Pop-in characteristic induced by nanoindentation in ZrB$_2$-SiC composites

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Abstract—In this research, instrumented nanoindentation tests were performed to determine the mechanical properties associated with pop-in events of the ZrB$_2$-SiC composites reinforced with and without the mixture of boron nitride nanotubes (BNNTs) and boron nitride nanoplatelets (BNNPs). The results show the sintered ZrB$_2$-SiC and (BNNT-BNNP)/(ZrB$_2$-SiC) composites have typical pop-in event, and the added mixture of BNNTs-BNNPs increases the critical load at pop-in, initial penetration depth and pop-in excursion at pop-in event. Moreover, the computed shear strength at which pop-in occurs increases with the mixture of BNNTs-BNNPs, which might be ascribed to Orowan-type strengthening effect. The indentation stress-strain curves of these ZrB$_2$-SiC composites were also reconstructed. This research is expected to facilitate a better understanding of the microscopic plastic deformation behavior of ZrB$_2$ and its composites.

Keywords—ceramic matrix composites; boron nitride nanotubes; toughness; spark plasma sintering

I. Introduction

ZrB$_2$-SiC, as an important member of ultrahigh-temperature ceramics (UHTC), has been considered a potential candidate material for aerospace applications because of its excellent combination of good oxidation resistance, low density, extremely high melting point and high hardness [1-3]. Nevertheless, low toughness-induced poor thermal shock resistance of ZrB$_2$-SiC composites still restrict their practical and potential applications [4]. Therefore, considerable efforts have been devoted to developing ZrB$_2$-SiC composites reinforced with graphite flakes [5], ZrO$_2$ particles [6], carbon fibers [7] and carbon nanotubes [8], in which carbon nanotubes are promising nanofillers in the ceramic matrix to improve fracture toughness due to their mechanical properties. However, the low starting oxidation temperature of CNTs (~ 400℃) [9] might degrade the mechanical properties of ZrB$_2$-SiC composite at elevated temperatures. By contrast, boron nitride nanotubes (BNNTs), a structural analogue of CNTs, not only possess excellent mechanical properties comparable to those of CNTs, but also exhibit higher starting oxidation temperature of BNNTs (~900℃) [10], which is expected to guarantee less degradation of high-temperature performances of the BNNT/(ZrB$_2$-SiC) composite. Also, the addition of soft and ductile BN platelets has been proven to be an attractive option to toughen brittle ceramics [5, 11]. More recently, the fracture toughness of ZrB$_2$-SiC composite reinforced with a mixture of boron nitride nanotubes (BNNTs) and boron nitride nanoplatelets (BNNPs) increases by up to 24.4% (from 3.73±0.11 to 4.64±0.36 MPa m$^{1/2}$) at 1.0% (BNNT-BNNP) weight fraction in our previous research [11].

Nanoindentation has been widely employed to provide valuable insights into the response of materials during deformation. On nanoindentation loading, distinct displacement burst on the load-displacement curve is commonly referred to as a pop-in event, which usually represents the sudden yielding of a tested material [12]. It is observed in crystalline materials are usually associated with the onset of plasticity, i.e., a sharp transition from purely elastic to plastic deformation. On a macroscopic scale, it is well known that the mechanical properties of a crystalline material often exhibit size-independent behavior. However, the local properties of a material tested through nanoindentation become depth and location dependent due to local variations in the internal material structure and the inhomogeneous deformation strain of the indentation, and the local properties of materials are totally different from those on a macroscopic scale. To the knowledge of the authors, there is little information on the microscopic mechanical response of ZrB$_2$ ceramics available in the literature.

In view of the present scenario, the aim of this research is to investigate the pop-in characteristic and its related micromechanical properties of ZrB$_2$-SiC composites reinforced with the mixture of boron nitride nanotubes (BNNTs) and boron nitride nanoplatelets (BNNPs) using nanoindentation, and the effects of the added BNNTs-BNNPs on the pop-in event were also elucidated.

