Journal of the European Ceramic Society 22 (2002) 2571–2576
www.elsevier.com/locate/jeurceramsoc

Processing and mechanical properties of materials in the Hf–N system

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Received 7 October 2001; received in revised form 10 February 2002; accepted 28 February 2002

Abstract

Samples of hexagonal α-Hf containing up to 30 at.% N in solid solution were made by a solid-state reaction. The brittle-to-ductile transition temperature increased as the %N increased. Steady-state compressive deformation has been measured from 20 to 1000 °C. The data for pure Hf could be fit using a threshold stress with a stress exponent of 5. The stress exponent of the Hf–N solid solution materials was between 5 and 8. The experiments could be interpreted on the basis of dislocation-controlled plasticity, with N acting as classical solid-solution hardening solutes. Transmission electron microscopy supported this interpretation. Published by Elsevier Science Ltd.

Keywords: Brittle–to–ductile transition (temperature); Dislication–based plasticity; Hf–N alloys; Hf–N solid solutions; Solid–solution hardening; Stress exponent; Threshold stress

1. Introduction

Currently, structural materials for use in high-temperature oxidizing environments are mostly limited to SiC, Si_3N_4, or oxide ceramics. However, these monolithic materials exhibit brittle behavior, which could cause failure in thermal cycling or rapid heating environments. Fiber- or whisker-reinforced composites based on these materials have been developed for applications involving temperatures below 1600°C. However, the low thermal conductivity of oxide matrices, and the oxidation behavior of the silicon-based nonoxide materials preclude their use. The development of structural materials for use in oxidizing and rapid heating environments at much higher temperatures is of great engineering importance. Additionally, the development of low-cost materials that can be fabricated into complex shapes by standard commercial processing techniques would also be of high value for many high-temperature applications, including thermal management, cutting tools, turbine engines, and rocket motors. Hafnium-based refractory materials may offer the possibility of an alternative material for high-temperature structural applications.

For structural design purposes, the thermomechanical properties of candidate materials must be fully characterized because a major concern for design is thermal cycling that can result in the thermal-stress failures. Knowledge of the ductile-to-brittle-transition temperature is necessary for thermostructural analysis and advanced design. Some plasticity is desirable.

Research has suggested that the addition of small atoms, such as nitrogen, into the interstitial sites of hafnium metal can increase the melting temperature[1] of the single-phase material (according to the Hf–N equilibrium diagram shown in Fig. 1), as well as increase hardness.[2] The Hf–C system has a more limited solubility range, and a less dramatic effect on melting temperature. Boron and oxygen also have limited solubility,[3–5] but the increase in melting temperature of α-Hf is not observed in those systems. Therefore, the Hf–N system was chosen for this study.

Uniaxial compression of polycrystalline Hf has been investigated at room temperature over a strain-rate range of 10^{-5}–$3.2\ s^{-1}$ by Subhash et al.[6] They combined stress–strain data with microstructural evidence that indicated yielding occurred by dislocation activity and that hardening was dominated by twinning. Ruano and

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0955-2219/02/$ - see front matter Published by Elsevier Science Ltd.
PII: S0955-2219(02)00118-8

