"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Nanocomposites"

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Nanocrystalline TiN Processing and Properties

With careful powder handling procedures and processing, the nanocrystalline TiN powders produced in our novel reactor undergo tremendous densification at 1400°C in a simple, pressureless sintering process to produce dense (99%) TiN materials [1]. In this quarter, efforts were devoted to microscopy studies of the nanocrystalline TiN to demonstrate that the mechanical properties are influenced by the ceramic microstructure [2]. Long ion milling times were required in order to prepare TiN samples for transmission electron microscopy due to the extreme hardness of this advanced ceramic material.

As shown in the previous report, the hardness values of the nanocrystalline TiN are among the highest reported in the literature [1]. Table 1 compares mechanical properties of TiN ceramics prepared using three different handling procedures: (1) pressureless sintering after exposing the TiN powders to air (EXP), (2) pressureless sintering while avoiding air exposure until after a pre-sintering step at 800°C (UN800), and (3) hot isostatic pressing (HIP) at 200 MPa without air exposure until final densification has been accomplished [3]. In all cases the sintering temperature was 1400°C.

Table 1. Mechanical properties of TiN sintered at 1400°C.

Sample	Hardness (GPa)	Fracture Toughness (MPa $m^{1/2}$)
EXP	15.7 ± 0.7	–
UN800	23.2 ± 1.9	4.0 ± 0.2
HIP	22.4 ± 1.5	4.2 ± 0.2

The hardness results indicate that there was a clear benefit to avoiding exposure to air prior to pre-sintering at 800°C, but that there was no improvement with the use of applied pressures up to 200 MPa. Figure 1 shows a SEM image of an EXP sample which had significant amounts of a second phase which was determined by EDAX to be oxygen-rich. The second phase was dispersed throughout the sample in small regions (20-100 nm) or larger regions (500-1000 nm), and substantial cracking was apparent at the interfaces. The phase segregation and cracking are likely responsible for the lower hardness value for the EXP sample.

Transmission electron microscopy (TEM) images of the UN800 and HIP samples are shown in Figures 2 and 3. Both preparations produced TiN materials that are fully dense (i.e., with no observable pores) by 1400°C without the need of sintering additives. The sample underwent normal grain growth during sintering, producing equiaxed grains of consistently ultrafine crystal sizes. Grain sizes were 140±15 nm for the UN800 sample and 155±20 nm for the HIP sample. High-resolution electron microscopy (HREM) images of these sintered TiN materials are presented in Figures 4 and 5. These micrographs clearly show the sharpness of the interfaces between grains. There were no observable glassy phases at the grain boundaries or triple junctions, which often result from the use of oxides added as sintering aids. Glassy interfaces are often the cause of diminished mechanical properties, especially at high tempertures. The use of nanocrystalline starting powders and careful handling procedures have eliminated the need for sintering aids, enabling densification to occur at a relatively low temperature of 1400°C. The resulting high-purity TiN materials with ultrafine microstructure give rise to outstanding properties, such as high hardness for structural applications.

A comparison of samples HIPed at different temperatures demonstrated that the application of pressure during sintering did not induce full densification at temperatures lower than 1400°C. Figures 6 and 7 are scanning electron micrscopy (SEM) images of TiN HIPed at 200 MPa at 1350°C and 1400°C, respectively. The grain size of the 1350°C sample is 80 nm, compared to 155 nm in the 1400°C sample. However, the 1350°C sample is less than 95% dense, while the 1400°C sample is 99% dense. The pressure dependence of sintering behavior can be explained by examining the driving force for the final stages of densification:

$$DF = (2\gamma/\rho + P_{app}/\delta) \quad (1)$$

where γ is the surface energy, ρ is the pore radius, P_{app} is the applied pressure, and δ is the density relative to theoretical. Where ρ=2.15 nm, for typical values of γ=1 J/m^2, P_{app} =200 MPa, and δ=0.90, the first term ($2\gamma/\rho$) is 930 MPa while the second term (P_{app}/δ) is only 222 MPa. The small particle size and non-agglomerated nature of the starting powders produce compacts with a narrow size distribution of ultrafine pores. These characteristics cause the surface energy term to dominate the densification driving force throughout the entire range of densification, obviating the need for applied pressure. Most importantly, as the material nears full density and the pore size shrinks to zero, the surface energy term increases while the applied pressure term decreases [4]. Consequently, it is not necessary to apply pressure to our TiN to achieve full densification at 1400°C. We obtain similar densities and grain sizes by pressureless sintering or by HIPing. For conventional materials with particles in the 1 μm size range, the applied pressure would be the controlling factor in densification.

