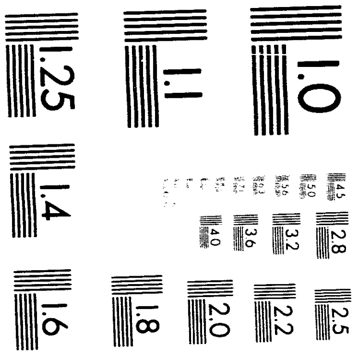
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Title: THE MECHANICAL PROPERTIES OF SINGLE CRYSTAL ALPHA-SILICON NITRIDE

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T. E. Mitchell

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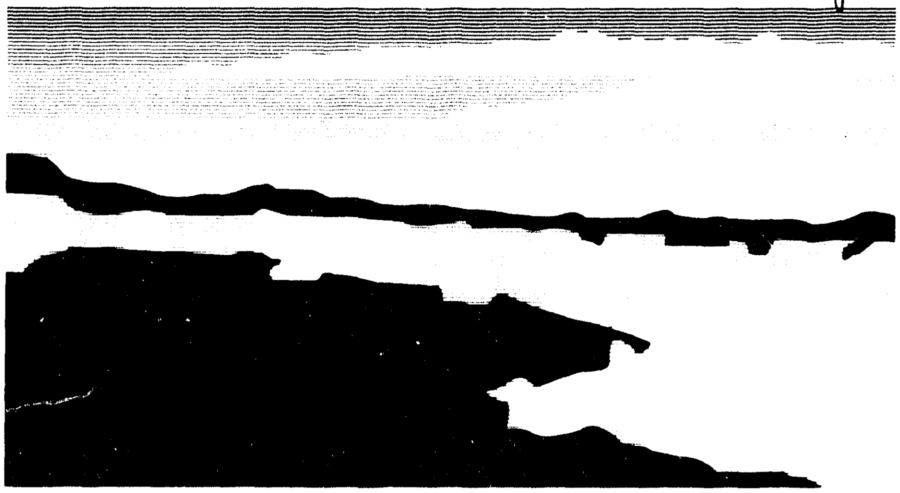

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The Mechanical Properties of Single Crystal α-Si3N4

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ABSTRACT

The ambient and high temperature mechanical properties of single crystal α-Si_3N_4 synthesized by chemical vapor deposition are reported. Crack patterns in the as-grown crystals and around Vicker's indentations reveal that significant residual stresses develop during growth. Indentation studies indicate that the cleavage is essentially isotropic in α-Si_3N_4 at 25°C as well as at 1400°C. Transmission electron microscopy on crystals which were deformed at high temperatures have confirmed the previous observation that high temperature slip occurs primarily on the (1011)[1120] system.

INTRODUCTION

Si_3N_4 is a key component in various existing and future high temperature structural applications in the automotive and aerospace industry. A fundamental understanding of the properties of Si_3N_4 may be accelerated by the study of single crystal Si_3N_4. There have been relatively few studies on the properties of single crystal α-Si_3N_4. In 1975 Niihara and Hirai reported that they obtained a limited amount of CVD α-Si_3N_4 single crystals, but were, however, unable to grow more [1, 2].

Niihara and Hirai studied the hardness anisotropy and applied the analysis by Brookes et al. which relates the active slip systems of a crystal to hardness measurements for different crystallographic orientations [3]. Niihara and Hirai's hardness anisotropy measurements were consistent with primary slip occurring on the (1100)<0001> system and inconsistent with slip occurring on the (0001)<1120> or the (1010)<1210> systems. Their results are in agreement with hardness measurements made by Mukerji et al. [4]. These results are also consistent with observations by Kossowsky that the most common Burgers vector in α grains from hot pressed Si_3N_4 is [0001] [5]; but it has not been shown that the (1100)<0001> system is primarily responsible for high temperature deformation of α-Si_3N_4. Suematsu et al. have recently reported that {1101}<1120> is the most commonly observed slip system in α-Si_3N_4 single crystals deformed in uniaxial compression at 1820°C [6]. In the following, we discuss recent high temperature fracture and deformation studies.

