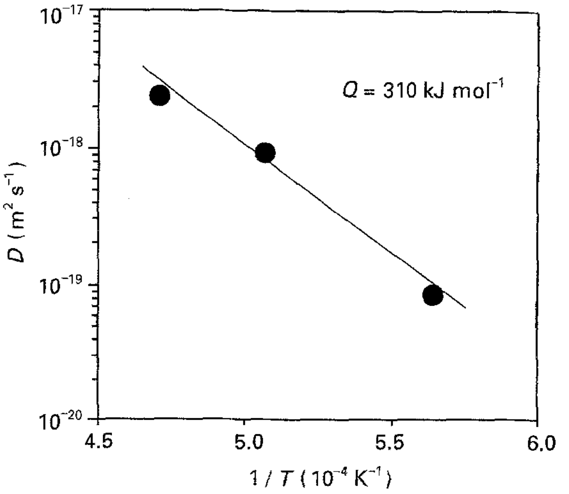

*Figure 4* Arrhenius plot of the diffusion coefficient of hafnium in pure tungsten preannealed at 2373 K for 1 h (grain size of 100 μm). The activation energy for lattice diffusion is 310 kJ mol$^{-1}$.

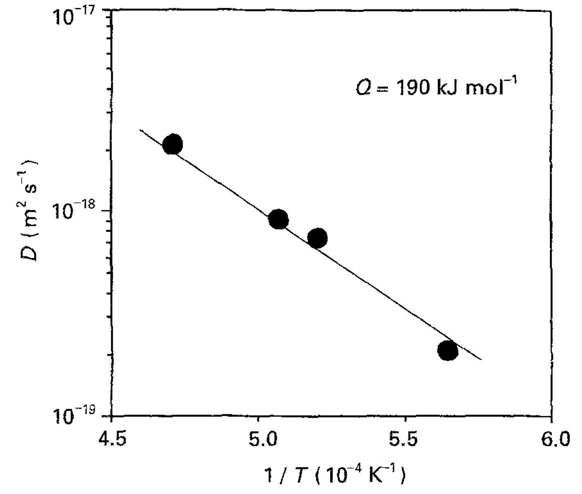

*Figure 5* An Arrhenius plot of the diffusion coefficient of hafnium in pure tungsten without the preanneal (grain size approximately 10 μm). The activation energy for grain-boundary diffusion is 190 kJ mol$^{-1}$.

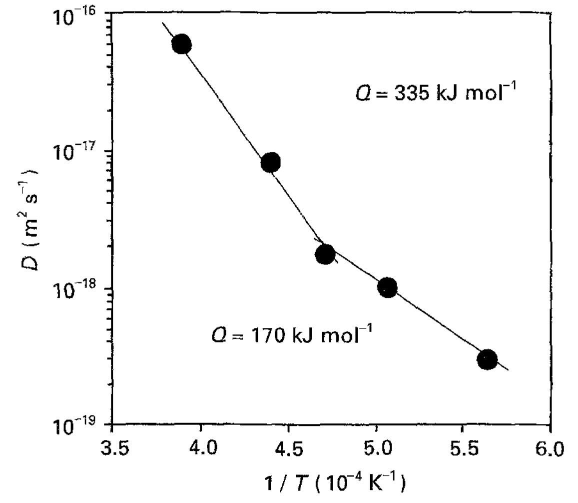

*Figure 6* Arrhenius plot of the diffusion coefficient of hafnium in W–HfC with a grain size of 10 μm. A change in slope indicates a transition from grain-boundary diffusion to lattice diffusion with increasing temperature.

clearly illustrates that the control sample did not exhibit any significant diffusion characteristic and any ion-beam effect can therefore be ignored.