II. Experimental

ZrB$_2$ powders with a size of ~2 μm (Wuxi Yu Long Electronic materials Co. Ltd., China) and nanosized SiC particles with a size of ~40 nm (predominately α-SiC, purity > 99%, Nanjing Emperor Nano Material Co. Ltd., China) were selected as starting precursors. The mixture of BNNTs-BNNPs was purchased from Xian Feng Nano Material Co. Ltd., (Nanjing, China), in which the diameter of BNNTs ranges from

several tens to hundreds of nanometers and the thickness of BNNPs is several tens nanometers. The powders of ZrB_2 and 20vol.% SiC were firstly mixed in ethanol using Si_3N_4 milling balls with a rotation rate of 300 rpm until 12 h. Then, the mixture of BNNTs-BNNPs were mixed with (ZrB_2-SiC) mixture in ethanol using Si_3N_4 milling balls with a rotation rate of 300 rpm for another 12 h. The three material compositions chosen here were ZrB_2-20vol.%SiC, 0.5 wt.% (BNNT-BNNP) /(ZrB_2-20vol.%SiC) and 1.0 wt.% (BNNT-BNNP) /(ZrB_2-20vol.%SiC), hereafter denoted as ZS, ZS-5BTP, and ZS-10BTP, respectively. After fully dried in an oven at 120℃, the resulting powders were loaded into a 20 mm graphite die and sintered under vacuum in SPS apparatus (Dr. Sinter 1050, Sumitomo Coal Co. Ltd., Japan) at 1550℃ and 40 MPa for 8 min. A heating rate of 150℃/min was employed to reach 1450℃, and 1550℃ was attained in the next 1 min.

Nanoindentation tests were conducted on the polished top surface of the sintered samples using NHT2 nanoindentation test system (CSM instrument, Switzerland) with a Berkovich tip, the load was applied up to a peak of 10 mN in 30s, where it was held for 10s, and then unloaded completely in 30s. In this research, 20 individual indentations were performed at 20 separate locations where the distance between the adjacent indentation marks was at least 10 μm. Also, the indenter tip radius R was evaluated by performing 0.1 mN load indentation test on a standard fused silica specimen, in which elastic modulus and Poisson's ratio of silica and diamond indenter were taken as 72 GPa and 1141 GPa, 0.17 and 0.07, respectively. Hence, the estimated tip radius was (205±23) nm as averaged on 15 tests. Nanoindentation residual marks were observed through optical micrography (OM, Shanghai Taiming Optical Instrument Co. Ltd.).

III. RESULTS AND DISCUSSION

Fig. 1a shows the typical OM image of nanoindentation residual marks (marked by white circles), and there are no obvious cracks observed. Also, it is clear that the granular SiC with a size of ~1-4 μm distribute uniformly in ZrB_2 matrix with an average grain size of ZrB_2 is ~2-4 μm [13]. Moreover, the distance of adjacent residual marks is about 10 μm, implying that each indentation distributes in different ZrB_2 grains.
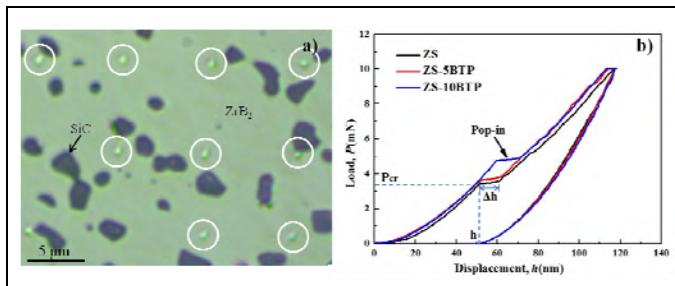

Fig. 1. OM image of typical nanoindentation residual marks a), and typical P-h curves with pop-in phenomenon on ZS, ZS-5BTP and ZS-10BTP composites b).

Representative nanoindentation load-displacement curves with typical pop-in characteristics on ZS, ZS-5BTP and ZS-10BTP samples are depicted in Fig. 1b, in which the critical