The microstructure and interfacial chemistry of the UN800 TiN were further examined using scanning transmission electron microscopy (STEM). Equipped with a windowless X-ray detector that has very high geometrical efficiency, STEM provides exceptional X-ray microanalytical capability with superb imaging resolution (1.4 Å). It was used to determine the composition of grains and grain boundaries in the sintered UN800 sample. We found no distinct variation in the composition throughout the sample. Such compositional uniformity and absence of oxide-containing interface will lead to superior mechanical properties and thermal stability, which are subjects of future studies.

Summary

Microscopy studies of nanocrystalline TiN produced in our laboratory and densified through a pressureless sintering process show a consistent ultrafine microstructure with grains of 140 nm and no glassy intergranular or secondary phases. Comparison of nanostructured TiN ceramics processed by different methods demonstrates that there is a clear benefit to avoiding exposure of the starting powders to air, but that pressure application during sintering (e.g., by HIPing at 200 MPa) was not necessary to achieve full densification at 1400°C. STEM analysis of a fully-dense UN800 TiN ceramic found no oxygen-rich regions in the grains or grain boundaries.

References

[1] J.Y. Ying, ONR Technical Report, June 30, 1997.

[2] D.T. Castro and J.Y. Ying, "Microstructure and Mechanical Properties of Nanocrystalline Titanium Nitride," to be submitted to *J. Am. Ceram. Soc.*

[3] D.T. Castro and J.Y. Ying, "Processing and Densification of Nanocrystalline Titanium Nitride," to be submitted to *J. Am. Ceram. Soc.*

[4] D.T. Castro, "Synthesis, Processing, and Properties of Nanocrystalline Nitrides," Sc.D. Thesis, Massachusetts Institute of Technology, Sept. 1997.

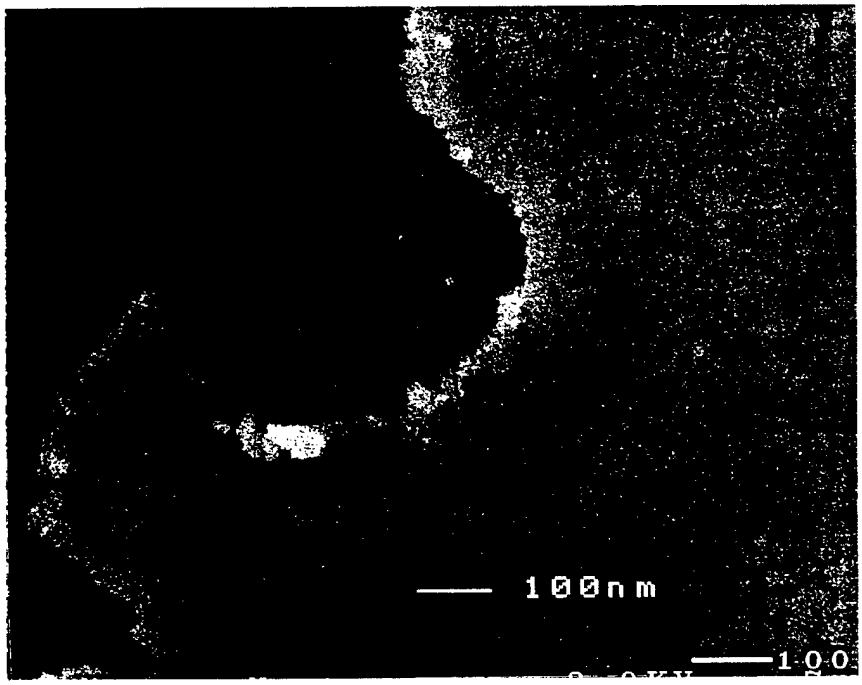

Figure 1. SEM image of nano-TiN EXP sintered at 1400°C.