Diffusion experiments were also conducted using tungsten substrates that have not undergone the preanneal process. These substrates possessed a smaller grain size. Results from the microstructure analysis show that the grain sizes in these specimens are of the order of 10 μm which is smaller than the diameter of the scan gate used (60 μm). This set of samples is denoted as W/10 μm. This implies that the diffusion process measured in this group will be dominated by grain boundaries. The effort to limit grain growth restricted the experiments to low temperatures (below 2123 K). Fig. 5 shows the results from this group of samples from which an activation energy for grain-boundary diffusion of 190 kJ mol$^{-1}$ is obtained for hafnium in pure tungsten. This is approximately half of the bulk diffusion energy which is consistent with the general observation that diffusion through grain boundaries requires less energy than through the lattice. Results from the diffusion study of hafnium in W-HfC are shown in Fig. 6. It should be noted that the original hafnium in the alloy could be disregarded because the contribution of hafnium diffused from the deposited layer was much larger than the amount of Hf in the HfC particles. The grain size of this group of samples remained at approximately 10 μm even after a high diffusion annealing temperature of 2273 K. Because the scan gate used for the SIMS analysis was 60 μm, the diffusion process determined in this set of samples corresponds largely to grain-boundary diffusion, at least at low temperatures. According to the Arrhenius plot, the low-temperature diffusion of hafnium is governed by a process with an activation energy of approximately 170 kJ mol$^{-1}$ (grain-boundary diffusion), whereas at temperatures above 2123 K, a higher activation of 335 kJ mol$^{-1}$ (lattice diffusion) is required for solute migration. This is illustrated in the two lines shown in Fig. 6. The ratio of activation energy for the two processes (lattice versus boundary) is approximately 2:1 which is consistent with the general observation in most metals. The similarity of the diffusion data obtained from pure tungsten and W–HfC indicates that the presence of HfC does not significantly affect the hafnium diffusion behaviour in tungsten.

To investigate the effects of the presence of dispersed HfC particles on grain growth, a W–HfC sample was vacuum annealed at 2573 K for 1 h. The distributions of hafnium as a function of depth were determined using SIMS prior to and after annealing. Results are shown in Fig 7a and b for the samples in the as-received condition and after annealing at 2573 K for 1 h, respectively. No hafnium coating was used in this experiment and therefore the hafnium signal is from the hafnium in the HfC particles. The vacuum-annealing process has rendered the surface of the sample free of hafnium owing to the high evaporation rate of hafnium at such an elevated temperature. The depleted surface serves as the driving force for the dissociation and subsequent outdiffusion of hafnium and carbon to the surface leading to a layer depleted of HfC particles. As a result of the formation of the depletion layer (pure tungsten with no or reduced HfC concentration near the surface), enhanced surface recrystallization has occurred. This is illustrated in Fig. 8 which shows the recrystallized grain structure on the surface. This indicates the importance of the dispersed carbide particles on retaining the grain structure at elevated temperatures. Chemical etching of the surface revealed that the thickness of the recrystallized layer is of the order of 1 μm, which agrees with the SIMS results.

