Scripta Materialia 117 (2016) 24–27

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

Plastic flow at the theoretical yield stress in ceramic films

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ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form 3 February 2016
Accepted 6 February 2016
Available online 27 February 2016

Keywords:
Hard coating
Dislocation nucleation
Micropillar compression
Deformation kinetics

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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http://dx.doi.org/10.1016/j.scriptamat.2016.02.008
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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]

$$\sigma = \frac{\Delta E_{\rm n}}{V} - \frac{kT}{V}\ln\left(\frac{kTN\nu_{\rm O}}{E\dot{\varepsilon}V}\right) \tag{1}$$

where $\Delta E_{\rm n}$ is the energy required for nucleation, V is the activation volume, N is the number of surface nucleation sites, $\nu_{\rm O}$ 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 $\sigma = 2.65\tau$.

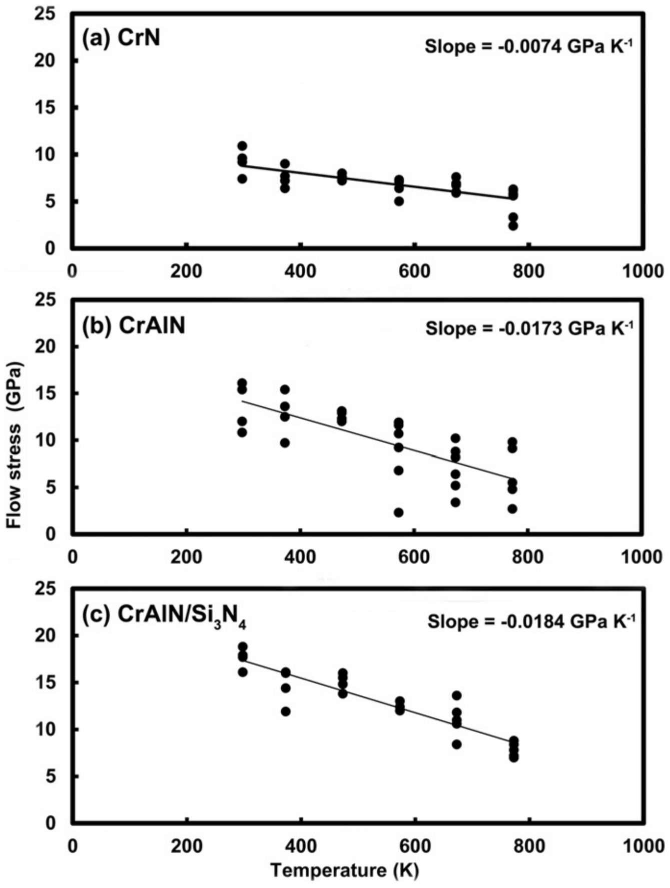

Fig. 1. The change of uniaxial yield stress with temperature for (a) CrN, (b) CrAlN and (c) CrAlN/Si_3N_4 coatings. Note that the change in the slope when the boundary phase is added is less than 6%, suggesting that the deformation is controlled by the CrAlN rather than the softer grain boundary phase.

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

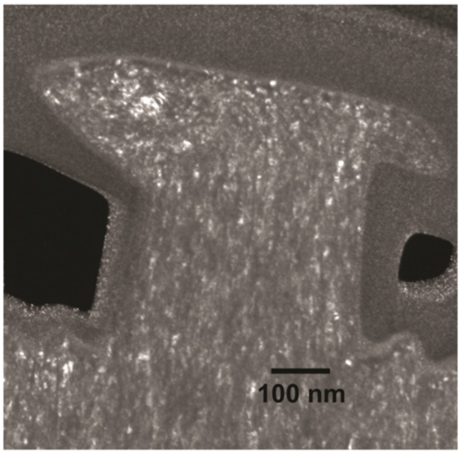

Fig. 2. A sample of CrAlN/Si_3N_4 that has been heavily deformed. Note that the grains appear to deform uniformly whereas in most materials deformation occurs on distinct slip bands [21].

