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Nanocomposite films of ZrN-Me (Me=Ag, Au, or Pd) were produced by reactive unbalanced magnetron sputtering and were found to form a dense and homogeneous microstructure whereby nanocrystals of Me are distributed evenly throughout the ZrN matrix. Interestingly, the Young's modulus was found to decrease much more dramatically with the increase in metal content for the ZrN-Ag system. A systematic *ab initio* study was undertaken to understand the mechanism of grain boundary sliding in these nanostructures. The maximum energy variation during the sliding was found to be the largest and the smallest for ZrN-Pd and ZrN-Ag, respectively. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2164391]

Grain boundary sliding was suggested by numerous researchers as a mechanism for improving ductility and providing super-plasticity of single phase ceramic nanocrystalline materials.[1–4] It is defined to be the relative displacement of two neighboring constituent grains in a direction parallel to the boundary interface.[5] It is a very complex phenomenon that strongly depends on the nature and the structure of the boundaries involved.

In the last five years, nanocomposite protective films have gained popularity among researchers because of their superior mechanical properties compared to the traditional single-phase films.[1,6,7] Most of the work, however, concentrated on the synthesis and characterization of these materials. For example, no systematic investigation has been carried out to understand the role of the interface in influencing the mechanical properties of these materials. From an experimental perspective, our knowledge of the interface and of the phenomena that occur during loading is very limited. This limitation is due to the lack of resolution of experimental techniques and by the fact that only fully relaxed structures can be observed.[8] However, computer simulations based on *ab initio* techniques offer the ability to examine details present at the microscopic scale that are not available experimentally. The techniques provide a reliable and an accurate description of the structural and electronic properties of these materials and provide an effective alternative to experimental observations. The only drawback to the *ab initio* approach is the fact that large scale investigations are precluded. Experimental and computational techniques may be utilized in tandem in order to understand the factors that affect the mechanical properties of these materials.

This paper reports on an attempt to understand and correlate the effect of grain boundary sliding on the mechanical properties of ZrN-Me (Me=Ag, Au, and Pd) nanocomposite thin films. These films were deposited by unbalanced magnetron sputtering, their structural properties were evaluated using x-ray diffraction and transmission electron microscopy, and their mechanical properties were estimated using nanoindentation. *Ab initio* density functional theory calculations

were carried out to investigate the microscopic origin of grain boundary sliding in these materials.

From the structural investigation, the films consisted of nanocrystals of Me that are distributed evenly throughout a ZrN matrix (Fig. 1). Nanoindentation measurements, reported in an earlier paper, were carried to evaluate the hardness and elastic modulus of the three sets of films.[9] The hardness H increased gradually with the increase in Me content, reached a maximum value, and then decreased dramatically. The elastic modulus E was found to decrease much more drastically for the ZrN-Ag system and much less significantly for ZrN-Pd as a function of Me content. The dramatic decrease in elastic modulus values cannot be explained in terms of the Young's modulus for Ag since the Young's modulus for Au is the smallest ($E_{Ag}=83$ GPa; $E_{Au}=78$ GPa; $E_{Pd}=121$ GPa).[10] A preliminary study allowed us to understand the correlation between the electronic structure at the interface of these three combinations of materials.[9] The dramatic change in the elastic modulus for the ZrN-Ag system was attributed to the weaker bonding mechanism at the in-
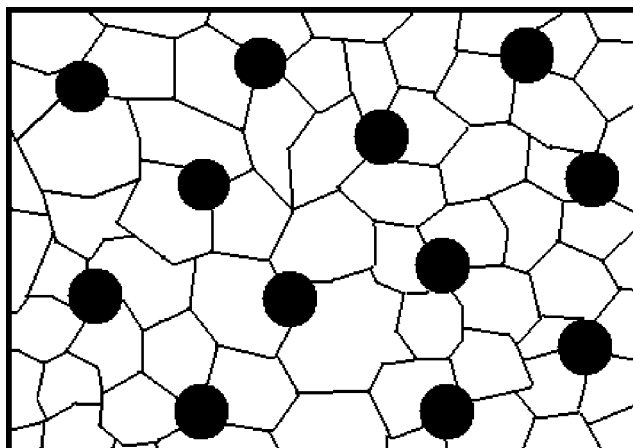

FIG. 1. Schematic diagram showing a typical architecture of the ZrN-Me system.

