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Fracture of hollow multiply-twinned particles under chemical etching

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ABSTRACT

The stress-strain state in a hollow decahedral small particle is modeled as that caused by a positive wedge disclination in an elastic hollow sphere. The stress and dilatation distribution in the particle is analyzed in relation to crack nucleation and the particle's catastrophic fracture during chemical etching. A two-stage process of the fracture is suggested, which includes nucleation of initial cracks along twin boundaries around their quintuple junction and subsequent pattern formation in a fivefold star-shaped crack at the junction. The critical sizes of the initial crack and the decahedral small particle at which this two-stage fracture process occurs, are estimated.

1. Introduction

Small crystalline particles composed of multiple cyclically twinned domains, commonly called "Multiply-Twinned Particles" (MTPs), are most interesting objects in materials science. They present a unique combination of unique characteristics (Gillet, 1977; Marks, 1994; Gryaznov et al., 1999; Hofmeister, 2004; Mayoral et al., 2010; Marks and Peng, 2016), among which the most notable are listed below:

(i) Fivefold symmetry axes which are impossible in bulk single crystals.
(ii) Typical decahedral and icosahedral shapes of equiaxial MTPs, and typical pentagonal cross sections of MTPs in the form of whiskers and wires, usually referred to as "pentagonal whiskers" and "pentagonal wires".
(iii) Characteristic strain-stress states and extremely high strain energy associated with the presence of quintuple junctions of twin boundaries (TBs).
(iv) Wide spectra of MTP sizes ranging from nanometers to micrometers.
(v) Different types of the MTPs including metals, metal oxides, semiconductors, proteins and viruses.
(vi) High percentage (up to 60-80%) of MTPs in populations of small particles of noble metals (Ag and Au) (Marks and Peng, 2016; Koga and Sugawara, 2003).

The physical origin of residual stresses in MTPs and the mechanisms of their relaxation have been the focus of many studies in the last decades. In these studies, the disclination concept (De Wit, 1972; Howie and Marks, 1984; Romanov and Kolesnikova, 2009) emerged as a natural and most convenient tool in theoretical modeling of MTPs. By using this concept, the stress-strain states and strain energies were calculated for decahedral (De Wit, 1972) and icosahedral (Howie and Marks, 1984) MTPs, as well as for pentagonal whiskers (De Wit, 1972). It was shown, both experimentally and theoretically, that the residual stresses can relax in the pentagonal particles through the nucleation of various crystal lattice defects such as dislocations, disclinations, low-angle grain boundaries and microtwins, as well as through the formation of open gaps, voids, lattice mismatched layers and inclusions (Gryaznov et al., 1991a, 1999; Marks and Peng, 2016; Romanov and Kolesnikova, 2009; Romanov et al., 1993; Pei and de Hosson, 2001; Kolesnikova and Romanov, 2007; Yasnikov and Vikarchuk, 2006, 2007; Yasnikov et al., 2015a; Fu et al., 2008; Langlois et al., 2008; Dorogin et al., 2010; Romanov et al., 2012; Gutkin and Panpurin, 2013, 2014; Yasnikov, 2013; Romanov et al., 2014; Yasnikov, 2014; Gutkin et al., 2015; Yasnikov et al., 2015b; Romanov et al., 2017). Moreover, surface

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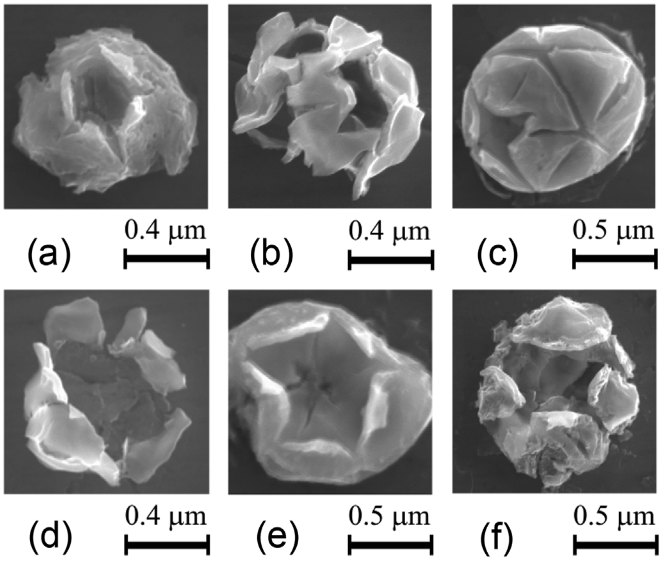

Fig. 1. SEM images of hollow copper ISPs (a–d, f) and DSPs (e) fractured during chemical etching. From Ref. (Yasnikov and Vikarchuk, 2006).

transformations can occur, resulting to the growth of surface whiskers (Romanov et al., 2012, 2014), which cause an additional previously unobserved nanodecoration to microparticles and provide extra surface for chemomechanical activity and possibly energy storage.

Although the reasons for the manifestation of the variety of stress relaxation modes in MTPs still remain largely unexplained, some of these modes are induced by external factors. A typical example is cracking and fracture of hollow decahedral and icosahedral small particles (DSPs and ISPs) of electrolytic Cu during chemical etching (Yasnikov and Vikarchuk, 2006).

Fig. 1 shows the morphology of the fractured surface of the particles after thinning of the particle shells by chemical etching (see Ref. (Yasnikov and Vikarchuk, 2006) for details). The surface seems to indicate that a number of multiple explosion-like fractures take place locally at some five-fold symmetry axes of the particles. It is worth noting that some photos in Fig. 1 show evidence of different stages in the fracture development starting from initial cracks, subsequent crack growth along TBs in the vicinity of their quintuple junctions, and final catastrophic fracture of these junctions with separation and buckling of some twin domains of the particle shells. For example, Fig. 1e shows both of these stages in a hollow DSP: the initial stage on the back side of the shell and the final stage on the front.

