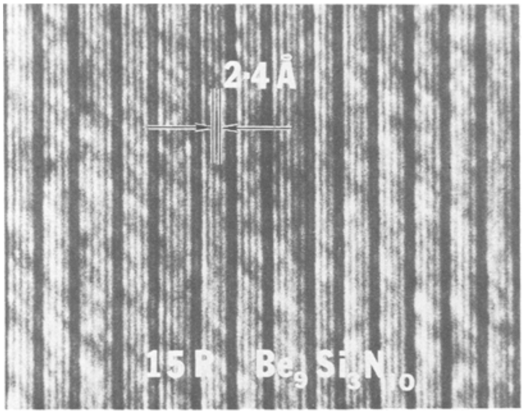

Figure 4 An adjacent region to that of Fig. 3. Departures form the ideal polytype arrangement are seen directly with some blocks comprising only four close-packed planes and others.

the unit cell consists of three symmetry related blocks of five close-packed layers. Similar results have been found in the Mg–Si–Al–O–N System where the metal: non-metal atom ratios are $M_m X_{m+1}$.

Observing the close-packed planes also allows departures from the ideal polytype arrangement to be examined directly. An example of this is shown in Fig. 4. Here, although the electron diffraction pattern again indicates an overall 15R structure there are faults in the block structure and instead of comprising five planes some of the blocks have six and others only four. By incorporating such faults the local composition varies from the exact $Be_9Si_3N_{10}$ composition. Very large variations in composition may occur in this manner, and a later publication will present detailed evidence for the resulting structures.

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References

1. D. P. THOMPSON, *J. Mater. Sci.* 11 (1976) 1377.
2. K. H. JACK, *ibid* 11 (1976) 1135.
3. K. H. JACK, private communication (1976).

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The estimation of the diffusion coefficient of oxygen in Cr_2O_3 from creep measurements

Chromium oxide plays an important role in the oxidation resistance of many steels. It is rapidly formed on the surface of the steel during service and provides a barrier to further oxidation between the metal and oxidant. The efficiency of this barrier depends on a number of factors such as the degree of adhesion between the oxide and the metal, the mechanical properties of the oxide and the diffusion coefficients of chromium and oxygen in the oxide. No creep data are available for chromium oxide and the present investigation was undertaken to provide such information. Additionally, it was intended to investigate creep in the region where creep is controlled by the stress-directed diffusion of vacancies (Nabarro–Herring creep) such that estimates of diffusion coefficients could be made from creep rates. NH creep depends on the migration of vacancies from grain boundaries stressed in tension to those under compression. The rate of creep $\dot{\epsilon}$, originally predicted by Nabarro [1] and Herring [2] is given by the expression

$$\dot{\epsilon} = B\sigma\Omega D/d^2kT, \qquad (1)$$

σ is the applied stress, Ω the atomic volume, d the grain size, D the effective diffusion coefficient for creep, k is Boltzmann's constant and T the temperature. B is a constant which depends on grain geometry and for equi-axed structures is close to 12. Thus since there are no disposable parameters in the equation, it permits estimates of the diffusion coefficient to be made from creep rate measurements with a reasonable degree of confidence.

This technique of estimating diffusivities indirectly from creep results is particularly useful in the case of many ceramic materials since the range of predominance of NH creep is often very extensive compared to, say, metallic systems. This is because dislocation movement is often difficult in ceramics, due to their higher shear moduli and for crystallographic reasons. Consequently, creep controlled by dislocation processes becomes correspondingly less important, thus extending the range of predominance of NH creep.

The starting material was chromium oxide of purity better than 99% in the form of submicron-sized powder. Specimens were prepared by vacuum hot-pressing the powder in a molybdenum die. The die consisted of a hollow cylinder of length 40 mm, diameter 25 mm and 10 mm bore. Molybdenum rams were used at a pressure of 16 MN m^{-2} and this produced material in excess of 96% of the theoretical density in about 2×10^3 sec at 1900 K. The rams were removed and cylindrical specimens were then drilled out of the sintered slug using a diamond-tipped hollow drill. The microstructure of a hot-pressed specimen is shown in Fig. 1. Note the absence of porosity. The material was then finally machined into cylindrical compression specimens having length 12 mm with a 4 : 1 aspect ratio.

Compression creep tests were performed, with the specimen held between two molybdenum plattens under a constant load transmitted by alumina push rods. Strain was measured using a transducer, set to gauge the distance between the loading platens via a series of alumina push rods. In this way any creep of the push rods could not contribute to the measured strain. All tests were performed in argon.

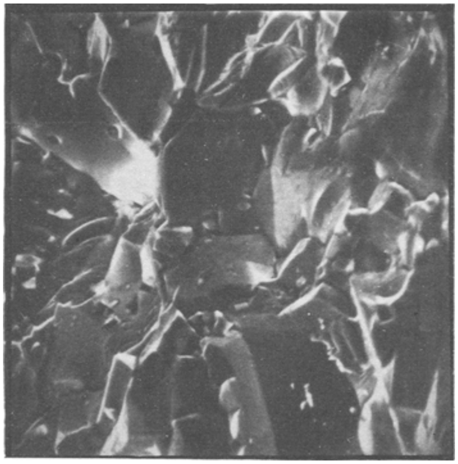

Figure 1 Scanning electron micrograph of fracture surface. (Grain size = 5 μm).