TABLE I. Details of the simulation cells and elastic constants for the ZrN, ZrN-Ag, ZrN-Au, and ZrN-Pd.

System	ZrN	ZrN-Ag	ZrN-Au	ZrN-Pd
Interface distance (nm)	⋯	0.2469	0.2661	0.2088
Lattice mismatch (%)	⋯	8	8	10
$E_{xx}=E_{yy}$	492	335	347	302
E_{zz}	492	154	208	326
B	245	135	186	226
C_{44}	123	54	64	101

terface between Ag and ZrN. The ability to design materials with the desired H and E is a powerful concept in tribology since it translates into the ability to enhance the resistance to plastic deformation, usually measured by the ratio H^3/E^2.[7] The advantage in utilizing a nanocomposite structure resides in the grain refinement that results from the competing events of the growth of two immiscible phases.[11] The film architecture that results from this grain refinement promotes hindering of dislocation motion and crack development at interfaces and enhances ductility by grain boundary sliding.[12] Among the investigated materials, the ZrN-Ag system showed the best resistance to plastic deformation as measured by the ratio H^3/E^2.

Electronic structure, elastic constants, and total energies were calculated within the density functional theory (DFT)[13] using the generalized-gradient approximation for the exchange correlation potential in the Perdew-Wang-Ernzerhof[14] version as implemented in the Cambridge Sequential Total Energy Package (CASTEP) software.[15–17] The experimental prototypes of the ZrN-Me interface cannot yet be experimentally determined. The nanocomposite nature of the structure and the relatively moderate lattice mismatch between the Me and ZrN (8% for Ag-ZrN and 10% for Pd-ZrN), make it very reasonable to assume that the interface structure is rather irregular. The interface model was chosen to balance the complexity of the realistic system and the simplicity enforced by the computational limitations. ZrN is kept in the NaCl structure and Me in the fcc structure. For simplicity, the ZrN(001)/Me(001) orientation is considered. A further simplification, imposed by the computational method, is the use of an interface structure with high symmetry and a relatively small supercell size. The calculations were performed with a supercell containing three layers of ZrN and one layer of Me. All the atoms were relaxed until the forces were <0.1 eV/Å.