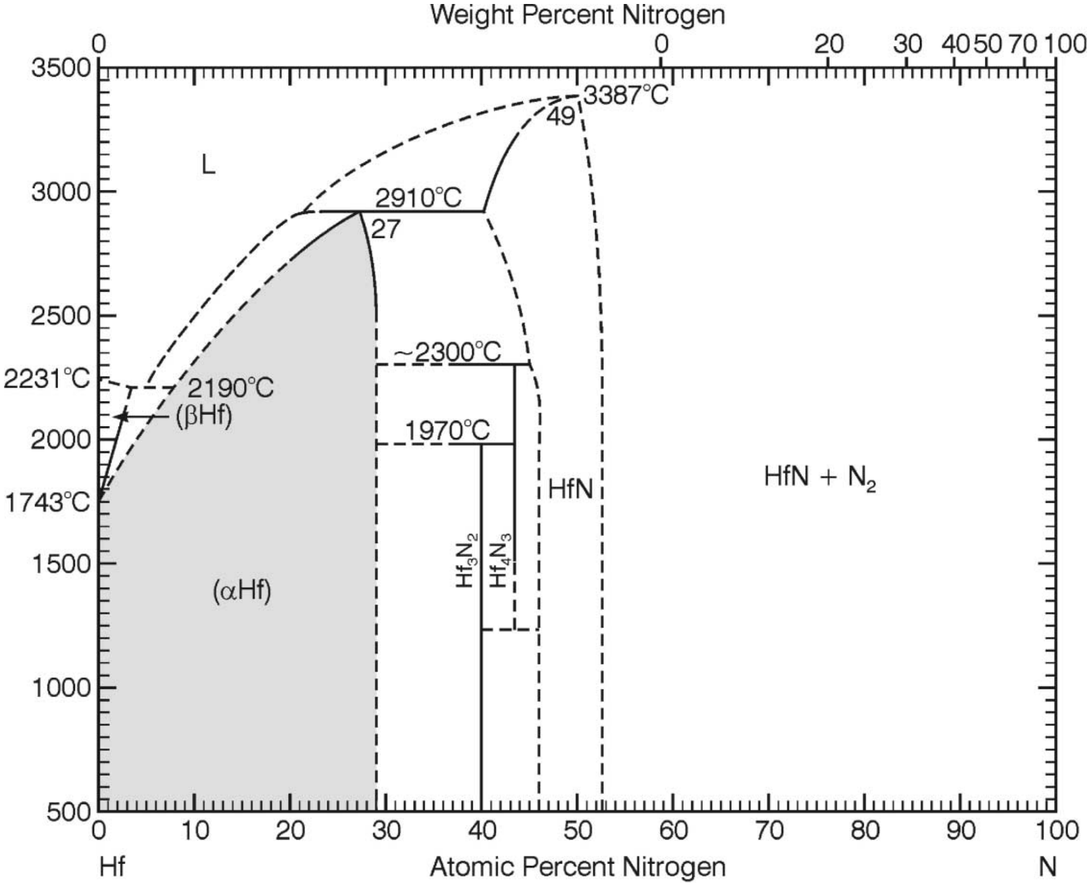

Fig. 1. The Hf–N phase diagram with αHf(N) region shaded.

Elssner[3] studied the behavior of bamboo-structured Hf–O and Hf–N for small concentrations (⩽1.2 at.%) between 77 and 500 K. They concluded that the flow stress is composed of two components, one the result of an interaction between dislocations and single solute atoms, and the other the result of a dislocation interaction with solute clusters. Oxidation studies previously performed on these materials in furnace and arc-jet facilities indicated that these materials exhibit good oxidation performance, i.e. they form a stable, adherent oxide scale and do not catastrophically oxidize.[7] This paper describes the processing, compression response, and characterization of single-phase materials in the alpha-hafnium region of the Hf–N phase equilibrium diagram (Fig. 1).

2. Experimental

Hafnium and Hf–N powders were blended into batches correlating to 2, 5, 10, 20, and 30 atomic percent N. The materials were densified by hot pressing at 1200–1900 °C and by isothermal heat treatments of powder compacts at temperatures of 1300–2300 °C in vacuum and under 1 atmosphere of helium.

Samples were machined, ground, and polished to 5×5×12 mm size for compressive testing. Tests were carried out at constant crosshead speeds in an Instron Model 1125 universal tester fitted with a furnace and a muffle tube for controlled atmosphere.[8] The temperature range for these experiments was from room temperature to 1000 °C, and the strain rates were 10^{-6}–10^{-3} s^{-1}. Room-temperature tests were conducted in air; the higher-temperature tests were conducted in static argon for the pure Hf samples and in static N_2 for the Hf–N samples.

To observe the microstructure after deformation testing, the samples were examined in a transmission electron microscope (TEM). TEM samples were prepared by using a diamond saw to cut a thin slice from the deformed sample at an angle of approximately 45° to the stress axis. The 3-mm disks were cut from the slice with a core drill, flat-polished to a thickness of ≈150 μm, and then dimple-polished to ≈15 μm thick. Finally, the specimens were ion-milled until perforation. TEM was performed in a Philips CM30 microscope in the

