



ENHANCING SUPERPLASTICITY OF ENGINEERING CERAMICS BY INTRODUCING BN NANOTUBES

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1 Introduction

Introducing carbon nanotubes (CNTs) into polymer or ceramic matrices has been a promising approach to obtain ultra-strong, extra-toughened materials as well as multifunctional composites. Most of the previous work on CNT composites has focused on strengthening and toughening of matrix materials at ambient conditions. However, there is *hitherto* a lack of information on mechanical behavior of these composites at elevated temperature. Recently, single-walled CNTs were found to undergo a superplastic deformation with an appealing 280% elongation at a high temperature (Huang J. Y.; Chen S.; Wang Z. Q.; Kempa K.; Wang Y. M.; Jo S. H.; Chen G.; Dresselhaus M. S.; Ren Z. F. *Nature*, **2006**, 439, 281.). This discovery implies the high probability for the potential usage of CNTs as reinforcing agents in engineering high-temperature ceramics with an improved ductility.

Here, for the first time, we demonstrate that a small addition of boron nitride nanotubes (BNNTs) can dramatically enhance a high-temperature superplastic deformation (SPD) of engineering ceramics. More specifically, 0.5 wt% addition of BNNTs leads to an inspiring brittle-to-ductile transition in Al₂O₃ ceramics even at a moderate temperature (1300 °C). For Si₃N₄ ceramics, 0.5 wt% addition of BNNTs could also decrease the true stress by 75% under

the same deformation conditions. In contrast, addition of micro-sized or nano-sized BN powders has no or negative effect on the superplasticity of these ceramics. The underlying SPD-enhancement mechanism is discussed in terms of inhibition of static and dynamic grain growth of matrix and energy-absorption mechanism of BNNTs. The unraveled capability of BNNTs to enhance the SPD behavior will make BNNTs promising components in cost-effective complex ceramics with good comprehensive mechanical properties.

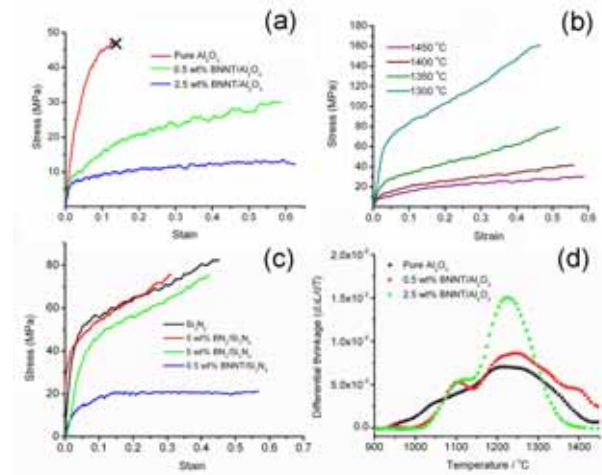
2 Results and discussion

2.1 superplastic deformation

SPD was performed on a machined 5×3×2.5 mm³ sample. Compressive force was applied on a 3×2.5 mm² sector at a constant crosshead-displacement-rate and released when a shrinkage reached half of the initial height (2.5 mm), as described in detail elsewhere. Obviously, under a constant strain rate of 10⁻⁴/s pure alumina ceramics underwent an elastic deformation at the beginning, but readily cracked when a true strain had reached 0.1 at 1450 °C. The fracture surface of the deformed pure alumina sample disclosed that Al₂O₃ grains obeyed dissolution-precipitation rule and dynamically grew to huge rough agglomerates via GB sliding. Cavitation was also evidently prevailing. If these cavities are not effectively accommodated through GB diffusion and/or grain dislocation, cavities would be transformed

into penetrable cracks and ultimately break the ceramics. In other words, accommodation length that proportional to a grain size dynamically mounted up in pure Al_2O_3 ceramics, which made ceramics brittle and incapable of superplastic deformation. More intriguingly, the deformation feature of Al_2O_3 ceramics is qualitatively changed via addition of BNNTs. The 0.5 wt% BNNT/ Al_2O_3 composite shows excellent SPD behavior with the true stress of only 7.5 MPa at 1450 °C. Because the strain rate increases during deformation tests due to a decreasing specimen height, the true stress under the initial strain rate is defined as the intersection of two lines extrapolated to the elastic and the plastic strain regions on the stress-strain curves. The true stress at 1400 °C is 14 MPa, which is only one third of reported value of a 10 vol% $\text{ZrO}_2/\text{Al}_2\text{O}_3$ composite (about 42 MPa). Moreover, it is striking to observe that the SPD behavior in 0.5 wt% BNNT/ Al_2O_3 composite is maintained even at a temperature as low as 1300 °C which is the lowest deformation temperature reported for alumina ceramics. Assuming stress exponent n is 2, an activation-energy of 298 ± 63 kJ/mol was obtained from plotting of the $\ln \dot{\epsilon}-1/T$ relationship. This value is far below the reported activation energy (600-800 kJ/mol) for alumina-based composites whose SPD behaviors were controlled by the diffusion and defect mechanism. It is also worth noting that besides a reduced initial grain size in the 0.5 wt% BNNT/ Al_2O_3 composite, the dynamic grain growth during deformation is also markedly suppressed accompanied with the minimized cavitation. Therefore, the accommodation length evolution was favorably slow to match the SPD processes, such as grain rotation, grain boundary sliding and grain boundary diffusion. Although there still presents abnormally-grown alumina grains, as reflected by the strain-hardening phenomenon (stress increases along with strain) and displayed by the strain-stress curve, surrounding small grains would act as fluidic balls that can promote the accommodation of cavities formed by the large grains sliding or rotation. The 2.5 wt% BNNT/ Al_2O_3 composite exhibits the similar low

true stress (7.1 MPa) at 1450 °C, but the strain-hardening phenomenon is largely alleviated.



2.3 SPD enhancement mechanism

First, the underlying attribution of BNNTs to superplasticity is due to their role in the suppression of static grain growth during a sintering stage, as displayed by the BNNT/ Al_2O_3 composite. This effect is owing to evenly distributed BNNTs located on the GBs of ceramics that effectively obstruct the mass transport between adjacent ceramic grains. Secondly, the imbedded BNNTs in the composites could dissipate the concentrated stresses during the superplastic deformation, which would further inhibit the dynamic grain growth when composites are under compressive stress at high temperature. Thirdly, a BNNT would be an efficient absorber of strain energy accumulated during the deformation. Distorted (bent, tense and twisted) BNNT layers during the deformation would be broken down and exposed the inner BNNT shells when the stress is over the threshold strength.

3 conclusion

In summary, the present results show that a small addition of BNNTs (especially 0.5 wt %) will make typical engineering ceramics, such as Al_2O_3 and Si_3N_4 , readily much more moldable at a high temperature while their other characteristic properties are not altered. On the contrast, BN micro- or nano-sized powders were found to be not beneficial for the superplastic deformation behavior.