First, equilibrium lattice constants and elastic constants were computed and the results of the simulation are reported in Table I. The elastic constants determine the reponse of the materials to an externally applied load and provide information about the bonding characteristics between adjacent planes, the anisotropic character of the bonding, and the structural stability. The elastic constants listed in Table I include: (1) Young's moduli $E_{xx}=E_{yy}$ and E_{zz}, which describe the material's response to linear strain in the xx, yy, and zz directions (zz is the direction that is parallel to the interface); (2) the bulk modulus B, which describes the material's response to uniform pressure; and, (3) c_{44}, which represents a shape change without volume change, and provides information about electronic response to shear strain.[18] It is, therefore, E_{zz} and c_{44} that give an indication of whether the investigated interface is prone to grain boundary sliding (zz
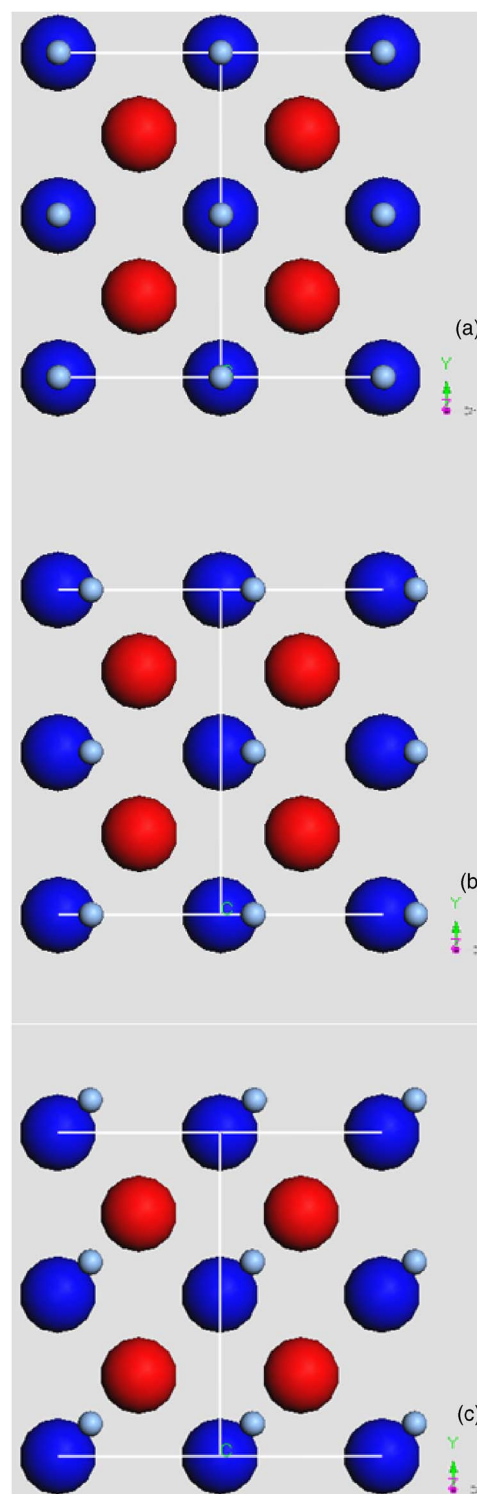

FIG. 2. Diagram describing the quasistatic evolution of the atoms to simulate grain boundary sliding: (a) initial position; (b) sliding in the [100] direction; and, (c) sliding in the [110] direction.

direction). The calculated E_{zz} and c_{44} values for Me=Ag indicate that grain boundary sliding can more easily occur during the loading of a ZrN-Ag film compared to the other two systems. In addition, the smallest distance between the ZrN and the Me layers occuring for Me=Pd (Table I) suggests that the strongest interfacial bond can be expected in the ZrN-Pd system.

Sliding was simulated quasistatically by rigidly shifting Me grain with respect to the ZrN grain by a small specified distance and then relaxing the structure to <1 meV/cell.
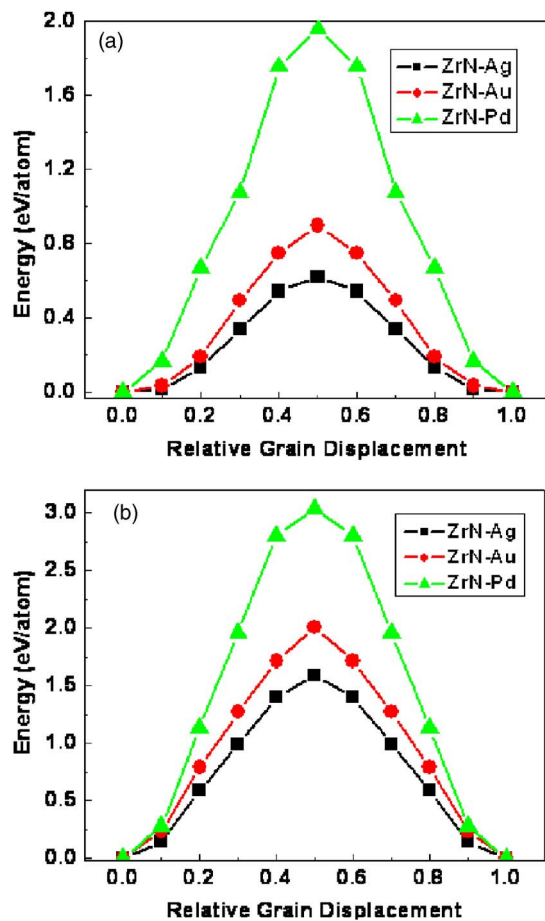
FIG. 3. Evolution of the grain boundary energy as a function of sliding in the (a) [100] and (b) [110] directions.