EXPERIMENTAL

Single crystals of α-Si_3N_4 were obtained by Praxair Coatings Technology, formerly known as Union Carbide Coatings. They were grown by the chemical vapor deposition of $HSiCl_3$, NH_3 and H_2 gases 1500°C at a pressure of 0.5 torr. The crystals were extracted using a diamond bit tool to cut around the polycrystalline base. Samples were cross sectioned and polished using diamond media. Laue x-ray diffraction was used to determine the crystallographic orientations and phases of individual crystals. Optical microscopy using polarized light revealed information on the crystal growth morphology. The fracture behavior studies and hardness measurements were carried out on polished specimens using a conventional Vickers hardness tester and a Nikon QM-2 hot hardness tester. Loads of either 200 or 300 g were used. For the high temperature indentation experiments, samples with the (1010) or (0001) face polished were attached to polycrystalline Si_3N_4 mounts using a high temperature alumina-based adhesive.

The high temperature uniaxial compression experiments were performed on an Shimadzu IS-10T testing machine equipped with a vacuum furnace. Transmission electron microscopy (TEM) was used to evaluate the dislocation structures in as-grown and deformed crystals. The specimen preparation for TEM involved cutting, grinding and polishing the specimens using diamond media. The specimens were then mechanically dimpled and ion milled using 5 KeV energy Ar ions. The TEM was performed with a Philips CM30 using an accelerating voltage of 300 KeV.

RESULTS AND DISCUSSION

Morphological characterization of as-grown crystals

The CVD process described above resulted in two general types of α-Si_3N_4 crystal. The first type grows as a prismatic needle parallel to the [0001] direction. Because these needles were the largest type of crystal, they were used in the high temperature deformation studies. They were not used in the indentation fracture studies because they contained surface and sub-surface mircocracks, and in some cases were polycrystalline in the core. The second type of crystal grows in the [1010] direction. Macroscopically, these crystals have a hexagonal shape (figure 1a); however, four of the sextants of the hexagonal cylinder are polycrystalline, as shown in figure 1b. The (1120) plane faces outward in the 'hexagon'. These [1010] crystals typically contain a single radial crack which is aligned parallel to the (0001) plane, as shown schematically in figure 1b. Presumably, the crack is present due to residual tensile stresses which develop upon cooling. Using a high power optical microscope, the crack opening was measured at 20 locations along the crack and a plastic strain was calculated for each location. The widest crack openings were 3.5 μm. Using a value of 300 GPa for the elastic modulus of Si_3N_4, these measurements (approximately 0.3% strain) yielded an estimated value of 0.9 GPa for the residual stress in the crystal. While the presence of tensile stresses is not surprizing, considering that the single crystal regions are constrained at the base and partially surrounded by polycrystalline Si_3N_4 (figure 1), the magnitude is larger than predicted considering the relatively small thermal expansion mismatch in α-Si_3N_4 grains [7].

Indentation Fracture and Deformation

The measured length of cracks produced by Vickers indentations did not change significantly with temperature. Using the measured crack lengths, the indentation fracture toughness was