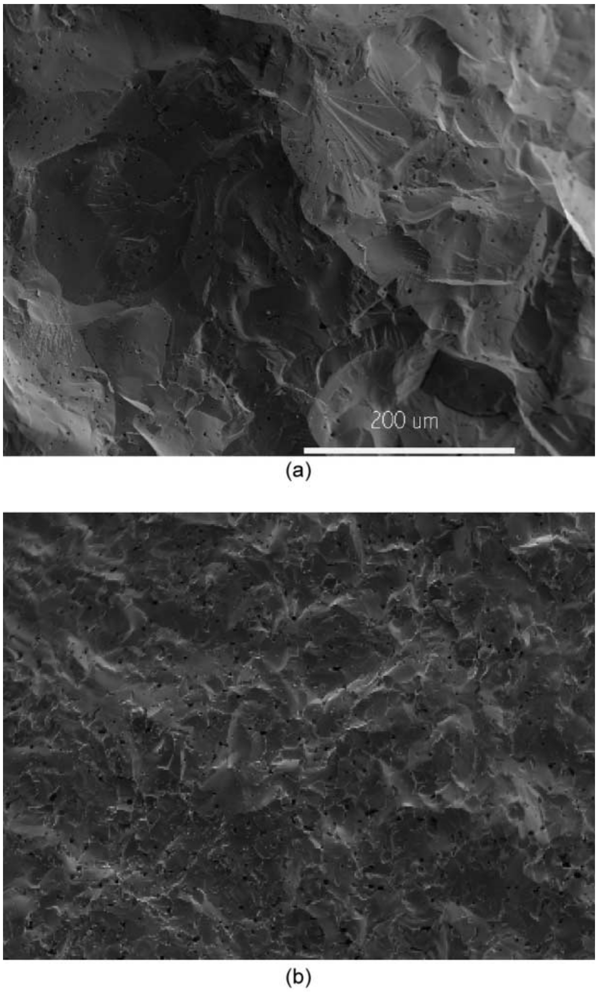

Fig. 2. SEM micrographs of Hf–5N (a) hot pressed and (b) sintered at 1500 °C. Bar = 200 μm.

Electron Microscopy Collaborative Research Center at Argonne National Laboratory.

3. Results and discussion

Sintering studies showed that compositions containing less than 10% N could be fully densified at temperatures below 1500°C in a carbon-free environment under 1 atm. of helium. Hot pressing these materials in graphite dies and a carbon-element furnace was found to induce rapid grain growth and carbon contamination, both of which contributed to producing low-strength, brittle materials. Microstructural examination also revealed a finer grain structure than in the hot-pressed materials (10 vs. 150 μm), as shown in Fig. 2. All materials tested and described in this paper were produced by pressureless sintering techniques.

3.1. Mechanical properties

The brittle-to-ductile transition (BDT) temperature for each composition was determined at a strain rate of 10^{-4} s^{-1}. BDT values as a function of N content are shown in Fig. 3. The transition temperature was a strong function of N concentration, increasing with N content. The Hf–2N composition deformed plastically above ≈400 °C, whereas the Hf–30N composition deformed plastically only above ≈1200 °C.

The results of stress–strain (elastic plus plastic) measurements at room temperature at a constant strain rate of 10^{-4} s^{-1} on various Hf–N solid solutions are shown in Fig. 4. The data indicated that fracture stress increased from ≈800 MPa for pure Hf to 1250 MPa for Hf–5N but decreased to ≈500 MPa for Hf–10N. Therefore, at this strain rate at room temperature, the fracture stress exhibits a maximum at intermediate N concentration. The results on the unalloyed Hf were compared to those reported by Subhash et al.[6] They reported a room-temperature yield stress of ≈800 MPa at a similar strain rate. Although their yield stress was comparable to our measured fracture stress, their material exhibited considerably more room-temperature ductility than did ours.

The strain rate vs. stress-data for the unalloyed Hf are shown in Fig. 5. The data could be fit to a phenomenological equation :

$$\dot{\varepsilon} = A(T)\sigma^{n}, \tag{1}$$

where $A(T)$ is a temperature-dependent constant and n is the stress exponent. The stress exponent is a sensitive function of temperature, decreasing as the temperature increases (Table 1). This may be the result of a temperature-dependent activation volume[3] or a temperature-dependent threshold stress, σ_o. The concept of a threshold stress, while unusual for a pure metal, appeared to yield a consistent description of the creep results, as shown in a linear plot of $\dot{\varepsilon}$ vs. σ (Fig. 6). The fits to a straight line exhibited excellent correlation factors of between 0.984 and 0.998. The intercepts define σ_o, the values of which were a strong function of temperature. Fit of the data to $\dot{\varepsilon} = (\sigma - \sigma_o)^n$, yielded an average stress exponent, n, of 5.

