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Mechanical instability of stressed grain boundaries during plastic deformation of zirconium carbide

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ABSTRACT

Grain boundaries are the elementary carriers of mechanical stress and chemical transport in polycrystalline materials. They are responsible for most macroscopic properties of them, particularly the mechanical performance. Most models take into account the ability of grain boundaries to slide each other assuming that surfaces do not suffer any deformation. However, one fact that is normally ignored is the mechanical distortion of flat boundaries under shear stresses. Indeed, such deformation is usually very small to play a significant role on the dynamics of point defects or dislocations. In this work, we will report the presence of a notably mechanical instability of flat boundaries under shear solicitation in zirconium carbide, giving rise to a periodic transversal shift. Such effect is the driving force for dislocation nucleation and annihilation, the main mechanism for high-temperature plasticity in this carbide.

1. Introduction

Plasticity is still a fascinating challenge for physicists and material scientists because it is a multiscale problem which demands description of matter from the atomic scale, the range of atomic bonding, to the mesoscale, the geometrical and topology of grain boundaries and ending at the macroscale, the range at which boundary conditions and shape factor of the piece are essential. Consequently, their rigorous study requires a bottom-up approach [1–4]. At this regard, many theoretical tools and techniques are available for atomistic description (density functional theory (DFT) [5,6], Molecular Dynamics (MD) [7,8], Ab Initio calculations [9,10]). On the contrary, mesoscopic analyses of grain boundaries are restricted to electron microscopic observations of post-mortem specimens [11,12] or pioneering techniques such as phase-field-like simulation codes [13]. Unfortunately, these latter ones cannot capture all the peculiarities of grain dynamics, such as switching, cavitation opening, local dislocation creation and annihilation [11–13].

Among the ceramic systems receiving special attention, ultra-high temperature carbides and nitrides play a central role. Zirconium carbide (ZrC) is one of the ultra-high temperature ceramics (melting point is approximately 3530 °C). Its high hardness (~25 GPa) and elastic modulus (~390 GPa), combined with a relatively low density (6.63 g/cm^3), makes this material particularly promising for thermomechanical applications at high temperatures. Furthermore, its elastic properties, together with the creep and corrosion resistance make this material suitable for many applications, such as crucibles, jet engines or supersonic vehicles. Due to the presence of metallic bonding, ZrC has thermal and electrical conductivities that are comparable to those of the metal zirconium [14–18]. ZrC has many of the general features exhibited by the monocarbides of the transition metals of the fourth and fifth groups. It is isomorphous with the other monocarbides having the NaCl-type structure and also exists over a wide range of carbon-deficient compositions [19].

Previous studies on the high-temperature plastic deformation of ZrC showed several features common with the structural changes occurring during the deformation of metals: dislocation glide with stress relaxation through dislocation climb and simultaneously the formation of a cellular structure with transition from the operation of a single slip system into the operation of multiple systems facilitating transverse slip. It is proposed in literature that the plastic deformation in this carbide is controlled by the diffusion of carbon and that carbon diffusion-assisted dislocation glide is the most

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probable rate-controlling deformation mechanism. However, the processes of grain boundary sliding and rotation of the grains can also accommodate plastic deformation and gives rise to the formation of intergranular pores at high temperatures [20–23].

This classical view presents a weakness: dislocations are usually emitted by Frank-Read sources located in the grain lattice. Since the observed dislocation density is concentrated in small regions of the grain, an elementary calculation can show that the critical stress for dislocation emission for sources of realistic size ($d < 100$ nm) in ZrC is too large to explain the low values of the applied stress required for plastic deformation. This paper reports the presence of mechanical instabilities of large periodicity along the sheared grain boundaries. The origin of these ones is modelled in the frame of classical theoretical approaches for analysis of the surface roughening (such as the Asaro–Tiller–Grinfeld instability of solid surfaces) and the correlation with superplasticity [24,25]. The surface roughening is responsible for the appearance of local stresses. These stresses drive dislocation emission to the bulk.

2. Experimental procedure

ZrC ceramics were prepared using a procedure described in Ref. [26]. Zirconium carbide powders (Grade B, H.C. Starck, Goslar, Germany) with an average particle size of 3–5 μm were considered. These powders were mechanically ball-milled in air with an equipment (SPEX 8000D, Spex CertiPrep, Metuchen, United States) having WC balls (6.7 mm in diameter; charge ratio of 4) for 3 h. The so-prepared powders were sintered to get a fully-dense polycrystalline specimen by spark plasma sintering (Dr. Sinter, Kanagawa, Japan) at 1900 °C for 5 min. The heating ramp was set as 100 °C/min and the uniaxial pressure of 75 MPa was applied upon heating and released at the end of the holding time.