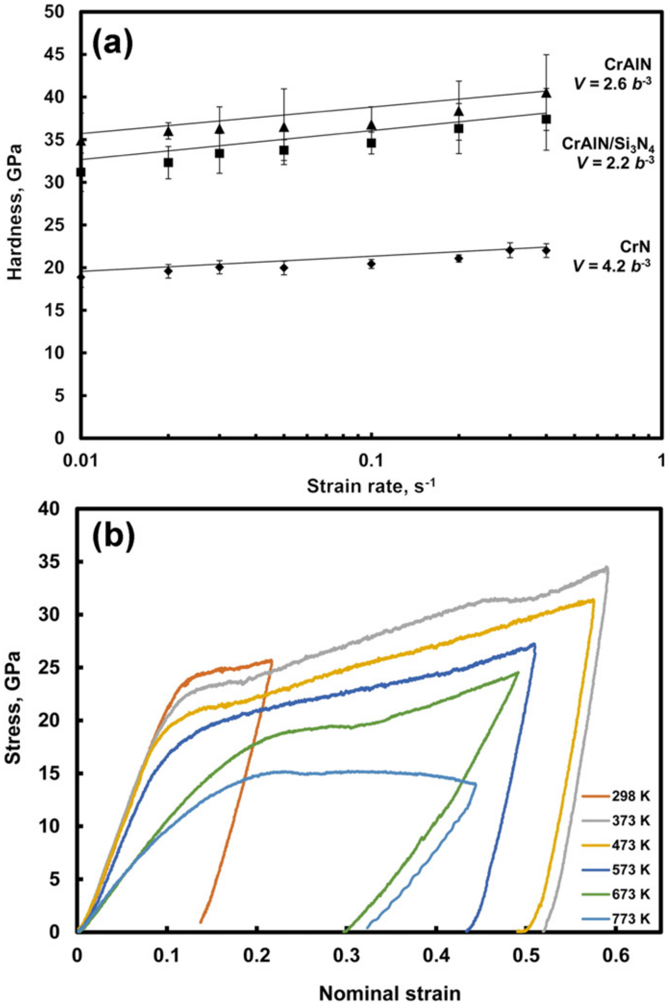

Fig. 3. (a) The change in the hardness with strain-rate. Note that introducing the grain boundary phase has no apparent effect on the deformation behaviour and (b) typical stress/strain curves at the different test temperatures for the CrAlN/Si_3N_4 coating.

sensitivity of the strain-rate m to the applied pressure, the hardness, can be expressed as [26]

$$m = \frac{dH}{d \ln \dot{\varepsilon}}, \tag{3}$$

and the activation volume V as

$$V = \frac{\alpha\, k\, T}{m} \cdot c \tag{4}$$

where α is a factor that relates the uniaxial stress to the shear stress, in this case 2.65, H is the hardness and c is the constraint factor, found experimentally to be 2.2 [21]. Whilst this approach is experimentally more direct, it has the disadvantage that the activation volume was only determined at room temperature.

The activation volumes measured from these results are approximately 2.2 b^3 for the CrAlN/Si_3N_4, 2.6 b^3 for the CrAlN and 4.2 b^3 for the basic CrN coating, assuming b is the Burgers vector of a partial dislocation on a {111}<110> slip system and equal to 0.176 nm. These values are of the magnitude expected for dislocation nucleation [16]. The activation energy for nucleation, ΔE_n, estimated from Eq. (1), using the value of the stress extrapolated to 0 K, i.e. 22.8 GPa, and the activation volume above, is approximately 1.7 eV. It should be stressed that this is only an estimate as the activation volume was measured at room temperature. Although this is greater than the 0.6 eV estimated for Cu [16], it is approximately consistent with the increase in stress associated with the increase in elastic modulus from 117 GPa for Cu to 395 GPa for the fine-grained CrAlN/Si_3N_4.

The hardness of the fine-grained materials has not come about here through the Hall–Petch effect. It arises because the decreasing grain size reduces the probability of a grain containing a dislocation source, somewhat analogous to the absence of heterogeneous nuclei in very small particles [27–29], so that flow requires dislocation nucleation. It has been suggested that amorphous material, often caused by focused ion beam milling [30], can give rise to the preferential operation of surface sources. Such sources might be expected to give rise to glide bands. However, these were not observed here suggesting the effect is not important in this system. Furthermore, the similarity between the CrAlN/Si_3N_4 and the CrAlN confirms the initial observation that the introduction of the amorphous Si_3N_4 grain boundary phase has little effect on the rate of flow and hence the hardness. Rather, the rate of deformation is controlled by the matrix CrAlN.

Consider a material made of CrAlN grains surrounded by a layer of amorphous Si_3N_4, Fig. 4. It has been shown that the CrAlN grains will deform once the shear stress becomes equal to that required to nucleate new dislocations. The deformation could occur either by each grain changing its shape by an amount similar to the overall strain, *affine* deformation, or alternatively by the grains changing their neighbours, in a manner somewhat akin to superplasticity, except that it is visualised that deformation of the grain occurs by plastic flow rather than by diffusion. The plastic strains, although large for a ceramic, are still too small to be able to reliably distinguish between the two possibilities.