To describe the fracture of the hollow particles, previous work (Yasnikov and Vikarchuk, 2006) focused on the case of an ISP. These authors used an expression for the strain energy (Romanov et al., 1993) E_{ISP} by employing the Marks-Yoffe stereo-disclination model (Howie and Marks, 1984) and associating the volume density of the total elastic energy of a disclination type defect with the average pressure P_{ISP} over the ISP volume V: $P_{\mathrm{ISP}} = E_{\mathrm{ISP}}/V$. Comparing P_{ISP} with the maximum pressure $P_{\max}$, which corresponds to the ultimate stress of the ISP material, they obtained a critical ratio $\xi_c = R_{\mathrm{in}}/R_{\mathrm{out}}$ of the inner (R_{in}) and outer (R_{out}) radii of the ISP and showed that for a hollow ISP of Cu with a characteristic outer radius of $\sim 0.5\,\mu$m, is $\xi_c \approx 0.87$ (Yasnikov and Vikarchuk, 2006). To answer the question of where is the place of crack nucleation in an ISP, the authors (Yasnikov and Vikarchuk, 2006) turned back from the Marks-Yoffe stereo-disclination model to the discrete disclination model (Howie and Marks, 1984) and suggested that the fracture originates at the disclination line which acts as a natural stress concentrator in real ISPs.

At first glance, the model and conclusions of the aforementioned analysis are in a good accordance with experimental images of the fractured hollow DSPs and ISPs shown in Fig. 1. However, there are at least two contradictory points to clarify. First, although the approximation of the effective average pressure is very attractive due its simplicity and effectiveness, it is noted that the Marks-Yoffe stereo-disclination model gives zero-values for the radial stress and compressive tangential normal stress at the inner surface of a hollow ISP (Gryaznov et al., 1991b). This means that the hydrostatic stress is also compressive and cannot initiate fracture there. Second, the area around discrete lines of singular positive wedge disclinations is always compressed within any version (classical (Romanov et al., 1992), strain-gradient (Gutkin and Aifantis, 1999a) or surface-stress (Rezazadeh Kalehbasti et al., 2014)) of the theory of elasticity and therefore it cannot serve as a nucleus for fracture. This conclusion is also in a good agreement with recent results of computer simulations of strain distribution in five-fold twins of diamond and silicon (Yu et al., 2017).

The main purpose of the present work is to cope with the above contradictions and shed some light on the fracture process as a channel of stress relaxation in hollow DSPs and ISPs. This process is obviously a micro- and nanoscale multi-physics phenomenon which we analyze with taking into account the structure, the morphology and the role of interfaces (TBs) of hollow DSPs and ISPs. It is worth noting that this work is within the scope of great interest to hollow crystalline nano- and microparticles which are the subject of many research efforts in over the world due to their promising applications in catalysis, gas sensors, filters, etc. (Cao and Zhu, 2008; Chen et al., 2012; Dubau et al., 2017; El Mel et al., 2015; Li et al., 2016; Niu et al., 2010; Peng et al., 2010; Sneed et al., 2015; Sturm et al., 2013; Sun et al., 2003; Yin et al., 2004; Zeng et al., 2016; Zuo et al., 2016).

2. The model

Following De Wit (De Wit, 1972), a DSP can be modeled as an elastic particle which contains a positive partial wedge disclination. To illustrate this idea, let us consider an undeformed body which consists of five face – centered cubic (FCC) crystals oriented with the $(1\bar{1}0)$ plane in the plane of the paper (Fig. 2a). Each crystal is in twin orientation with respect to the adjacent one, so that AC, AD, AE, and AF are TBs. The angle between each pair of (111) and $(\bar{1}\bar{1}1)$ planes is 70°32'. Therefore, the resulting polycrystal has a wedge BAB′ with an apex angle of 7°20'. If the two sides of this wedge are brought together they will form a TB while at the same time a positive wedge disclination is created at A, where five TBs terminate (Fig. 2b). Thus, the final configuration has no wedge-like cusp BAB′ but contains a partial disclination of strength $\omega = +7°20'$ which creates inhomogeneous elastic strains and stresses in the polycrystal.

Next, let us consider a hollow DSP, which contains a positive wedge disclination of strength $\omega = +7°20' \approx +0.128$ rad in the quintuple junction of five TBs (De Wit, 1972) as schematically shown in Fig. 3a, where the disclination line is denoted by the black triangle in the top sketch and the dashed line in the bottom sketch. As noted above, the line of positive disclination cannot be a nucleus of fracture. On the other hand, the quintuple junctions of TBs in hollow DSPs and ISPs appear as fracture sources in the SEM images of Fig. 1. Therefore, we assume that the fracture process starts with the nucleation of cracks along the TBs in the vicinity of the disclination line but not at it (Fig. 3b), this being the first stage of fracture in hollow DSPs and ISPs. The second stage involves a process of pattern formation in a fivefold star-shaped crack which also includes the disclination line (Fig. 3c). The transition between these two stages of fracture occurs when the first-stage cracks become large enough to ensure that the tensile stress (strain) concentration at the crack tips prevails over the compressive stress (strain) level near the disclination line and the corresponding stress intensity factor reaches some critical value.

To support our assumption for such fracture development in a hollow DSP by numerics, let us model the DSP as an elastic spherical shell containing an axially symmetric positive wedge disclination. Indeed, the initial shape of hollow DSPs and ISPs imaged in Fig. 1 was