Specimens were cut into parallelepipeds of $2.5 \times 2.5 \times 5.0\ mm^3$ and subjected to uniaxial compression creep testing using a method and equipment described elsewhere [27,28]. Two pads of the same materials were used between the testing samples and the silicon carbide rams to avoid indentation of the rams during deformation. The specimens were deformed inside one furnace of tungsten heating element under argon atmosphere. The applied stress (σ) was in the range of 40–95 MPa at temperature (T) in the range 1600–1650 °C. In this condition, the strain rates were always within the 10^{-7}–$10^{-5}\ s^{-1}$. After concluding the tests, the temperature was cooled down very fast (100 °C/min) while keeping the load on the tested specimen until the temperature was below 700 °C. This procedure avoids dislocation annihilation at the grain boundaries during cooling.

Steady state creep rate was fitted to the applied stress and temperature according to the classical Dorn equation [29]:

$$\dot{\varepsilon} = A\sigma^n \exp\left(-\frac{Q}{kT}\right) \quad (1)$$

In this equation, $\dot{\varepsilon}$ is the creep rate, σ is the applied stress, k is the Boltzmann constant, T is the temperature and n, Q are parameters commonly-named as the stress exponent and the activation energy, respectively. The constant A is just a fitting parameter.

The values of n and Q determine the deformation mechanism together with the microstructural observations, which should be consistent with the proposed mechanism. These values were measured after sudden changes (jumps) of either the stress or the temperature, keeping the other quantity constant.

The post-mortem specimens were characterized using scanning electron microscopy (SEM, S5200, Hitachi, Japan). The SEM observation were done on polished surfaces that where chemically etched for 3 min using $HF:HNO_3:H_2O$ solution in a volumetric ratio of 1:1:3. More detailed observations were made using a transmission electron microscopy (TEM) (H-800, Hitachi, Japan) operated at 200 kV. The TEM specimens were prepared using the conventional method involving successive steps of mechanical thinning, dimpling and ion beam milling.

3. Results

Fig. 1 shows a typical strain-rate versus strain test at different stress and temperature conditions. Steady state deformation rates were measured after a very short transient regime. The values of both the stress exponent and the activation energy are given in the plot after each jump. In Fig. 1, the total deformation is ~25% at the end of the creep test, where the deformation is homogeneous and the specimen remains intact. At constant temperature ($T = 1600$ °C) the steady state strain rates follows a classical power law dependence with the applied stress. The results show that the stress exponent n is approximately $n = 3.5 \pm 0.5$ (Fig. 2). With respect to the activation energy, it can be fitted to a constant value $Q = 616 \pm 12$ kJ/mol.

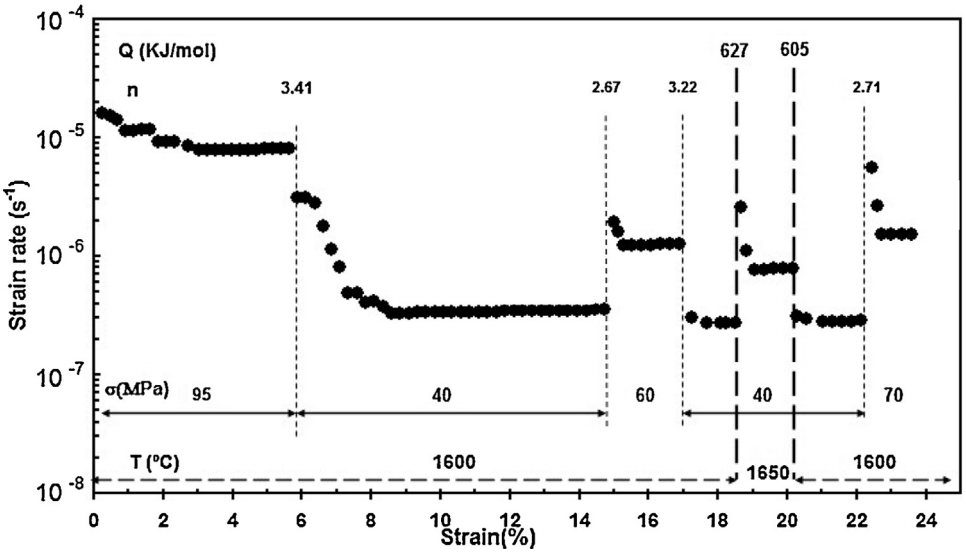

Fig. 1. Strain rate versus strain creep test at 1600–1650 °C. The values of the stress exponent and activation energy determinations after discontinuous change of stress or temperature are given at the transition line between stages.