load at pop-in (P_{cr}), initial penetration depth (h), and pop-in excursion (Δh) were marked. It is evident that the values of P_{cr}, h and Δh at pop-in increase with the addition content of BNNTs-BNNPs mixture. The average parameters of critical load at pop-in, initial penetration depth and pop-in excursion for these sintered composites were listed in Table I. Also, statistical distributions of measured critical loads of the three composites are shown in Fig. 2a. The scatter of P_{cr} could be ascribed to the difference in the mechanical properties of ZrB_2 grains due to grain orientations, the surface defects, grain boundary and so on. As compared with ZS sample, it is evident from Fig. 2a that the main peaks of P_{cr} for ZS-5BTP and ZS-10BTP increase to ~3.90 mN and ~4.90 mN, respectively, strongly indicating that the addition of BNNTs-BNNPs could enhance the critical load which is necessary for pop-in event in the (BNNT-BNNP)/(ZrB_2-SiC) composites. As can be seen in Fig. 2b, a plot showing the critical load at pop-in as a function of pop-in excursion for each sample, it is clear that critical load at pop-in increases with the pop-in excursion. It is also interesting to note that the range of pop-in excursion increase with the addition of BNNTs-BNNPs mixture.
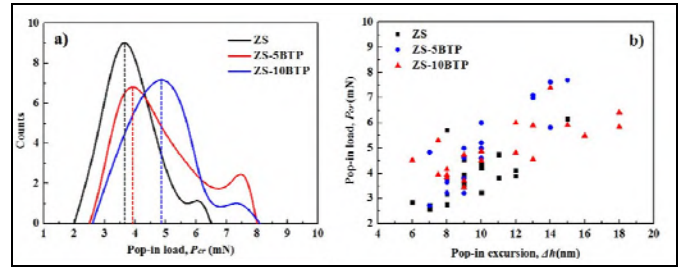

Fig. 2. Distribution curves of critical loads at pop-in events a) and variation of critical loads as a function of pop-in excursion in ZS, ZS-5BTP and ZS-10BTP composites b).

It is well known that the most widely accepted explanation of pop-in is homogeneous dislocation nucleation due to the fact that the shear stress at which pop-in occurs matches well with the theoretical shear strength of the tested material, and pop-in event can be used to mark the initiation of dislocation motion that occurs upon the onset of plastic deformation. On the basis of Hertz elastic contact theory, when a spherical tip indenter presses into the flat surface material, the critical load (P_{cr}) and the maximum shear stress (τ_{max}) satisfy the following equations [14]:

$$\tau_{max} = 0.31 P_0 \tag{1}$$

$$P_0 = \left(\frac{6 P_{cr} E^{*2}}{\pi^3 R^2} \right)^{1/3} \tag{2}$$

where, P_0 is the maximum pressure underneath the indenter tip, P_{cr} is the main peaks of critical load at pop-in, R is the spherical radius of Berkovich indenter tip, E^* is the reduced elastic modulus of the tested composite and diamond tip. According to the equation (1) and (2), the maximum shear stresses of ZS, ZS-5BTP and ZS-10BTP composites were calculated, as shown in Fig. 3. To further examine the yielding

of sintered samples, the theoretical shear strength of ZrB_2 (39-41 GPa) [15] was compared to the maximum shear stress of each sample induced under the indenter. The range of the maximum shear stress reflects that the range of critical loads at which pop-in events was observed to occur for each sample. As can be seen in Fig. 3, most of the computed maximum shear stresses of the three composites are higher than that of the theoretical shear strength of ZrB_2, but also the added mixture of BNNTs-BNNPs slightly increases the shear strength of the sintered ZrB_2-SiC composites. As reported in our previous research [11], the fracture toughness of a ZrB_2-SiC composite increases by up to ~24.4% (from 3.73±0.11 to 4.64±0.36 MPa m1/2) at 1.0% (BNNT-BNNP) weight fraction. Hence, it is clear that the added mixture of BNNTs-BNNPs is expected to significantly improve the toughness of ZrB_2-SiC composites without comprising its mechanical strength.

TABLE I. POP-IN PARAMETERS AND MECHANICAL PROPERTIES OF (BNNT-BNNP)/(ZrB_2-SiC) COMPOSITES

	P_{cr} (mN)	h (nm)	Δh (nm)	E^* (GPa)	τ_{max} (GPa)
ZS	3.67±2.2	51±8.1	9.4±4.5	360±30.2	40±6.7
ZS-5BTP	3.84±2.7	54±9.5	10.2±5.5	358±32.8	41±8.5
ZS-10BTP	4.90±2.5	61±7.6	11.1±4.4	356±33.8	45±6.7

