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On the relevance of kinking to reversible hysteresis in MAX phases

N.G. Jones [a], C. Humphrey [a], L.D. Connor [b], O. Wilhelmsson [c], L. Hultman [d], H.J. Stone [a], F. Giuliani [e], W.J. Clegg [a,*]

[a] Department of Materials Science & Metallurgy, 27 Charles Babbage Rd, Cambridge CB3 0FS, UK
[b] Diamond Light Source, Harwell Science & Innovation Campus, Didcot OX11 0DE, UK
[c] Sandvik Heating Technology AB, SE-734 27 Hallstahammar, Sweden
[d] Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden
[e] Department of Materials, Imperial College, London SW7 2AZ, UK

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Abstract

This paper examines the idea that reversible hysteresis in MAX phases is caused by the formation, growth and collapse of unstable, or incipient, kink bands. In situ X-ray diffraction of polycrystalline Ti_3SiC_2 in compression showed that residual elastic lattice strains developed during the first loading cycle and remained approximately constant afterwards. These residual strains were compressive in grains with a low Schmid factor and tensile in grains with a high Schmid factor, consistent with previous observations of plastically deformed hexagonal metals. In contrast, incipient kink bands would be expected to collapse completely, without any residual strain. Elastoplastic self-consistent simulations showed that reversible hysteresis is predicted if some grains yield by slip on the basal plane, while others remain predominantly elastic, giving both the experimentally observed magnitude of the work dissipated and its dependence on the maximum applied stress. The reversible hysteresis in single crystals was studied by cyclically indenting thin films of Ti_3SiC_2 and Ti_3SiC_2/TiC multilayers on Al_2O_3 substrates. The work dissipated in the multilayer films was greater than in Ti_3SiC_2 alone, despite the reduction in volume fraction of Ti_3SiC_2. Reversible hysteresis was also observed during indentation of single-crystal cubic MgO, demonstrating that this behaviour can occur if there are insufficient slip systems to accommodate the strain around the indentation. These results show that reversible hysteresis is associated with conventional dislocation flow, without the need for unstable kinking.

Keywords: Mechanical properties; X-ray synchrotron radiation; Lattice strains; Polycrystal; MAX phases

1. Introduction

A group of ternary, layered carbides and nitrides, known as MAX phases, show a large reversible hysteresis when they are repeatedly loaded and unloaded. This effect is seen in a wide range of materials, both in polycrystals under compression [1–4] and in single crystals during indentation [5–11]. The hysteretic behaviour has been divided into two types: Type I, where all cycles are completely reversible, as in Ti_3SiC_2; and Type II, where the first loading cycle causes some permanent strain, as in graphite, after which the behaviour is completely reversible [3]. Both have generally been associated with crystals that have anisotropic, often hexagonal structures, with a c/a ratio typically >1.5 [3].

It is well known that in soft hexagonal metals, such as Cd or Zn [12,13], dislocations move much more easily on the basal planes than on the prismatic or pyramidal planes. However, if the soft slip planes are oriented so that they are parallel to the loading axis, deformation can occur by kinking, where two dislocation walls are nucleated by the

* Corresponding author.
E-mail address: wjc1000@cam.ac.uk (W.J. Clegg).

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sequential breaking of individual crystal planes [14]. Each wall contains dislocations gliding on the basal plane with the same Burgers vector, but of opposite line vector to the opposing wall. Inspired by these ideas, Barsoum and co-workers [15,16] have suggested that deformation in MAX phases can also take place by kinking and it is often stated that the linear features observed in deformed structures are the walls of kinks [17,18].

The driving force for the formation of a kink comes from the extra work done by the applied force and the changes in elastic energy in the body. It is resisted by the attractive forces between the dislocations formed by breaking of the crystal planes. In a manner similar to a crack under tension, a kink must reach a minimum length before it becomes stable [14]. Therefore, in any deforming material, there may be kink bands shorter than this critical value, so that when the material is unloaded these subcritical kinks, termed incipient kink bands, will disappear completely. It is thought that the formation, growth and subsequent collapse of these small kinks gives rise to the reversible strain on cyclic loading [1]. In a polycrystal, kinking is thought to occur in those grains whose basal planes are approximately parallel to the loading axis. However, grains with slip planes on which the resolved shear stresses are higher will deform by dislocation motion [1]. In both cases, agreement has been obtained between observations and an analysis based on these ideas, in particular that the work dissipated in a reversible cycle is proportional to the square of the maximum applied stress [3].