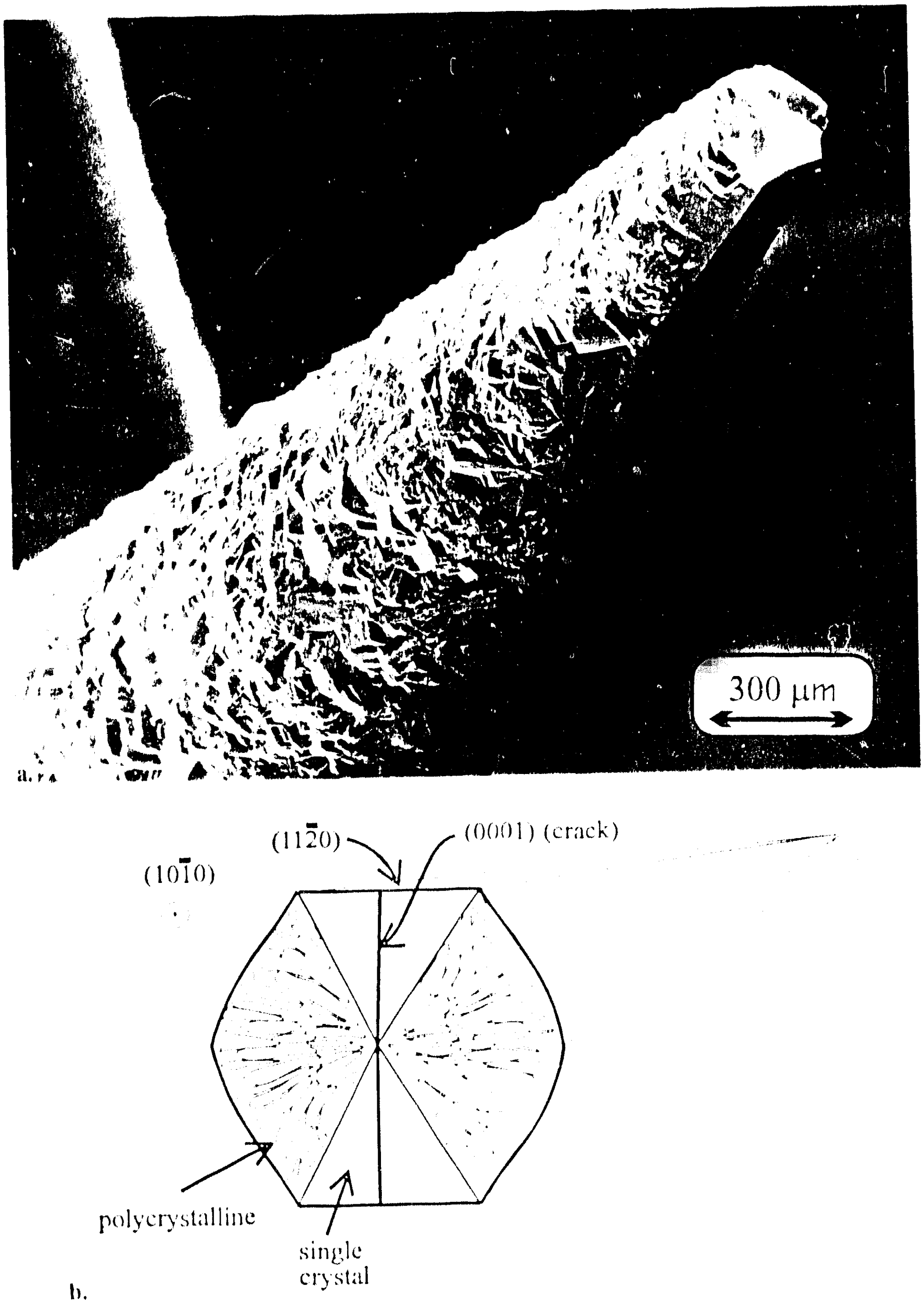

FIGURE 1a. Scanning electron micrograph of pyramidal α-Si_3N_4 needle growing in the [1010] direction. **b.** schematic of cross section of needle shown in 1a

calculated according to the analysis by Anstis et al [8], assuming penny-shaped cracks. Cracks tend to be somewhat longer when they are oriented radially with respect to the hexagonal shape of the crystal. It is clear that the residual stress influences the indentation stress field.

Figure 2 shows that the indentation fracture toughness does not vary significantly with temperature. At room temperature the penny-shape of the indent cracks was confirmed by placing an indent several indent diameters from the edge of the crystal and viewing through the transparent side face of the crystal. Thus, at room temperature the fracture mechanics analysis of indent cracking according to Anstis et al. is strictly valid. However, at temperatures above about 800°C the cracking pattern changes, as illustrated in figure 3 for 25°C and 1400°C indents. Lateral cracking is also apparent in figure 3. Strictly, the aberrant crack patterns invalidate the use of the Anstis analysis in calculating the fracture toughness. While the cracking pattern remains virtually identical for all temperatures above 800°C for a particular orientation in a given area of the crystal, it changes when the orientation is changed. Figure 4 shows two indents at 900°C where one is rotated 35° with respect to the other. Because the degree and type of plasticity under the indent may be anisotropic, the indentation stress field may be a function of the crystal orientation with respect to the indent. However, clearly the cleavage anisotropy in α-Si_3N_4 must be relatively small; otherwise the two cracking patterns in figure 4 would be similar. To confirm that the cleavage is relatively isotropic, a more rigorous fracture mechanics approach is necessary. Furthermore, while some of the residual stress in the crystal is relieved through the basal plane cracking, it is expected that the uncracked portions of crystal contain a significant magnitude of stress, thus influencing the indentation cracking.