Table 1
Stress exponent values for Hf–N compositions

at.%N	n (1000°C)	n (8500°C)	n (750°C)	n (600°C)
2	Not tested	Not tested	6.5	Not tested
5	4.9	5.9	Not tested	8.2
10	Not tested	Not tested	15[a]	Broken
20	6.0	Broken	Broken	Broken

[a] Based on two experiments.

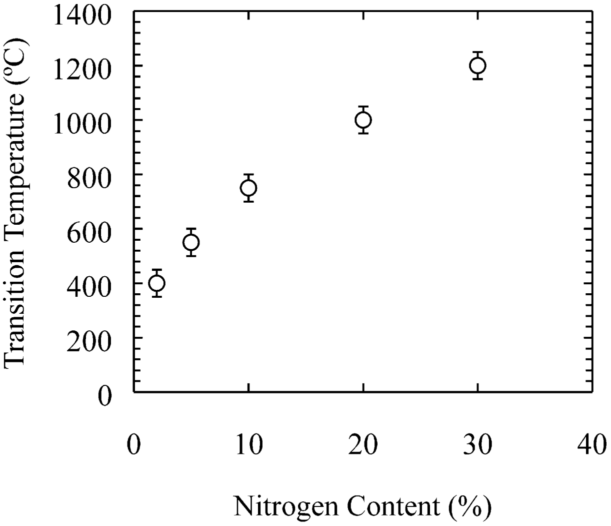

Fig. 3. Brittle-ductile transition temperature for Hf samples with different nitrogen content.

Stress-vs-strain data for Hf–5N at $\dot{\varepsilon} = 10^{-4}$ s^{-1} are shown in Fig. 7. This composition was brittle at $T \leqslant 400$ °C, but deformed into a steady state (as indicated by the zero work-hardening rate) for higher temperatures. Steady-state deformation was achieved above the BDT temperature for the Hf–2N, Hf–5N, and Hf–10N. Strain-rate-change experiments were performed, and the stress exponents derived from the experiments were between ≈5 and 8 for all compositions in the temperature range where the materials exhibited sufficient plasticity. It appears that the stress exponent for the solid solution could be slightly dependent on temperature, as the *n*-values tended to be higher at the lower temperatures. The limited ductility of some of the compositions precluded more detailed experiments.

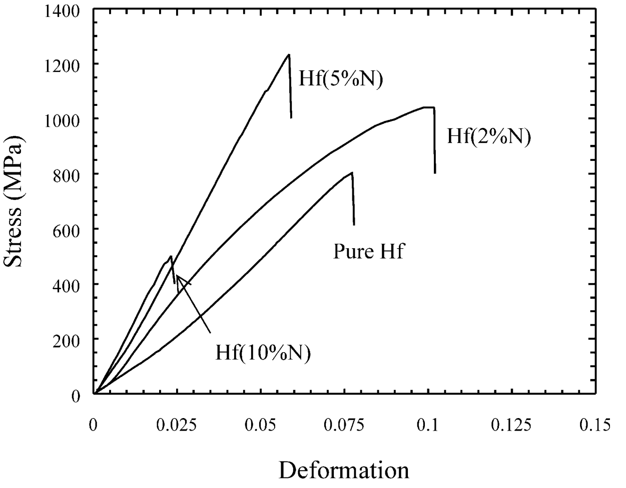

Fig. 4. Fracture stress for Hf–N materials deformed at $\dot{\varepsilon} = 10^{-4}$ s^{-1} at room temperature.

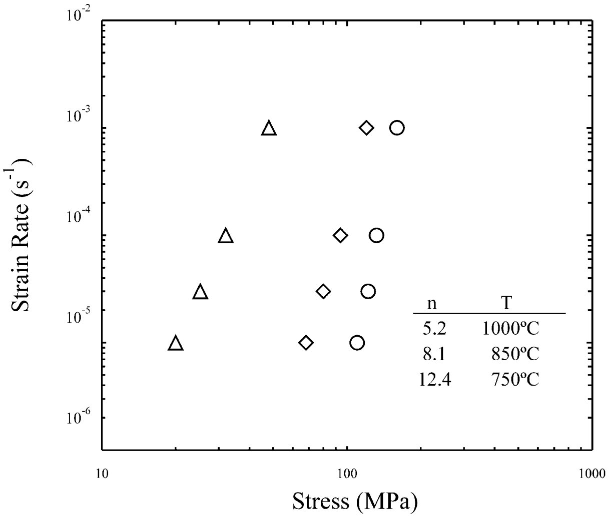

Fig. 5. Stress vs. strain rate at various temperatures for pure Hf: (△) 1000 °C, (◇) 850 °C, (○) 750 °C.