However this deformation occurs, the grain is contained within a layer of the grain boundary phase, so that after some initial elastic transient, flow will cease unless the grain boundary phase also deforms. That a large yield drop is not seen in the stress/strain curves, Fig. 3(b), once nucleation starts, as it is in metal crystals, suggest that any elastic transients are rather small. The importance of any deformation is this grain boundary layer, which must in any event be very highly constrained, is unclear, although it may be that it helps limit grain boundary failure.

The mechanical analogue of this is two dashpots in parallel, although one may add a spring to each side, if one wishes to include elastic transients. For simplicity, we ignore these transients here. The deformation of the body occurs by the deformation of both phases occurring at rates that allow the deformation in one phase to be completely accommodated by the deformation of the other. In other words, the rate of deformation of both phases together is dependent on the stress required to drive deformation at a given rate in each component. The measured behaviour will reflect the process requiring the most work. As the incorporation of the silicon nitride has marginal effect on the rate of deformation, this suggests that the CrAlN is more resistant to deformation than the amorphous Si_3N_4.

This is consistent with the hardness of an amorphous silicon nitride film being measured as 19 GPa, whereas that of the CrAlN was approximately 36 GPa. This implies that previous ideas that the hardness is diminished by the grain boundaries are incorrect. Weakening of the boundaries could promote cracking, decreasing the wear resistance. However, the observation that the wear resistance is improved [31] suggests that such cracking, and therefore any weakening, does not occur. Such fine-grained microstructures are therefore a reliable approach to obtaining the highest possible yield strengths in a brittle hard coating.

Fine-grained CrAlN/Si_3N_4 yields when the shear stress on the CrAlN grains reaches $G/19$, close to the theoretical shear strength, where dislocations are nucleated. This leads to slip taking place by the nucleation of dislocations within each grain. This is consistent with the observation that slip bands do not form across the whole pillar, as is commonly observed. It is also found that the deformation behaviour is determined by the CrAlN grains, rather than by the grain boundary Si_3N_4 phase. This is expected if one considers that deformation of the CrAlN/Si_3N_4 requires that both the crystal phase and the grain boundary phase must deform,

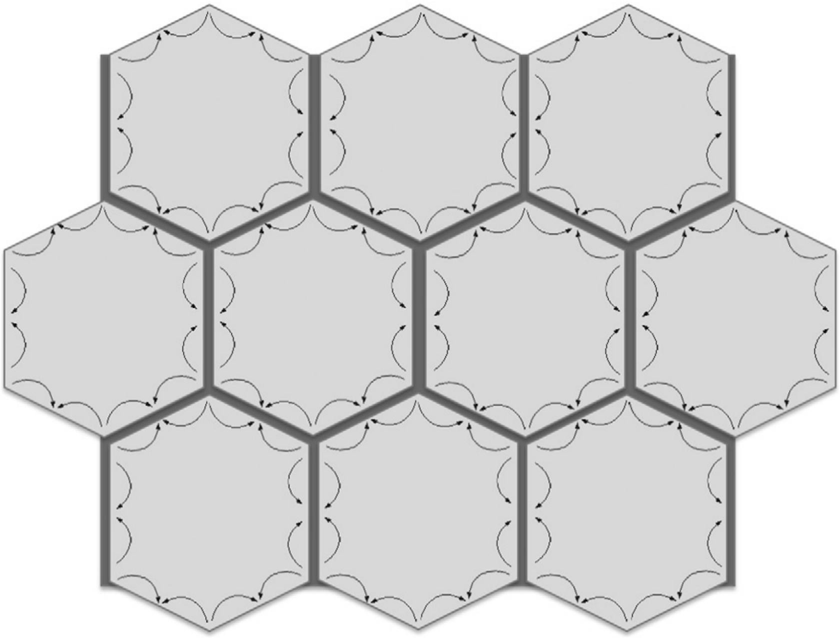

Fig. 4. A schematic of the microstructure of the CrAlN/Si_3N_4 coating, showing the CrAlN grains, each surrounded by an amorphous Si_3N_4 grain boundary phase. For the body as a whole to deform, both CrAlN and Si_3N_4 must deform.

as CrAlN is harder than the Si_3N_4. This therefore gives a robust way of maximising both the yield stress and hardness of a thin ceramic film.

Acknowledgements

This research was funded by A*STAR, Singapore and the Engineering and Physical Sciences Research Council (EPSRC) and Rolls-Royce Strategic Partnership (EP/M005607/1). Aidan Taylor commented on the manuscript. Additional research data supporting this publication are available as supplementary files.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scriptamat.2016.02.008.

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