Two different translational states that correspond to the sliding along the [100] and [110] directions were investigated (Fig. 2). Figure 3 shows the evolution of the energy during sliding along these directions for the three ZrN-Me systems with the initial translational state set at (0,0). The sliding distance is expressed as a percentage of the lattice parameter for the supercell. The smooth and periodic energy profile is a clear indication that no remarkable and sudden rearrangements of atoms occur during sliding. The "sliding" of atoms is a continuous process. The energy minima occur when the Me atoms are on top of the N atoms. Figure 3 indicates that sliding is more favorable in the [100] direction for all three systems. The smallest maximum energy variation during sliding occurs for the ZrN-Ag material and the largest for the ZrN-Pd case. These results are in accord with experimental findings confirming that grain boundary sliding occurs more readily in the ZrN-Ag system when compared to ZrN-Pd.[9]

The present investigation combines a theoretical and a computational approach to understand the mechanical properties of nanocomposite protective films. The properties of these materials depend on the following factors: (1) The intrinsic properties of the constituent phases, (2) the film architecture, and (3) the interfacial energy. In this study, the film architecture varied in a consistent fashion to span similar architectures for the three systems with different metals. In spite of the fact that the intrinsic properties of the constituent phases did not vary considerably, any observed changes in the mechanical properties of the nanocomposite structure did not follow the rule of mixtures. The present study represents a step to address the role of the interface in a systematic fashion. We feel that the use of first principles techniques would provide an insight that could explain some of the properties of these materials. These computational tools have significant potential in designing nanocomposite structures. A more systematic investigation is currently being conducted to address the correlation between the various possible architectuctures and the mechanical properties of these materials.

[1] A. A. Voevodin and J. S. Zabinski, Comp. Sci. Technol. **65**, 741 (2005).
[2] R. W. Siegel and G. E. Fougere, Mater. Res. Soc. Symp. Proc. **362**, 219 (2002).
[3] T. G. Langdon, Mater. Sci. Forum **189–190**, 31 (1995).
[4] J. Schiotz, F. D. Di Tolla, and K. W. Jacobsen, Nature (London) **391**, 561 (1998).
[5] C. Molteni, N. Marzari, M. C. Payne, and V. Heine, Phys. Rev. Lett. **79**, 869 (1997).
[6] S. Vepek, M. G. J. Vepek-Heijman, P. Karvankova, and J. Prochazka, Thin Solid Films **476**, 1 (2005).
[7] J. Musil, P. Karvankova, and J. Kasl, Surf. Coat. Technol. **139**, 101 (2001).
[8] P. Ballo, N. Kioussis, and G. Lu, Phys. Rev. B **64**, 024104 (2001).
[9] S. M. Aouadi, P. K. Shreeman, Q. Ge, J. Xu, and S. R. Mishra, Appl. Phys. Lett. **87**, 041902 (2005).
[10] W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants*, 15th ed. (Longman, London, UK, 1993).
[11] I Petrov, P. B. Barna, L. Hultman, and G. E. Greene, J. Vac. Sci. Technol. A **21**, S117 (2003).
[12] S. Zhang, D. Sun, Y. Fu, and H. Du, Surf. Coat. Technol. **167**, 113 (2003).
[13] R. M. Dreizler, and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
[14] J. P. Perdew, K. Berke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[15] V. Milman, V. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya, and R. H. Nobes, Int. J. Quantum Chem. **77**, 895 (2000).
[16] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[17] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys. Condens. Matter **14**, 2717 (2002).
[18] S. J. Jhi, J. Ihm, S. G. Louie, and M. L. Cohen, Nature (London) **399**, 132 (1999).