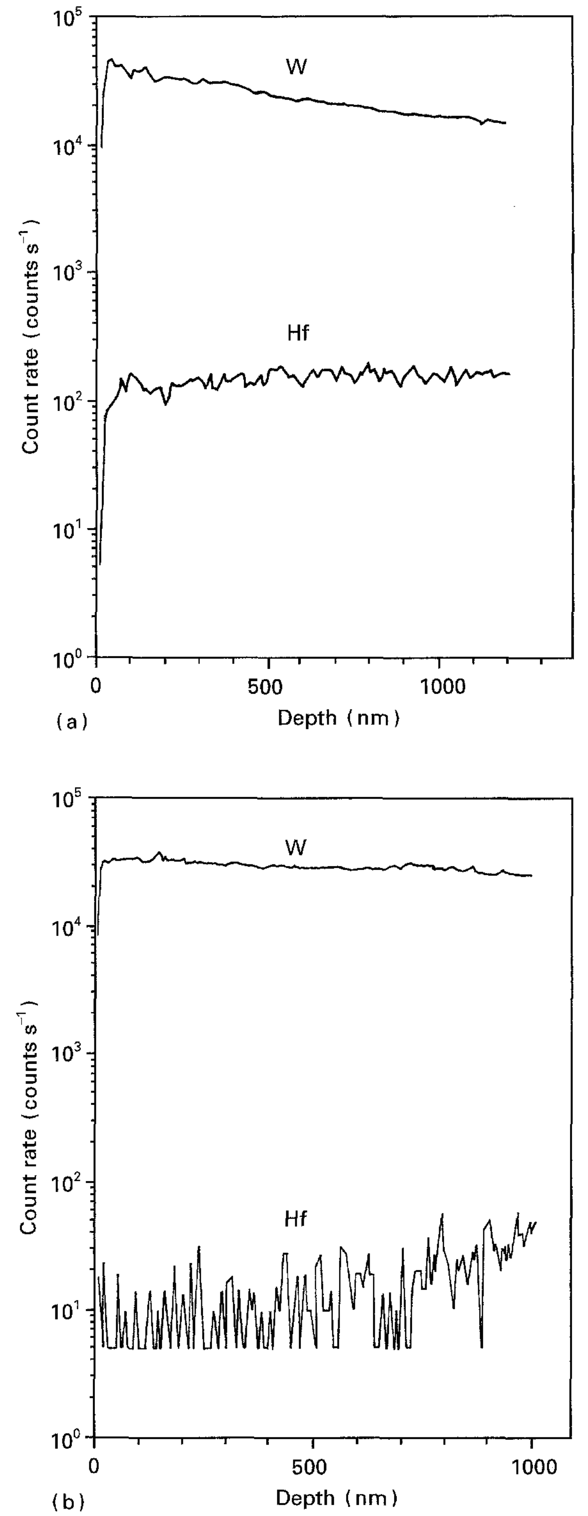

*Figure 7* Depth distribution, measured by SIMS, of hafnium in a W–HfC sample (a) prior to annealing and (b) after annealing at 2573 K for 1 h. The isotopes analysed were $^{177}$Hf and $^{184}$W.

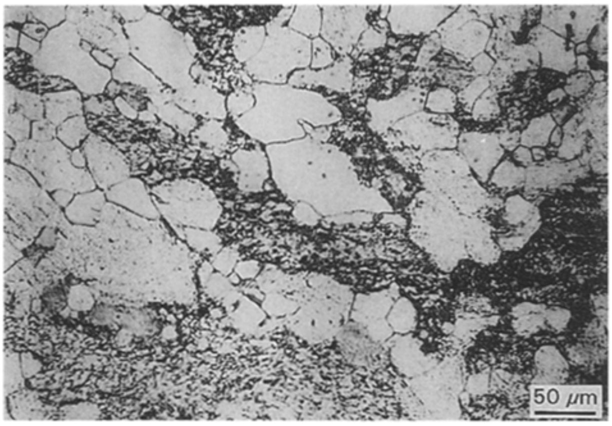

*Figure 8* Microstructure of the W–HfC sample vacuum annealed at 2573 K for 1 h showing surface grain growth due to dissociation of near-surface HfC particles.

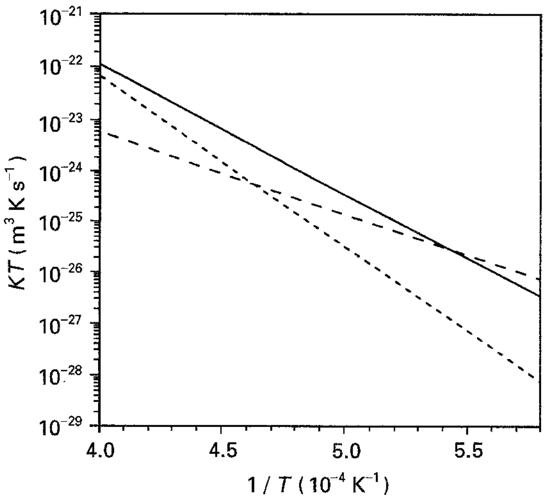

*Figure 9* A comparison of the coarsening behaviour of HfC in tungsten from three different studies: (– – –) present work, (———) Klopp *et al.* [3], (- - -) Chen [5].