The hardness decreased appreciably as a function of temperature, as shown in figure 5. Crystals which were indented on the (1100) faces exhibited Vickers hardness numbers which were on average 40 - 55% higher than those for the (0001) crystals. These results (i.e., figure 5) are in agreement with the room temperature Vicker's hardness measurements by Suematsu et al [6], considering the standard deviation of both studies. In the present study, the standard deviation is 2 -3 GPa, except for the room temperature measurements, where it is 5.0 GPa for both orientations. Figure 5 is also in fair agreement with earlier work by Niihara who observed that the (1100) oriented crystals had an average Knoop hardness about 20 - 25% higher than the (0001) orientation [2].

As was shown by Daniels and Dunn [9], and more completely by Brookes et al. [3], Knoop indentation measurements may be used to evaluate operative slip systems in crystals. In their analysis, the effective resolved shear stress underneath a Knoop indent, τ_c', is given by [3]

$$\tau_c' = F/2A \cos\lambda \ \cos\phi \ (\cos\Psi + \sin\gamma) \qquad (1)$$

where F is the applied force at the indent facet, A is the cross sectional area, λ is the angle between the slip direction and the stress axis, ϕ is the angle between the slip plane and the stress axis, Ψ is the angle between the axis of rotation in the slip plane and the indenter edge, and γ is the angle between the slip direction and the indenter edge. By comparing values of $(\tau_c' \ A/F)^{-1}$ for three different slip systems, Niihara and Hirai found that their Knoop measurements were consistent with slip occurring on {1010}[0001]. However, they did not

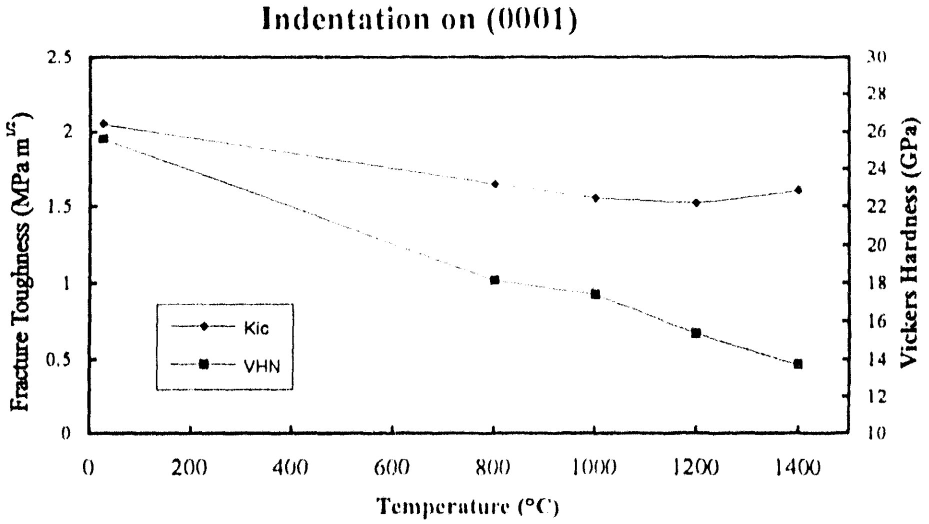

FIGURE 2. Indentation fracture toughness and Vickers hardness as a function of temperature.

