$6.6\,\mathrm{MPa\,m}^{1/2}$. However, the fact that the stress intensity factor is not constant along these boundaries may indicate that the reflecting spot regions are not analogous to the mirrors observed in glass fracture surfaces which are bounded by crack branching.

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The Vickers micro-hardness of non-stoichiometric niobium carbide and vanadium carbide single crystals up to 1500° C

This communication describes the micro-hardness of VC and NbC single crystals up to 1500° C and the temperature dependency of the relaxation behaviour of indentation. These results are compared with a previous study of TiC single crystals [1]. There has been some controversy [1–8] as to whether the activation energy for high-temperature deformation in transition metal monocarbides is coincident with that for the lattice diffusion of carbon, which is also clarified by the present study.

Single crystals were prepared by an *r.f.* floating zone process, in an Ar atmosphere of 3 atm, as for TiC [9, 10]. The composition of these crystals corresponds to $\mathrm{VC}_{0.88}$ and $\mathrm{NbC}_{0.80}$ determined by chemical analysis. The single crystals have high dislocation densities (10^6 to $10^7\,\mathrm{cm}^{-2}$), which cause the generation of subgrain boundaries. The crushed samples of $\mathrm{NbC}_{0.80}$ crystals contain a little precipitated $\mathrm{Nb_2C}$ confirmed by X-ray powder diffraction methods. The electrical resistivities of $\mathrm{VC}_{0.88}$ and $\mathrm{NbC}_{0.80}$ are 69 and $135\,\mu\Omega\,\mathrm{cm}$, respectively. The arrangement of vacancies in $\mathrm{VC}_{0.88}$ corresponds to an ordered state judging from the behaviour of the electrical resistivity of VC_x at various vacancy concentrations, including its arrangement studied by Williams [11].

The single crystals of VC are large enough to enable the hardness on three planes to be measured, while NbC is limited to only the (1 0 0) plane because of difficulty in preparing crystals as long as VC. The experiment at room temperature was carried out using a Vickers micro-hardness tester, Akashi Seisakusho Ltd. High-temperature indentation was performed using a Nikon high-temperature micro-hardness tester Model QM [1].

Fig. 1 shows the anisotropy hardness of VC and NbC single crystals at room temperature. The hardness anisotropy is less pronounced than in TiC [1], which would be due firstly to the non-stoichiometry of the crystals and secondly to the possibility of formation of ordering of vacancies [12, 13]. The anisotropy in the (1 0 0) planes

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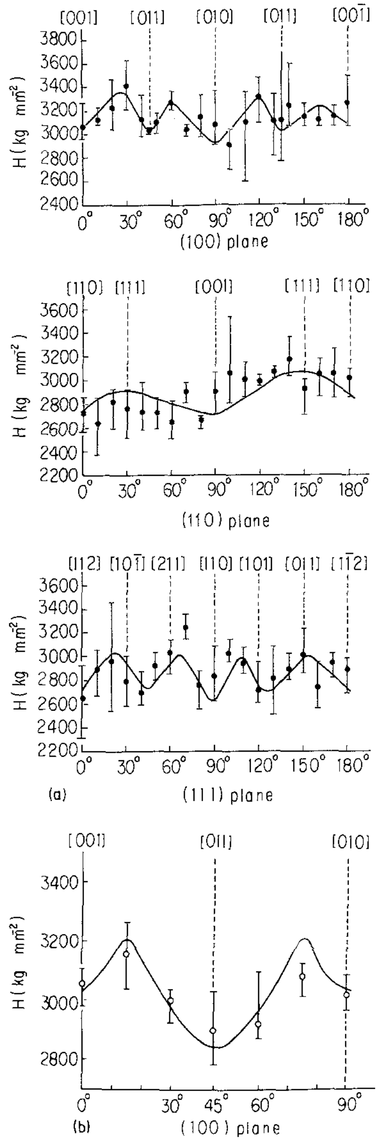

Figure 1 Periodicity of the hardness curves. (a) $VC_{0.88}$ (b) $NbC_{0.80}$.