## 4. Discussion

The coarsening process is usually more complicated than that illustrated in Equations 1 and 2. As discussed by Bhattacharyya and Russell [13] and Ardell [14], no single theory is capable of describing all the coarsening data for any given alloy system. Furthermore, the activation energy for coarsening is usually sensitive to the environmental conditions, making data comparison even more difficult. It is therefore not the intent of this paper fully to address the coarsening process in the tungsten alloy of interest, but rather to formulate a better understanding by correlating coarsening rates with hafnium diffusion. Two other investigations [3, 5] have examined the coarsening rate of HfC in tungsten in a manner similar to that employed in this study. Results from the three studies are compared in Fig. 9. The activation energy for coarsening extracted from the three studies ranges from a low value of 293 kJ mol$^{-1}$ [5] to a high value of 635 kJ mol$^{-1}$ [3]. This discrepancy is due to the experimental statistical inaccuracy associated with TEM analysis which was the method employed in all three studies. It is reasonable to assume that the coarsening rate depends on the diffusion of the slower of the two species. Chen [5] suggested that the fundamental process governing coarsening in this system was the diffusion of carbon. Their analysis was based on the assumption that carbon diffusion was slower than hafnium and the diffusion of carbon was, therefore, the rate-limiting step for the coarsening process. Experimental studies [8, 9] have yielded the activation energy of carbon diffusion in tungsten from 180–226 kJ mol$^{-1}$. The diffusion of carbon is expected to be interstitial in nature and the activation energy of about 170 kJ mol$^{-1}$ is certainly reasonable. Activation energy for tungsten self-diffusion [9–11] is of the order of 540 kJ mol$^{-1}$ (from 485–640 kJ mol$^{-1}$) and it is unlikely that carbon interstitial diffusion would be near such high values. It is commonly assumed that hafnium diffuses via vacancy exchange (substitutional diffusion) and therefore should possess an activation energy similar to that of self diffusion. The assumption by Chen [5] that hafnium diffuses faster than interstitial carbon is inconsistent with the occupational states of the two solutes. Direct measurements have not been made to determine the diffusion of hafnium in tungsten prior to the present investigation. It is the purpose of this study to measure the grain-boundary and lattice-diffusion behaviour of hafnium in pure tungsten and the W–HfC alloy of interest to help clarify the coarsening mechanism. Results from this study show that the presence of HfC does not significantly affect the diffusion behaviour. The lattice-diffusion energy was determined to be 335 kJ mol$^{-1}$ (for hafnium in W–HfC) whereas the grain-boundary diffusion was controlled by an energy approximately half of that amount. These energies are considerably less than the tungsten self-diffusion energies reported, but higher than carbon-diffusion energy. A study by Braun and Rudy [15] indicates that hafnium solute in a tungsten matrix has a linear misfit factor of about + 10% (hafnium solute is larger than tungsten). The misfit strain due to the presence of hafnium would result in a reduction in the diffusion barrier for hafnium diffusion, consistent with the observation that the diffusion energy of hafnium in tungsten is less than that for tungsten self-diffusion. In addition, the pre-exponential term ($10^{-10}$ m$^2$ s$^{-1}$) is smaller than that for self diffusion (of the order of $10^{-4}$ m$^2$ s$^{-1}$). Again the size misfit of hafnium leads to an attractive potential between tungsten lattice vacancies and hafnium solutes. This strong correlation suppresses the effectiveness of the hafnium solutes diffusing long distances.