Figure 2. TEM image of nano-TiN UN800 sintered at 1400°C.

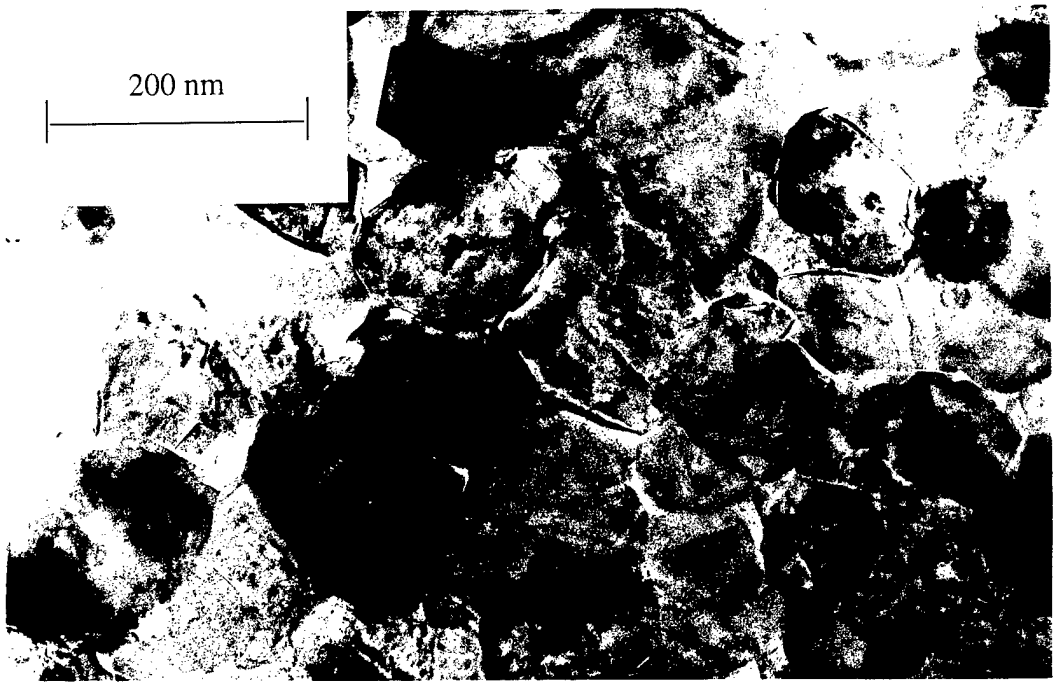

Figure 3. TEM image of nano-TiN HIPed at 1400°C, 200 MPa.