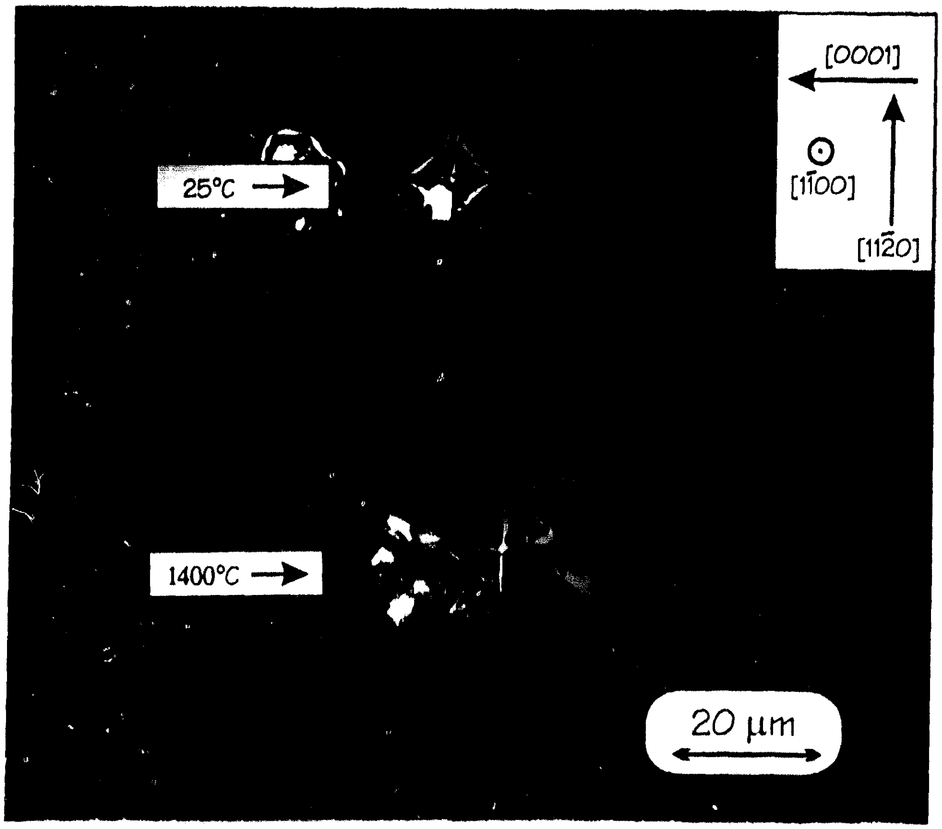

FIGURE 3. Vickers indentation on (1010) plane, at 25°C and 1400°C, showing change in cracking pattern.

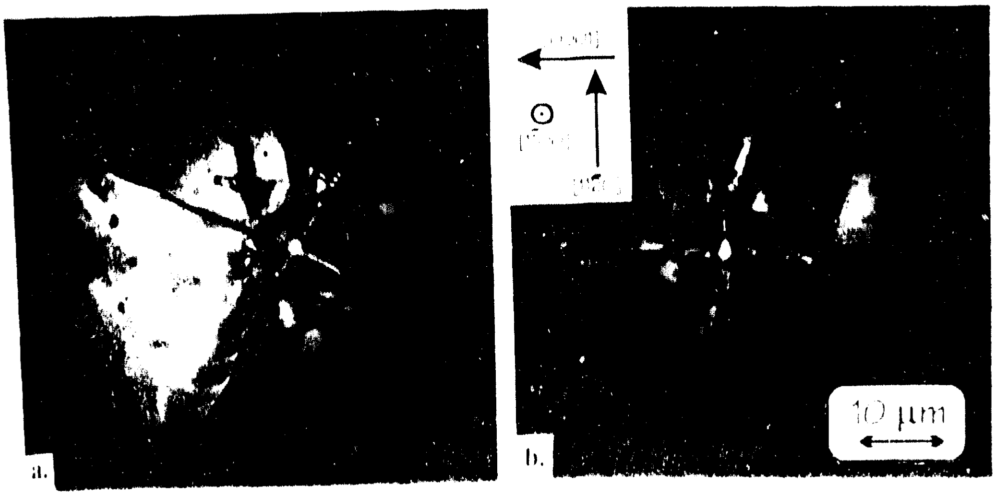

FIGURE 4. Vickers indentation on $(10\bar{1}0)$ plane at 1400°C: a. 5° off-axis; and b. 0° off-axis of $[11\bar{2}0]$