Fig. 8 presents limited data on the yield stress (defined as the intercept between the stress-vs.-strain curve at $\epsilon = 0.002$) as a function of concentration, C = (% N). The data were obtained at 850 °C, with $\dot{\varepsilon} = 10^{-4}$ s^{-1}. The fit to a $C^{1/2}$ was reasonable.

3.2. TEM analysis

A TEM micrograph from a representative area of the Hf–5N alloy deformed to $\varepsilon \approx 0.045$ at 850 °C is shown in Fig. 9. It can be seen that the deformation produced dislocations. No dislocations were seen in TEM analysis of undeformed samples.

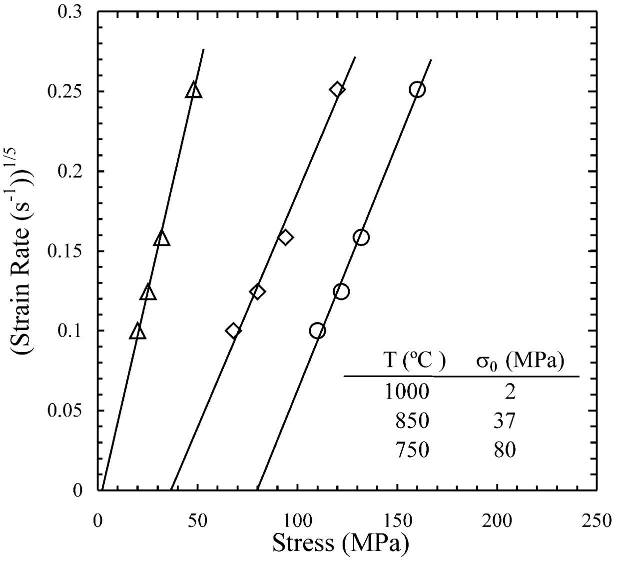

Fig. 6. Threshold stress vs strain rate corrected with $1/n$ at various temperatures for pure Hf: (△) 1000 °C, (◇) 850 °C, (○) 750 °C.

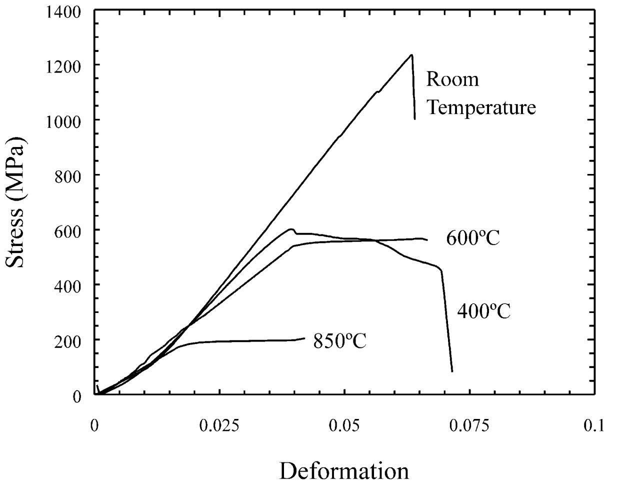

Fig. 7. Stress vs deformation for Hf–5N deformed at $\dot{\varepsilon} = 10^{-4}$ s^{-1} at different temperatures.

3.3. Discussion

The goal of our alloy-development program has been to identify and fabricate strong high-temperature materials. The Hf and Hf–N alloys tested exhibited mechanical responses that were typical of hardened metals.

As shown in Fig. 3, the DBT temperature of the Hf–N alloys increased with increasing N concentration. Pinning of dislocation glide by N solutes is the obvious explanation that has been used by Ruano and Elssner.[3] TEM observation confirmed significant dislocation activity in the plastically deformed samples, consistent with this explanation.

Although the DBT temperature data followed an expected trend, the room-temperature fracture stress exhibited two surprises. First, the strongest alloy was the Hf–5N. Increases in N concentration to 10% decreased the fracture strength (Fig. 4). Second, for a standard strain rate of 10^{-4} s^{-1}, it was expected that pure Hf would be fully ductile, as was found by Subhash et al.[6] Instead, it exhibited only limited plastic deformation before fracture.

