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Plastic flow at the theoretical yield stress in ceramic films

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ABSTRACT

Using fine-grained ceramic films based on chromium nitride, and suppressing fracture by using microcompression, it is shown that plastic flow at the theoretical yield stress can be obtained in brittle materials, with shear yield stresses of ~$G/24$ at room temperature, which extrapolate to ~$G/19$ at 0 K. Surprisingly, it is also found that the rate of deformation, and hence the hardness and the yield stress, are determined not by the soft, glassy grain boundary phase in the fine-grained materials, but by the harder crystal phase.

The removal of material when two surfaces rub against one another is one of the most important processes in determining the useful lifetime of components: from hip prostheses to hard, ceramic films on metal cutting and forming tools. Hardness is usually considered to be the most important property of a material for increasing the wear resistance. However, it has been observed that this may be moderated by the Young's modulus, E, so that H/E is the controlling variable, where H is the hardness [1]. It has been suggested that this applies when wear is occurring by plastic flow. However, in a given system, the elastic modulus often changes only by relatively small amounts, so that the greatest changes to the wear resistance would still be obtained by increasing the yield stress, and hence the hardness of the film material.

In transition metal nitrides and carbides, deformation occurs by dislocation flow, rather than, say, twinning. At low temperatures the preferred slip system is $\{110\}\langle 1\bar{1}0\rangle$ [2,3]. However at higher temperatures, dislocations move on the $\{111\}$ plane, dissociating into partials with a Burgers vector of $a/2\langle 1\bar{1}0\rangle$ [4]. If the dislocation density were negligible, then yielding could only occur once the applied stress was sufficient for dislocation nucleation [5]. Simulations predict that the precise values depend on the geometry of the surface, with small steps enabling dislocation nucleation at stresses between $G/10$ and $G/20$ [6]. However, experimental measurements on metal whiskers with diameters of the order of a micron, and thought to be dislocation free [7], give values of the order of $G/40$. Furthermore, once dislocations have nucleated, there is normally a substantial drop in the yield stress for further flow [7–10].

It has been shown that when a sample with micron-sized dimensions is compressed, the driving force for cracking diminishes as the sample size decreases [11]. This increases the stress required for fracture, so that it may exceed the yield stress. In this case, the material will plastically deform rather than break. Plasticity at very high stresses can be achieved in very small fibres or particles of the order of 10 nm in size in brittle materials [12]. However, loose particles or fibres are of little use when abrasive wear resistance is required. This requires continuous films, so that any approach must ensure that the film is sufficiently hard.

One way of doing this is to greatly reduce the grain-size. Ceramic films, typically of transition metal nitrides, often mixed with aluminium in solid solution, can now be routinely made with grain-sizes <10 nm, by doping with silicon, giving a microstructure in which each grain is surrounded by a grain boundary phase of amorphous silicon nitride [13]. However, although it has been suggested that flow may not occur until the theoretical yield stress is reached [14], it has, so far, not proved possible either to demonstrate this or, more importantly, to determine the stress at which the onset of flow occurs, because of the inherent brittleness of the transition metal nitrides.

The aim of this work, therefore, is to exploit the effect of size on the fracture stress to study the deformation behaviour of such fine-grained CrN-based films, to understand whether deformation requires dislocation nucleation, comparing their behaviour with that of more conventional CrAlN-based coatings.

The coatings were made by physical vapour deposition using the cathodic arc method and were ~5 μm thick. The amorphous Si_3N_4 was made by unbalanced magnetron sputtering. Micropillars, 380 nm in diameter with an aspect ratio of 2.5, were milled using focused ion beam milling and compressed in situ in a scanning electron microscope at a

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displacement rate of 5 nm s^{-1}, giving a uniaxial strain-rate of $5 \times 10^{-3}\,s^{-1}$, at temperatures ranging from 298 to 773 K [15]. The hardnesses and Young's moduli of the coatings were measured by nanoindentation at room temperature. Thin films for transmission electron microscopy were thinned using focused ion beam milling and examined at 300 kV.

Dislocation nucleation is considered to be a thermally activated process, in which part of the work required to nucleate a new dislocation comes from the applied stress and part comes from thermal activation. Conventional chemical kinetics shows that the uniaxial stress σ required to drive dislocation nucleation to give a uniaxial strain-rate $\dot{\varepsilon}$, which varies according to [16]

$$\sigma = \frac{\Delta E_n}{V} - \frac{kT}{V} \ln\left(\frac{kTN\nu_O}{E\dot{\varepsilon}V}\right) \tag{1}$$

where ΔE_n is the energy required for nucleation, V is the activation volume, N is the number of surface nucleation sites, ν_O is the attempt frequency and E is the Young's modulus. The first term on the right hand side gives this stress required for nucleation at 0 K, while the second term gives the rate at which the stress decreases, which varies approximately linearly with increasing temperature. Extrapolating the data in Fig. 1 back to 0 K, gives a uniaxial, compressive stress required for nucleation of 22.8 GPa.

To estimate the corresponding shear stress acting on the slip planes in the individual grains of the polycrystalline film, requires a relationship between the shear stress required for slip in a single crystal and the applied uniaxial stress. Two bounds have generally been considered. The first, due to Sachs [17], is where the grains support the same stress; the second, due to Taylor [18] assumes the grains undergo the same strains. These give lower and upper bounds respectively. The former predicts that $\sigma = 2.23\tau$, while the latter gives $\sigma = 3.06\tau$. The real value is thought to lie somewhere between the two [19]. For simplicity, we have taken the arithmetic mean, giving $\sigma = 2.65\tau$.