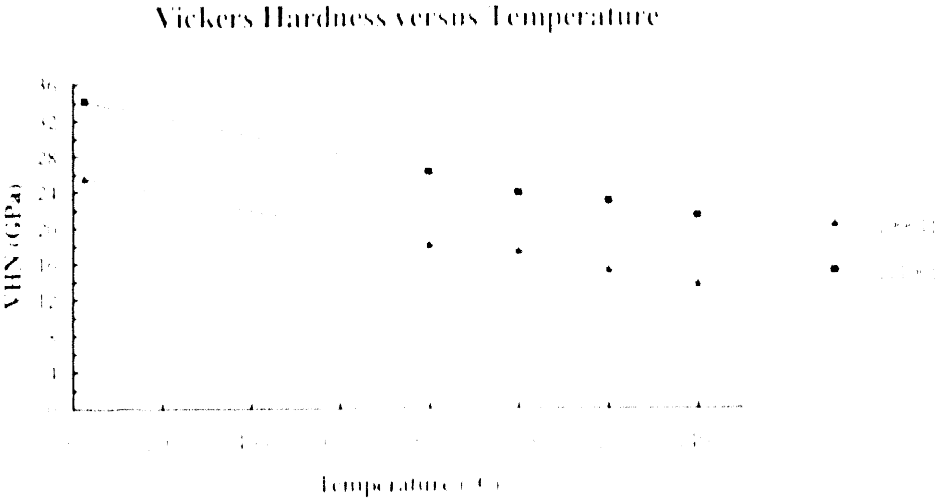

FIGURE 5. Vickers hardness as a function of temperature for two orientations

Table 1 **Values of $(\tau_c'A/F)^{-1}$ compared with Niihara and Hirai's Knoop Hardness Measurements [2].**

Indenter Plane	{0001}		{1010}		{1120}	
Indenter Axis	<1010>	<1120>	<0001>	<1120>	<0001>	<1010>
Slip System						
{1010}[0001]	3.1	2.6	46.6	2.6	37.5	2.9
{1011}<1120>	3.2	2.9	2.7	3.2	3.7	4.9
Hardnesss (GPa)						
25°C	27.91	26.2	34.86	31.51	34.76	32.76
1500°C	15.22	12.63	19.35	14.76	18.02	14.32

evaluate values of $(\tau_c' A/F)^{-1}$ for the {1011}[1120] system, which was observed by Suematsu et al. as the most common slip system in α-Si_3N_4 deformed uniaxially at 1820°C [6]. In the present study, extensive transmission electron microscopy on samples deformed uniaxially at 1820°C confirmed the earlier observation by Suematsu et al. that {1011},<1120> is the most prevalent slip system. Table 1 shows the calculated values for the (1011)[1120] and (1010)[0001] slip systems. Also shown are the Knoop hardness measurements of Niihara and Hirai [2]. It is seen that the measurements are consistent with slip occurring on {1010}[0001], as Niihara and Hirai concluded.

It must be noted that while the resolved shear stress analysis has been successful in describing deformation anisotropy in cubic crystals, it has not been as successful for hexagonal systems [10]. Also, a true comparison of Niihara's Knoop-indentation results with the uniaxial deformation results requires a full understanding of the stress field under the indent. The only way to confirm that Knoop indentation deformation involves the{1010}[0001] system, is to conduct transmission electron microscopy in the vicinity of a Knoop indent. Indentation studies in conjunction with TEM are currently in progress in our group.

CONCLUSIONS

From the results presented above, and from earlier work [5], it appears that any cleavage anisotropy in α-Si_3N_4 is relatively small, both at high temperatures and ambient. It has also been shown that Niihara and Hirai's hardness anisotropy measurements are not consistent with slip occurring on {1101}<1120>, the slip system which was observed in α-Si_3N_4 deformed at high temperatures. The unambiguous identification of the slip systems responsible for deformation underneath a Knoop indent requires electron microscopy in the vicinity of indentations at various temperatures.

ACKNOWLEDGEMENTS

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