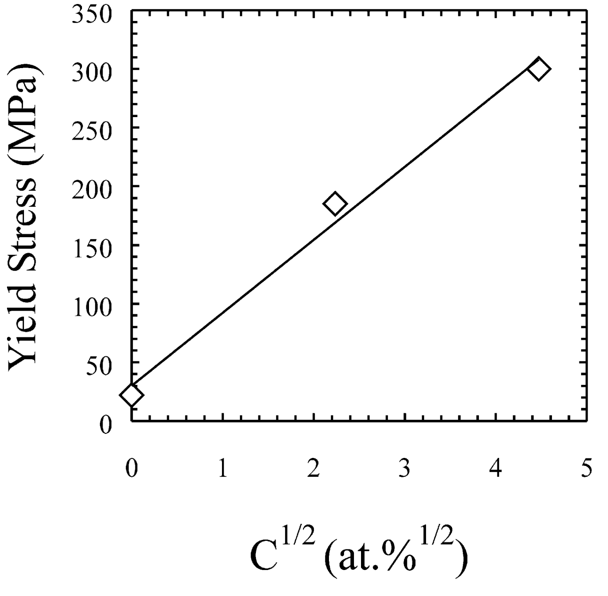

Fig. 8. Yield stress as a function of (at.%N)$^{1/2}$ measured at 850 °C using a strain rate of 10^{-4} s^{-1}.

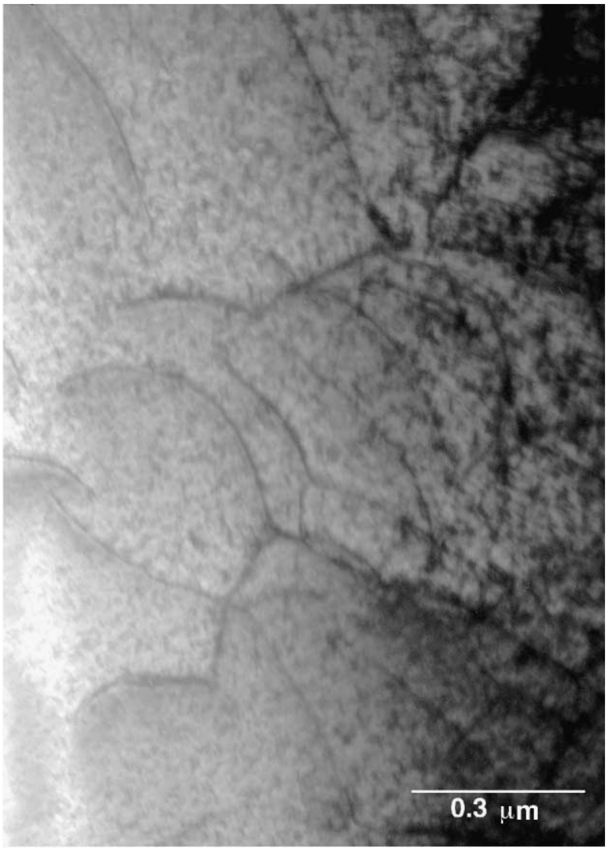

Fig. 9. TEM micrograph of Hf–5N alloy deformed at 850 °C.

Fracture will occur when the fracture stress is lower than the flow stress. Solute atoms and clusters affect the flow stress[3] and could also affect the surface energy by segregating to grain boundaries. This may modify the fracture energy. Therefore, it is possible that the maximum in room-temperature fracture stress observed for the Hf–5N alloys is a fortuitous result of a combination of the two effects. More experiments are clearly needed.

It is believed that dislocation–solute interactions were responsible for flow and fracture in the pure Hf as well. The specimens in this study were prepared from powders. Residual O was doubtless present because the samples were not processed under reducing conditions due to the potential formation of HfH_2. As discussed previously, this residual O would reside at interstitial sites, becoming additional obstacles to dislocation motion.[3] The effect on mechanical properties would be reduced ductility and, in the absence of fracture, an increased flow stress. It is also possible that the microstructures of the ductile Hf were different than the microstructures used here. Our samples were prepared by powder metallurgy, whereas the Hf used by Ruano and Ellsner[3] contained large bamboo grains.