indicates that the slip systems are co-existent [12, 13] with $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ and $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$. The former is predominant in NbC [13] while in TiC the $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$ system is found [1]. The anisotropy factors, $2C_{44}/(C_{11}-C_{12})$, of TiC, VC and NbC single crystals obtained by measurement of the elastic constants [14] exceed unity, indicating that the resistance to shear deformation in the [0 1 0] direction on the (1 0 0) plane is larger than that in the [1 $\bar{1}$ 0] direction on the (1 1 0) plane. This is explained qualitatively by the fact that the hardness is proportional to yield stress and the hardness of TiC [1] and VC (Fig. 1) in the (1 0 0) plane in the $\langle 0\,0\,1\rangle$ direction is larger than that in the $\{1\,1\,0\}$ plane in the $\langle 1\,1\,0\rangle$ direction.

Cracks observed at each corner at room temperature diminish at 800 and 1100° C in $VC_{0.88}$ and $NbC_{0.80}$, respectively, causing slip traces of the $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ system as in TiC [1, 15]. This is explained in terms of the dislocation mobility corresponding to the kneeck in a logarithmic plot of hardness versus homologous temperature T/T_m represented in Fig. 2. In the case of $VC_{0.88}$, additional kneeck caused by the order–disorder transition of vacancies exists as is confirmed by Kohlstedt [7] for $VC_{0.83}$.

The creep test was performed by varying the loading time under a given load at constant temperature in the plastic region. The indentation

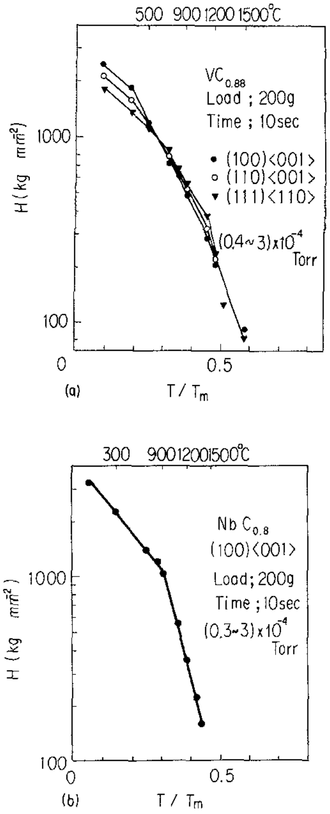

Figure 2 A logarithmic plot of hardness versus homologous temperature.

TABLE I Values of constant m and activation energy Q

	m	Q (kcal mol^{-1})	
		Present results	From diffusion data
TiC (1 0 0)[0 0 1]	3.85	80.4	91.3 [17] – 95.3 [18]
(1 1 0)[0 0 1]	4.05	81.2	
(1 1 1)[1 1 0]	3.73	77.0	
VC (1 0 0)[0 0 1]	4.27	85.6	85.0 ± 0.5 [19]
(1 1 0)[0 0 1]	4.07	83.2	
(1 1 1)[1 1 0]	3.79	79.8	
NbC (1 0 0)[0 0 1]	3.91	90.4	88.2 [20]

hardness decreases with increase in loading time. A series of straight lines were obtained as shown in Fig. 3. The activation energy, Q, for creep and the constant, m, expressed by the following equations are calculated (Table I).

$$B/t = H^m \exp(-Q/RT) \qquad [16]$$
$$H = A \exp(-BT)$$

where A and B are constants, R is the gas constant, t is the loading time, and T is temperature. The constant m is 4 to 5, and the activation energy is close to that obtained for self-diffusion of carbon in carbide [17–20]. Therefore, a common slip mechanism governed by carbon diffusion and dislocation climb can be presumed.