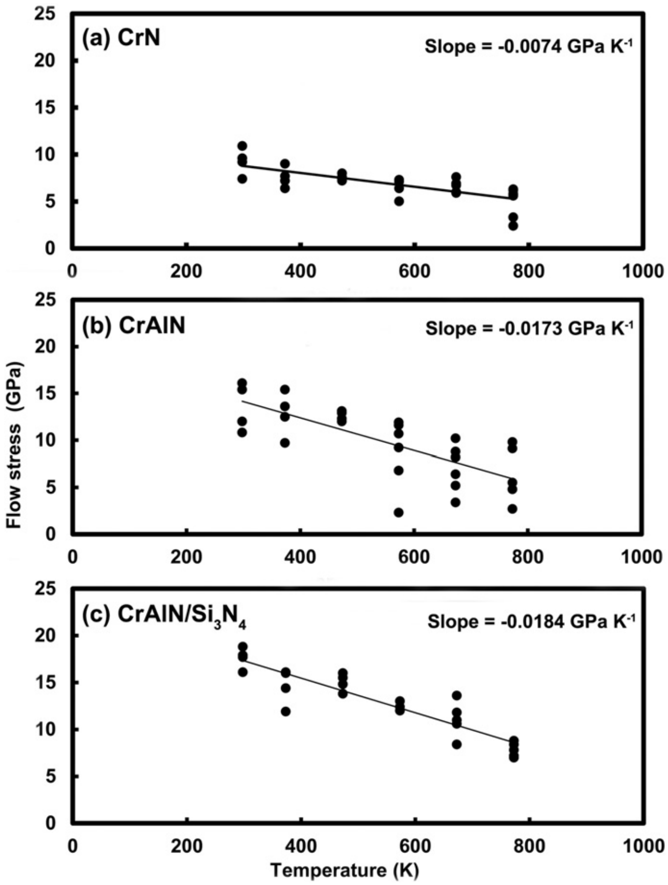

Fig. 1. The change of uniaxial yield stress with temperature for (a) CrN, (b) CrAlN and (c) CrAlN/Si_3N_4 coatings. Note that the change in the slope when the boundary phase is added is less than 6%, suggesting that the deformation is controlled by the CrAlN rather than the softer grain boundary phase.

Using the Young's modulus of the CrAlN/Si_3N_4 coatings measured by nanoindentation of 395 GPa, and taking the Poisson ratio as 0.2 [20], a shear modulus of 165 GPa is estimated. Using this, with the factor above of 2.65 and the measured yield stress of 18.3 GPa, gives a shear yield stress, at room temperature, of $G/24$, close to that required for dislocation nucleation. At 0 K this can be extrapolated to approximately $G/19$, in the range of the values for dislocation nucleation. This suggests that deformation occurs by the nucleation of dislocations within each 10 nm grain. This is also consistent with the observation that slip bands are not seen when fine-grained CrAlN/Si_3N_4 is deformed, Fig. 2 [21], although slip bands are normally seen both in bulk materials and in micropillar deformation [11,22,23].

It can be seen from Fig. 1, that the stress required for nucleation with temperature varies in the same way for the fine-grained CrAlN/Si_3N_4 as it does for the CrAlN, when there is no grain boundary phase. This suggests that the rate of deformation is controlled by the crystalline CrAlN matrix phase, rather than the grain boundary phase. This is perhaps not surprising if dislocation nucleation is occurring in the crystalline phase. However, it has been generally thought that the rate of deformation, measured using indentation, is controlled by grain boundary processes [24].

To confirm that this effect was not an artefact associated with the micropillar testing, the strain-rate sensitivity was measured using nanoindentation of the complete film, Fig. 3(a). Again, the rate of change of hardness with strain-rate appears to be little affected by the introduction of the grain boundary phase. The processes occurring have been characterised by measuring their activation volumes. The hardness data was used to determine these, as the activation volume is contained in the logarithmic term in Eq. (1), whilst the values of terms such as the attempt frequency or the number of surface nucleation sites are very uncertain.

To do this it is assumed that the strain-rate and flow stress can be approximately represented by single values [25], as conventionally done. These are given by

$$\dot{\varepsilon} \approx \frac{\dot{h}}{h} \approx \frac{1}{2}\frac{\dot{F}}{F}, \tag{2}$$

where $\dot{h}$ and $\dot{F}$ are the displacement rate and loading rate respectively, h and F are the maximum displacement and force respectively. The

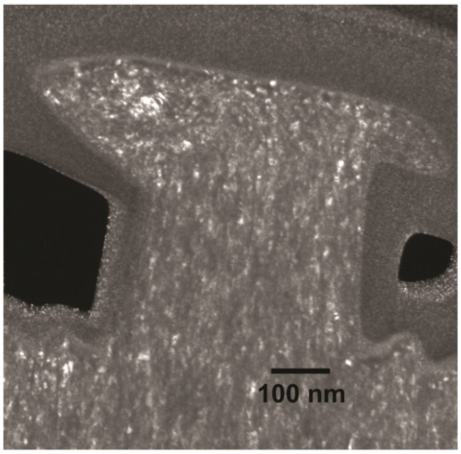

Fig. 2. A sample of CrAlN/Si_3N_4 that has been heavily deformed. Note that the grains appear to deform uniformly whereas in most materials deformation occurs on distinct slip bands [21].