The apparent existence of a temperature-dependent threshold stress for plastic deformation of Hf is also consistent with effects of solutes. In addition to providing thermal energy for overcoming obstacles to dislocation motion, higher temperatures imply increased diffusion and less stable solute atmospheres around dislocations.[9] One of the consequences of dislocation-impurity interactions can be an increase in the apparent steady-state stress exponent.[10] The average n value for the Hf was ≈ 5 and that of the Hf–N alloys was nearly 7. These values are larger than classical theories would predict,[11,12] but, again, are consistent with effects of solutes.

The fact that yield stress in the Hf–N alloys correlated well with a $C^{1/2}$ fit strongly supports an interpretation of effects of solid-solution hardening.[9] This fit was surprisingly good given that its underlying model is based on dilute solid solutions. We can only speculate that the dependence is the result of the cluster concentration rather than the concentration of the single N solute interstitials. The dislocation activity revealed by the TEM observations supported the conclusions of plastic deformation via dislocation motion.

Future plans include continuation of studies of strength/ductility responses in the Hf–N system. We intend to focus next on the HfN phase field. As the bonding and crystal structure are very different from those of the α-Hf(N) phase, it is expected that the properties and deformation mechanisms will be vastly different. More detailed TEM will be required to determine deformation kinetics and dislocation–solute interactions.

4. Conclusions

Hexagonal α-Hf containing up to 30 at.% N have been prepared, and compression tests were performed to characterize the strength and ductility of the materials. The fracture stress measured at room temperature has a maximum value for 5% N. The brittle-to-ductile transition temperature increases with increasing N content. Stress exponents measured from steady-state compressive deformation up to 1000 °C are between 5 and 8, and indicate a dependence on temperature. Transmission electron micrographs reveal the presence of dislocations in the deformed Hf–N materials. All experimental results can be interpreted on the basis of dislocation-controlled plasticity with the N (and N clusters) acting as classical solid-solution hardening solutes. This material shows promise for high- temperature structural applications in oxidizing atmospheres.

Acknowledgements

The processing of Hf–N materials was performed at the Naval Surface Warfare Center under the sponsorship of the Office of Naval Research. The work performed at Argonne National Laboratory was sponsored by the US Department of Energy, under Contract W-31–109-Eng-38. The authors are grateful to S. Fishman of ONR and D. Haught and S. Waslo of the US Department of Energy for providing funding for this program.

References

1. Okamoto, H., The Hf–N (Hafnium-nitrogen) system. *Bull. Alloy Phase Diagrams*, 1990, **11**(2), 146–149.
2. Johansson, B., Sundgren, J. and Helmerson, U., Reactively magnetron sputtered Hf–N films. II. Hardness and electrical resistivity. *J. Appl. Phys*., 1985, **58**(8), 3112–3117.
3. Ruano, O. and Elssner, G., On solid solution hardening in Hf–O and Hf–N alloys. *J. Less Common Metals*, 1977, **52**, 153–162.
4. Rudy, E., Windisch, S., Part I. Related binary systems. Volume IX. Hf–B System, *Ternary Phase Equilibria in Transition Metal–Boron–Carbon–Silicon Systems*, 1966, Tech Rep. AFML-TR-65–2, pp. 1–42.
5. Kubaschewski-von Goldbeck, O., *Phase Diagrams, Hafnium: Physio-chemical Properties of its Compounds and Alloys*. International Atomic Energy Agency, Vienna, 1981.
6. Subhash, G., Ravichandran, G. and Pletka, B. J., Plastic deformation of hafnium under uniaxial compression. *Metall. Mater. Trans*., 1997, **A28A**, 1479.
7. Wuchina, E., Opeka, M., unpublished results, 1997.
8. Routbort, J. L., Work hardening and creep of MgO. *Acta Metall*., 1982, **30**, 663.
9. Hirth, J. P. and Lothe, J., *Theory of Dislocations*. McGraw-Hill, New York, 1968.
10. Goretta, K. C., Routbort, J. L., Kallend, J. S. and Bloom, T. A., Effect of cation impurities on stress exponents of binary oxides. *J. Mater. Sci. Lett*., 1986, **5**, 391.
11. Frost, H. J. and Ashby, M. F., *Deformation-mechanism Maps*. Pergamon Press, Oxford, 1982.
12. Garofalo, F., *Fundamentals of Creep and Creep-rupture in Metals*. McMillan Co, New York, 1965.