In this research it was found that the activation energy of hafnium lattice diffusion in tungsten (335 kJ mol$^{-1}$) does not correspond to the observed coarsening energy. According to Equation 2, the term $KT$ depends on the surface energy, $\gamma$, atomic volume, $V_m$, diffusivity, $D$, and solute solubility, $C_e$. The first two terms ($\gamma$ and $V_m$) do not depend on temperature and should not contribute to the activation barrier for coarsening. In previous analysis of coarsening of HfC in tungsten, the observed activation energy is attributed solely to the diffusivity term. This is only true if the concentration of the solute $C_e$ is either temperature independent or below the solubility limit. Klopp *et al.* [3] have examined a W–Hf–C system and included the temperature-dependent solubility to evaluate the activation energy. However, a solution energy of 34 kJ mol$^{-1}$ was employed based on the data obtained from the binary W–Hf system [16] without carbon. Data from the binary phase diagram show that the solubility of hafnium in tungsten is of the order of several per cent within the temperature range investigated. However, the presence of carbon leads to the formation of hafnium carbide. The large binding energy of the carbide significantly reduces the solubility of hafnium in the matrix. The effect of carbon has been demonstrated in a study involving the ternary W–Hf–C system [17]. Results from that study indicate that the solubility of hafnium in the ternary system is strongly associated with the solubility behaviour of carbon. Based on the solvus line of the W–C phase diagram [18], the solubility was found to be governed by an energy of solution of approximately 125 kJ mol$^{-1}$. Owing to the strong carbide-forming tendency of hafnium, this higher energy of solution value of 125 kJ mol$^{-1}$ is appropriate for describing the solubility of hafnium in W–Hf–C ternary alloys. The observed energy for coarsening (480 kJ mol$^{-1}$) is thus the sum of the activation energy of the diffusion of hafnium (335 kJ mol$^{-1}$) and the energy of solution of hafnium in W–HfC (estimated at 125 kJ mol$^{-1}$).

According to Fig. 6, the long-range diffusion of hafnium in W–HfC can be divided into two regimes. Grain-boundary diffusion dominates at low temperature and lattice diffusion at high temperature. The temperature regime examined in this and earlier coarsening studies is sufficiently high so that lattice diffusion should dominate. However, it is expected that even at lower temperatures where normally grain-boundary diffusion is important, the coarsening rate would still be governed by lattice diffusion. The homogeneity of the alloy composition and microstructure ensures that there is no net flux of solute across the grain boundaries. The flow of hafnium (as well as carbon) atoms during the coarsening process can be treated as an intragranular process. The rate-limiting step is, therefore, the flux of the solutes between particles within each grain and only lattice diffusion needs to be considered.

In the fore-mentioned analysis, the rate-limiting step for coarsening is assumed to be the diffusion of hafnium (slower of the two species). This implies that the energy of dissociation for the HfC particles into hafnium and carbon atoms is smaller than the diffusion energy of hafnium in tungsten. The coarsening of the HfC particle requires the dissociation of the particles into individual hafnium and carbon atoms. The enthalpy change during the dissociation of the HfC has been measured and estimated to be 210 kJ mol$^{-1}$ [19], lower than the observed coarsening energy. However, the dissociation of the HfC structure into isolated hafnium and carbon atoms in the tungsten matrix and subsequently the recombination of the atoms to coarsen the HfC particles would involve a significant strain due to volume misfit. Each HfC molecule occupies a volume of $5 \times 10^{-29}$ m$^3$, whereas a hafnium atom has a volume of $2 \times 10^{-29}$ m$^3$. Carbon atoms occupy interstitial sites in the tungsten lattice and therefore contribute to a slight compressive strain. The dissociation of HfC into individual species in the lattice therefore involves a lattice dilation of $3 \times 10^{-29}$ m$^3$, and the recombination of the atoms would cause a lattice compression of the same magnitude. This volume change is of the same magnitude as the atomic volume of tungsten ($1.6 \times 10^{-29}$ m$^3$). This suggests that the diffusion of tungsten (or vacancies) will be necessary to relieve the stress for the dissociation and recombination processes in which case the coarsening energy should be related to the self-diffusion energy of tungsten, which has been reported to range from 485–640 kJ mol$^{-1}$ [9–11]. This lattice transfer phenomenon has been reported to occur in α-iron with $Fe_3C$ particles [20]. Available experimental data do not permit a definitive identification of the exact coarsening controlling process of HfC in tungsten at this time.