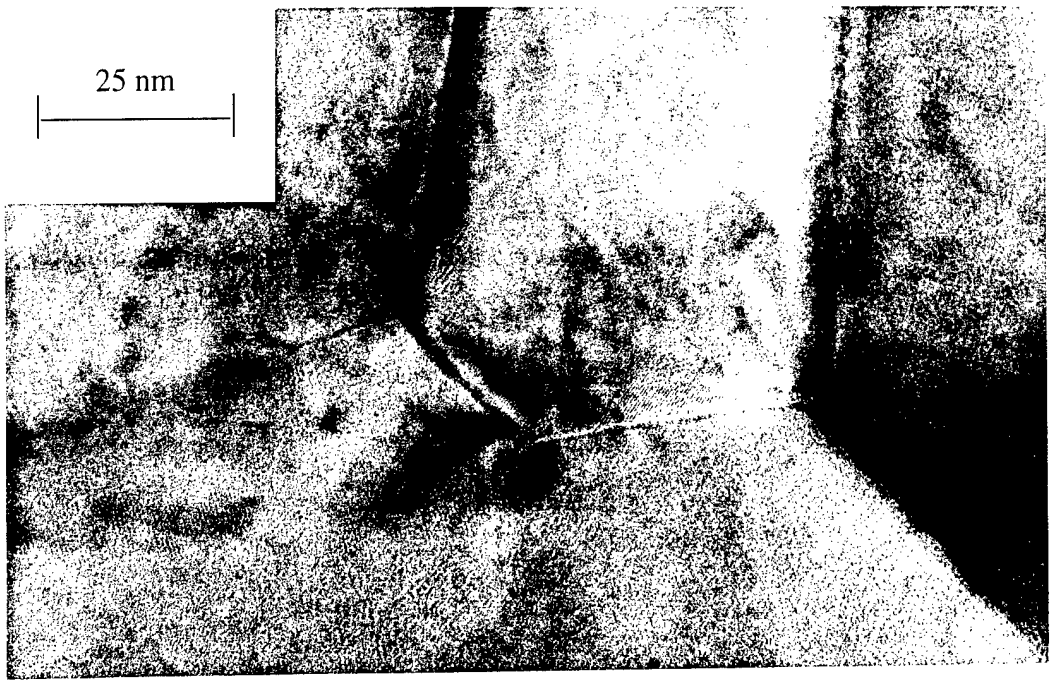

Figure 4. HREM image of triple junctions in nano-TiN UN800 sintered at 1400°C.

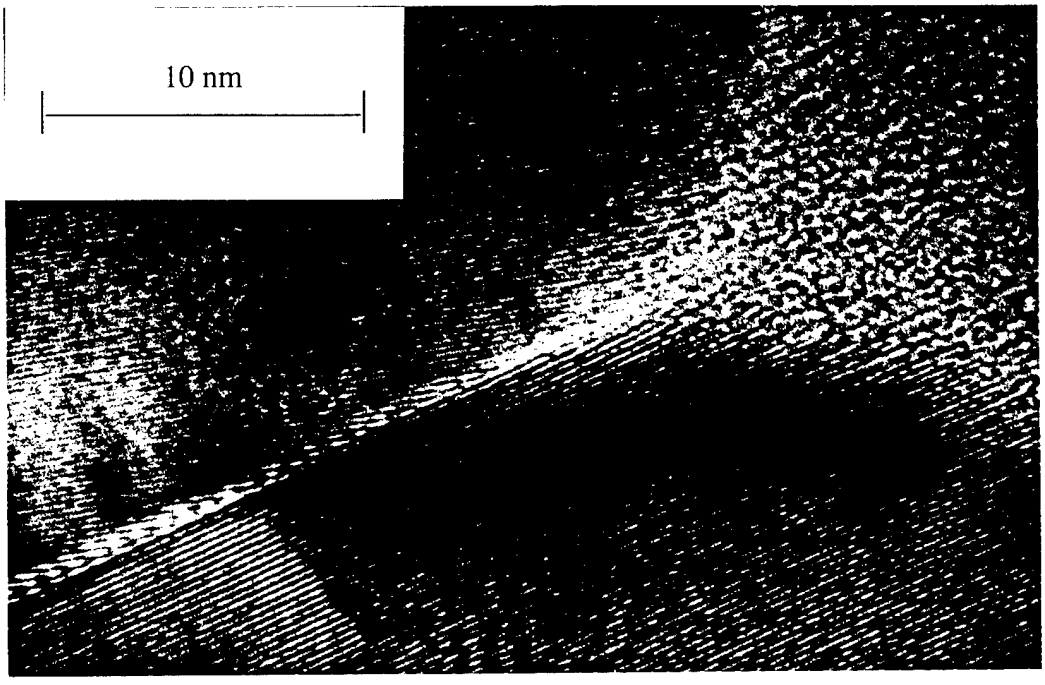

Figure 5. HREM image of intersection of grains with (111) and (200) orientations in nano-TiN UN800 sintered at 1400°C.