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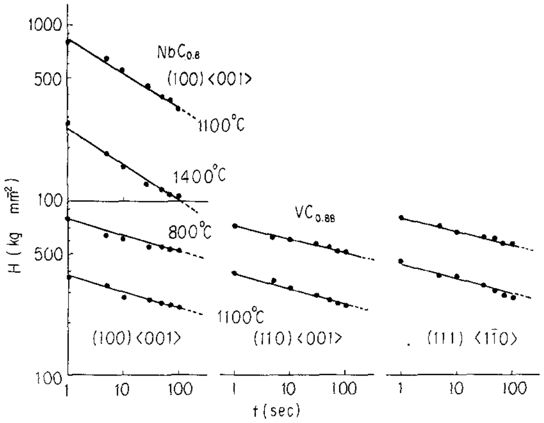

Figure 3 Relation between indentation stress and loading.

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Comments on "The chemistry of dicalcium silicate mineral"

I read with great interest the review article on C_2S* [1], and I wish to raise a few points.

We studied the polymorphic transformation scheme of pure γ-C_2S (stoichiometric value of Ca : Si = 2.85) using a Guinier–Lenné high-temperature X-ray camera [2]. From our observations we presented a revised stability diagram of C_2S polymorphic forms. The transformation scheme in Fig. 1 is somewhat different to those suggested by Niesel [3] and Midgley [4].

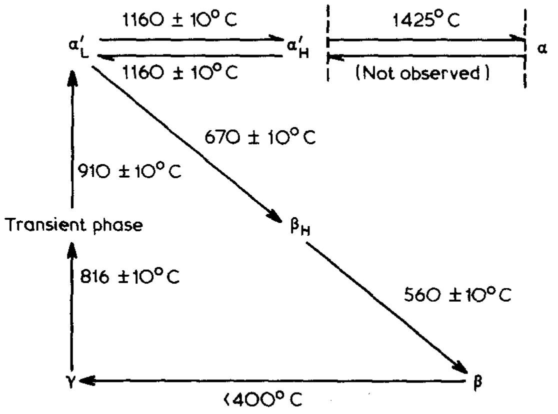

Figure 1 Stability diagram of C_2S polymorphs.

From our investigations it was found that, on heating, γ-C_2S transforms to an orthorhombic phase (named the "transient phase") at 816° C. At 910° C, α'_L-C_2S appears. A slow rate of heating ($40^\circ\,C\,h^{-1}$) yields α'_H-C_2S at 1165° C, whereas with rapid heating ($100^\circ\,C\,h^{-1}$) α'_H-C_2S fails to appear even at 1250° C (the limit of the apparatus). During cooling, α'_H-C_2S inverts to α'_L-C_2S at 1165° C and then to the β_H phase at 670° C. With further cooling β-C_2S appears at 560° C and finally, at ambient temperatures, a mixture of β- and γ-C_2S is obtained. Samples air-quenched from 1250° C also produce a mixture of β- and γ-phases at room temperatures. The crystallite particle size is seen to affect the transformation temperatures by only 10° C [3]. No evidence of superstructuring between the α'_H- and α'_L-C_2S was found [5]. The cell parameters of all these forms have been calculated from the X-ray powder patterns using a set of standard computer programs (COMPUTE, DECAL and modified CELL) (Table I). Our β_H-phase is seen to resemble Midgley's α'_m-C_2S [4].

TABLE I Lattice parameters of C_2S polymorphs

Form	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Crystal system	Space group
γ-C_2S	5.086	11.213	6.773	–	Ortho	P*bnm*
β-C_2S	5.427 ± 0.004	6.629 ± 0.004	9.148 ± 0.006	94.57	Mono	$P2_1/n$
β_H-C_2S	5.364 ± 0.009	6.709 ± 0.012	9.299 ± 0.016	91.51	Mono	$P2_1$
Trans. phase	10.978 ± 0.015	18.567 ± 0.026	6.740 ± 0.010	–	Ortho	$Cmc2_1$
α'_L-C_2S	11.020 ± 0.030	18.696 ± 0.050	6.758 ± 0.020	–	Ortho	P*mcn*
α'_H-C_2S	10.734 ± 0.009	19.072 ± 0.016	6.656 ± 0.006	–	Ortho	P*nmm*

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*Cement chemists' standard notation: C = CaO, S = SiO_2, N = Na_2O, P = PO_3.

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