The variation of steady-state creep rate with stress is shown in Fig. 2 for three different test temperatures. Two regions are noted; the high stress region where creep rate varies strongly with stress, and the region at lower stresses where creep rate varies in a linear manner with stress. These regions are characteristic of dislocation and NH creep respectively. Note that the transition stress between the two mechanisms, ~40 MN m^{-2}, is considered higher than the corresponding value for metallic systems (typically ~1 MN m^{-2}). The effective diffusion coefficient for creep, $D_{\text{creep}} = \dot{\epsilon}_{\text{m}} d^2 kT/B\sigma\Omega$, can be calculated from values of the creep rate measured in the region linear in stress. These are plotted in Fig. 3 for various values of reciprocal temperature. Also plotted are the values obtained from radio-tracer experiments for both chromium [3] and oxygen diffusion [4]. Clearly, the effective diffusion coefficient for creep is in excellent agreement with the oxygen ion diffusion coefficient. This agreement indicates the expected feature that creep is controlled by the slower moving species and also confirms Hagel's value [4] for the oxygen diffusion coefficient given by,

$$D_{\text{oxygen}} = 1.59 \times 10^{-3} \exp(-4.19 \times 10^5/\text{RT})\,\text{m}^2\,\text{sec}^{-1} \qquad (2)$$

In the temperature range 1350 to 1675 K, fine-grained chromium oxide creeps by power law

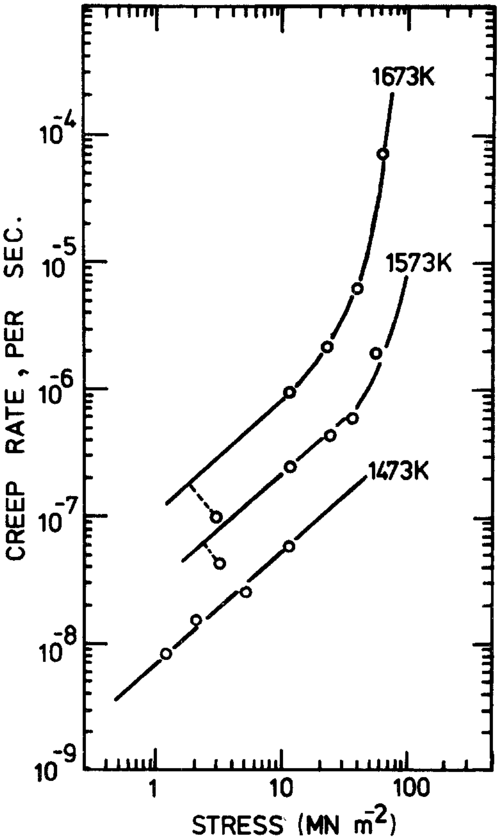

Figure 2 The variation of creep rate of Cr_2O_3 with stress for various temperatures.

creep at stresses in excess of 40 MN m^{-2} and by Nabarro–Herring creep at lower stresses. In this latter region, creep is controlled by diffusion of the slower moving species, in this case oxygen ions. The effective diffusion coefficient for creep is in excellent agreement with reported radio-tracer data and thus provides an independent check on the value for oxygen ion diffusion in chromium oxide.

Acknowledgements

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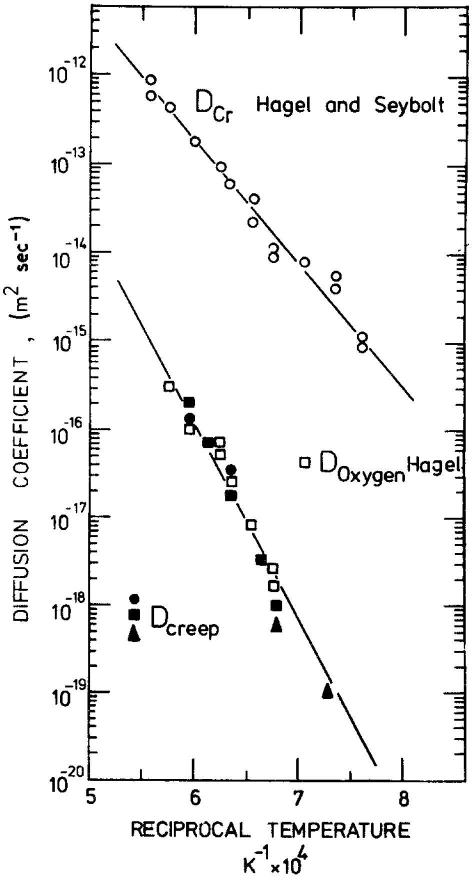

Figure 3 Comparison of the effective diffusion coefficient for creep of Cr_2O_3 with the tracer diffusivities of chromium and oxygen.

References

1. F. R. N. NABARRO, "Strength of Solids" (The Physical Society, London, 1948) p.75.
2. C. HERRING, *J. Appl. Phys.* **21** (1950) 437.
3. W. C. HAGEL and A. U. SEYBOLT, *J. Electrochem. Soc.* **108** (1961) 1146.
4. W. C. HAGEL, *J. Amer. Ceram. Soc.* **48** (1965) 70.

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