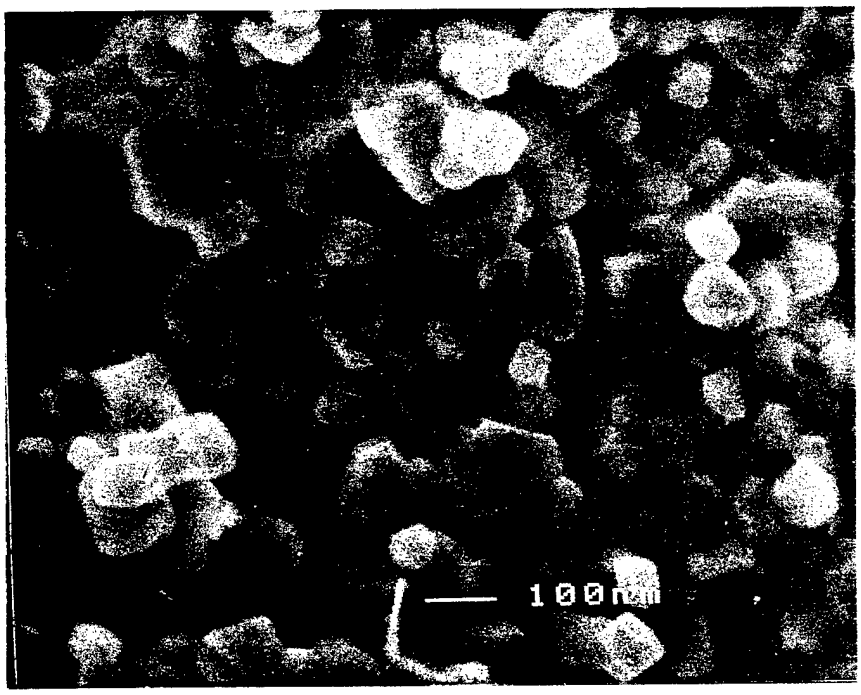

Figure 6. SEM image of nano-TiN HIPed at 1350°C, 200 MPa (<95% dense).

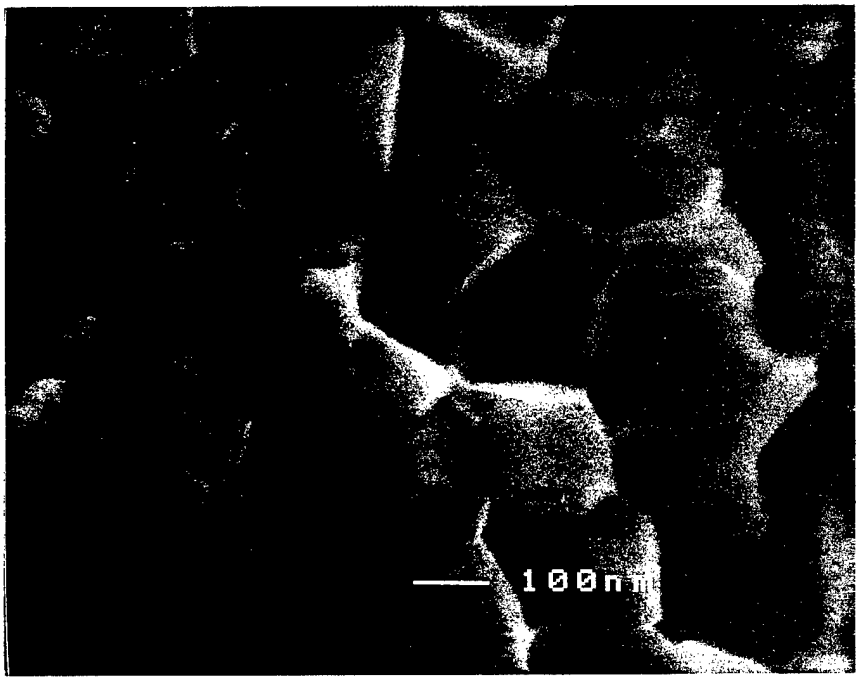

Figure 7. SEM image of nano-TiN HIPed at 1400°C, 200 MPa (99% dense).

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13. ABSTRACT *(Maximum 200 words)*

This report describes the microstructural characterization of nanocrystalline titanium nitride (TiN) produced in our forced flow reactor. Microscopy studies of TiN densified through a pressureless sintering process show a consistent ultrafine microstructure with grains of 140 nm and no glassy intergranular or secondary phases. Comparison of TiN ceramics processed by different methods demonstrates that there is a clear benefit to avoiding exposure of the starting powders to air, but that pressure application during sintering (e.g., by HIPing at 200 MPa) was not necessary to achieve full densification at 1400°C. STEM analysis of a fully-dense UN800 TiN ceramic found no oxygen-rich regions in the grains or grain boundaries.

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