## 5. Effects of coarsening on grain recrystallization and creep

Dispersion-strengthened W–HfC alloys derive their superior high-temperature mechanical properties (creep in particular) from the presence of the HfC particles. These particles restrict grain growth and dislocation motion, both of which are beneficial for creep resistance. The Hall–Petch relationship [21, 22] indicates that grain growth will lead to a weakening of the material. The upper temperature limit of the dispersion-strengthened W–HfC alloys will, therefore, be governed by the recrystallization temperature, which is a function of the size of the particles. The critical radius of the particle, $r_c$, to prohibit the recrystallization can be calculated using the equation [23]

$$r_c = 3 f_v d_G / 4 \qquad (6)$$

where $d_G$ is the grain diameter and $f_v$ is the volume fraction of the particles. Particles larger than this critical size are ineffective for inhibiting recrystallization. A more complex equation which includes subgrain formation yields a similar result [24]. Experimental data obtained from microstructure analysis indicate that the grain of a W–0.4 mol % HfC alloy is elongated and the average length of the grains was measured at 40 μm and the average width of the grains was 10 μm. Because Equation 6 assumes the grains to be spherical in shape, an effective diameter for the grain is needed. The average grain can be assumed to be an ellipsoid with a longitudinal cross-section as described by $x^2/20^2 + y^2/5^2 = 1$. The effective diameter of the grain can be estimated by equating the surface area of the effective sphere with the surface area of the ellipsoid. Substituting the appropriate parameters into Equation 6, a critical radius of 85 nm was obtained for the alloy of interest. A similar approach but using the volume of a sphere and volume of an ellipsoid yielded a critical radius of 75 nm.

The coarsening behaviour of HfC in tungsten can be estimated by combining Equations 1 and 2. The radius of HfC can be calculated at a given temperature, time and initial size, and is given by

$$r(\mathrm{m}) = [1.3\times10^{-12}\,t/T \times \exp(-480\,000/RT) + r_0^3]^{1/3} \quad (7)$$

where $t$ is in seconds, $R$ is in J mol$^{-1}$ K$^{-1}$. In the alloy investigated, $r_0$ was found to be 20 nm and significant recrystallization occurred after annealing at 2673 K for 1 h. Using these values ($r_0 = 20$ nm, $T = 2673$ K, and $t = 3600$ s), the radius was calculated to be 89 nm. Experimental results from this study show that the recrystallization temperature for a 1 h anneal is below 2673 K (between 2623 and 2673 K). Therefore, the value of 89 nm is the upper limit of the radius to inhibit recrystallization. This result is in agreement with a critical radius value between 75 and 85 nm, estimated from Equation 6.

Because measurements of HfC particle coarsening possess a large degree of uncertainty, as illustrated in the scatter of the data shown in Fig. 9, the average of three independent studies (Klopp *et al.* [3], Chen [5], and this study) will provide better estimates of the growth rates of the HfC particles. Averaging of the three rates yields

$$r(\mathrm{m}) = [2.8\times10^{-13}\,t/T \times \exp(-470\,000/RT) + r_0^3]^{1/3} \quad (8)$$

The growth behaviour of the particles at any temperature can be estimated as a function of time. This is illustrated in Fig. 10 for three temperatures, 1700, 1800 and 1900 K. The horizontal line indicates the estimated critical radius of HfC, which is equal to 80 nm. According to this growth behaviour, significant degradation of the materials would occur after 35 years at 1700 K and after 5.5 years at 1800 K. This lifetime would be significantly reduced to a year at 1900 K.

To investigate the effect of particle coarsening on creep deformation, a creep equation for dispersion-strengthened alloys has been developed of the form [3, 6, 25–27]

$$\dot{\varepsilon} = C(\sigma - \sigma_p)^n \quad (9)$$

and

$$\sigma_p = \kappa G b / L \quad (10)$$

where $C$ is the creep constant containing the temperature dependence, $n$ is the stress exponent, $\kappa$ is a constant related to the effectiveness of the particles as strengthening agent, $G$ is the shear modulus, $\boldsymbol{b}$ is the Burgers vector, and $L$ is the inter-particle distance. The particle stress, $\sigma_p$, describes the stress interaction between dislocations and the finely dispersed particles [27]. The coarsening data of the HfC particles are used to predict the time evolution of $\sigma_p$ through the $L$ term which increases with coarsening. Utilizing this creep equation with the appropriate parameters shows in Table II, the creep deformation of W–0.4 mol % HfC with an applied uniaxial stress of 20 MPa was calculated at a temperature of 1800 K is shown in Fig. 11. Curve (a) in the figure corresponds to the creep strain with HfC particle coarsening and curve (b) represents the case without HfC particle coarsening. This result indicates the importance of coarsening in dispersion-strengthened alloys and coarsening degradation becomes more pronounced as the temperature increases.