In indentation, the work dissipated has been observed to vary with the maximum stress, in the same manner as in the uniaxial compression tests [1,3]. Generally, where the number of slip systems was restricted, e.g. basal slip only in Ti_3SiC_2, changes of orientation had little effect [5]. However, if changing the orientation caused the number of operative slip systems to increase, the work done in a reversible hysteresis loop decreased [9].

In the process of kinking, it is considered that the work dissipated is associated with the plastic work done during both the growth and subsequent collapse of the kink, while the reversibility of flow is associated with the attractive forces between the dislocations in the kink band wall, with a smaller contribution from the relaxation of dislocation pile-ups. However, as the incipient kink band collapses, the attractive forces between the opposing walls increase, such that the band will be able to collapse completely [1,10,11], provided effects such as dislocation entanglement are minimal. Easy flow, with no cross-slip and dislocation interaction, has indeed been observed in these materials [19], so that any residual strains in the sample once it had been unloaded would be negligible. Other sources of elastic strains, such as the generation of long-range lattice strains [20–24], are also considered to be negligible [3]. However, to date, no direct evidence has been obtained for unstable, or incipient, kink bands.

Experimental studies of both polycrystalline and single-crystal Ti_3SiC_2 have been carried out, seeking to examine the idea that this reversible hysteresis is associated with kinking. By using in situ synchrotron X-ray diffraction during compression testing, direct measurements can be obtained of the volume averaged elastic strains that develop in a polycrystalline MAX phase as it is cyclically deformed, and in particular, the sign and magnitude of the elastic strains in grains of different orientations. Additional data on the cyclic deformation behaviour of Ti_3SiC_2 has been obtained by comparing the cyclic indentation behaviour of single-crystal thin films of Ti_3SiC_2 and multilayers of TiC/Ti_3SiC_2, to investigate the effect of reducing the volume fraction of Ti_3SiC_2. The extent to which reversible hysteresis can be obtained in other materials has also been studied through measurements of the well-characterized cubic material, MgO.

2. Experimental

2.1. Materials

2.1.1. Polycrystals

Cylindrical, polycrystalline specimens were made by electrical discharge machining of a commercially produced, hot-pressed bar of Ti_3SiC_2 (3-ONE-2, Voorhees, NJ, USA). The samples for ex situ cyclic compression testing had a diameter of 6 mm and length of 15 mm, whilst those for in situ diffraction experiments had a diameter of 3 mm and a gauge length of 7 mm. The material had a non-random texture and a somewhat bimodal grain structure, with some large grains, ~25 μm, in a matrix of grains with a mean size of 8 μm.

2.1.2. Single crystals

TiC (0 0 1) and Ti_3SiC_2 (0 0 0 1) single-crystal films, as well as TiC (1 1 1)/Ti_3SiC_2 (0 0 0 1) multilayers, were grown on Al_2O_3 (0 0 0 1) substrates by unbalanced magnetron sputtering under ultrahigh-vacuum conditions, as described in Ref. [25]. The TiC/Ti_3SiC_2 had layers of equal thickness, each of 10 nm. The single crystal of MgO (MTI Crystal, Richmond, CA, USA) had an (0 0 1) orientation.

2.2. Ex situ testing

Initial ex situ tests were carried out to confirm that the polycrystalline material showed reversible hysteresis. Samples were cycled five times from zero to a peak stress of 400 MPa under load control at an equivalent strain rate of 5×10^{-6} s^{-1} with the strain in the axial direction being measured using a strain gauge (Kyowa, Japan) attached directly to the sample surface.

2.3. In situ X-ray diffraction

In situ loading of the polycrystalline Ti_3SiC_2 was conducted on the I12 beamline at the Diamond Light Source. The beamline was configured in Debye–Scherrer transmission geometry, and a monochromatic incident beam of