In the cooling process after sintering of these (BNNTs-BNNPs)/(ZrB_2-SiC) composites, we can expect BNNTs and/or BNNPs are in residual compression and ZrB_2 grains in residual tension owing to the fact BNNTs and BNNPs exhibit much smaller coefficient of thermal expansion (CTE) values than those of ZrB_2(~6.7×10-6 K^{-1}) and SiC (~4.3×10-6 K^{-1}) [16], respectively. Moreover, theoretical analysis has shown the highly localized residual stresses in the vicinity of these nanofillers would be larger enough to create the dislocations [17, 18]. Hence, the pre-existing dislocations would form in the close vicinity of these BNNTs and/or BNNPs in the ZrB_2-SiC composites during the process cooling from the processing temperature. It is well known that ZrB_2 combines a mixture of covalent, metallic and ionic bonds. As compared with conventional ceramics, ZrB_2 crystal is believed to yield much through plastic deformation associated with the dislocation movement before failure. Some of these pre-existing dislocations around the BNNTs and/or BNNPs can move and disperse into the matrix in the process of further plastic deformation due to the presence of metallic bonds, and most of these dislocations are sessile at the room temperature owing to predomination of covalent bonds in the ZrB_2 crystal structure. These sessile dislocations restrict the movement of both these movable dislocations and the newly formed dislocations. Therefore, they would form loop-like configuration around the nanofillers [19], which is similar to the Orowan loops formed around the nanoparticles in metal matrix nanocomposites when the dislocations by-pass these nanoparticles on the slip plane. Such a dislocation configuration leads to an assumption that the Orowan-type strengthening the effect might be operative.
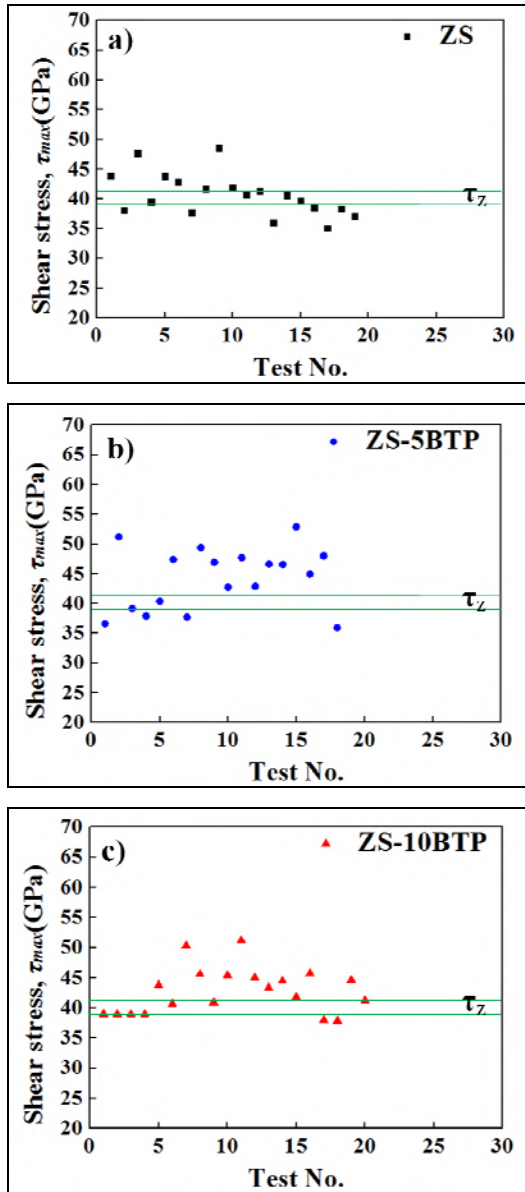

Fig. 3. Computed maximum shear stresses of a) ZS, b) ZS-5BTP and c) ZS-10BTP, in which the green lines represent the upper and low limits of ZrB_2 theoretical shear strength.

IV. CONCLUSION

Pop-in characteristics and related mechanical properties of the (BNNT-BNNP)/(ZrB_2-SiC) composites were investigated using instrumented nanoindentation tests. The results show the sintered ZrB_2-SiC and (BNNT-BNNP)/(ZrB_2-SiC) composites have typical pop-in event, and the added mixture of BNNTs-BNNPs increases the critical load at pop-in, initial penetration depth and pop-in excursion at pop-in event. Moreover, the computed shear strength at which pop-in occurs increases with the mixture of BNNTs-BNNPs, which might be ascribed to Orowan-type strengthening effect.

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