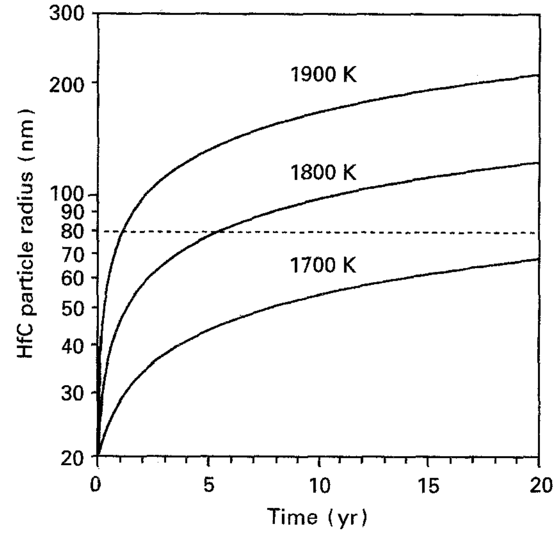

*Figure 10* Coarsening of HfC particle at 1700, 1800 and 1900 K.

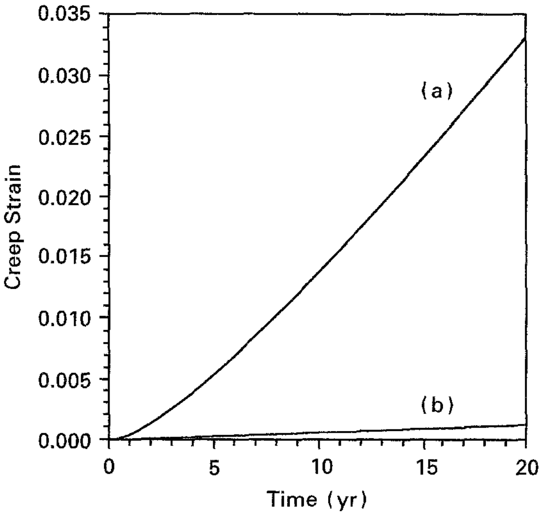

*Figure 11* Prediction of creep deformation in the W–HfC alloy at 1800 K (a) with HfC particle coarsening, and (b) without HfC particle coarsening.

TABLE II Parameters used for determining creep of W–0.4% HfC

| $T$(K) | $C$(MPa$^{-4}$s$^{-1}$) | $n$ | $\sigma_p$(MPa) at $t = 0$ | $L$ (μm) at $t = 0$ |
|---|---|---|---|---|
| 1800 | $7.0\times10^{-16}$ | 4 | 15 | 0.365 |

## 6. Conclusion

The activation energy for coarsening of hafnium carbide in tungsten was determined to be 480 kJ mol$^{-1}$. This value compares favourably with earlier results from Klopp but is significantly higher than that obtained by Chen. Lattice diffusion and grain-boundary diffusion energies of hafnium in tungsten and W–HfC were measured and found to be 335 and 170 kJ mol$^{-1}$, respectively. The diffusion process was found to be unaffected by the presence of HfC. The observed coarsening behaviour was compared with similar data in the literature and subsequently examined in light of the hafnium diffusion results obtained. It appears that the coarsening process is controlled by the diffusion of the hafnium atoms (the slower of the two species) as well as the effective solubility limit of hafnium in tungsten. The presence of carbon significantly reduces the solubility of hafnium and increases the heat of solution of hafnium to the level of the less soluble carbon. The observed coarsening energy (480 kJ mol$^{-1}$) is the sum of the diffusion energy of hafnium in W–HfC (335 kJ mol$^{-1}$) and the heat of solution (125 kJ mol$^{-1}$). The effects of the coarsening on recrystallization and creep deformation at elevated temperatures for dispersion-strengthened W–0.4 mol % HfC were also estimated.

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