

7-18-2005

Correlation Between Interfacial Electronic Structure and Mechanical Properties of ZrN–Me (Me=Ag, Au, or Pd) Nanocomposite Films

S. M. Aouadi

Southern Illinois University Carbondale

P. K. Shreeman

Southern Illinois University Carbondale

Q. Ge

Southern Illinois University Carbondale

J. Xu

University of Memphis

S. R. Mishra

University of Memphis

Follow this and additional works at: http://opensiuc.lib.siu.edu/phys_pubs

© 2005 American Institute of Physics

Published in *Applied Physics Letters*, Vol. 87 No. 4 (2005) at doi: [10.1063/1.2001141](https://doi.org/10.1063/1.2001141)

Recommended Citation

Aouadi, S. M., Shreeman, P. K., Ge, Q., Xu, J. and Mishra, S. R. "Correlation Between Interfacial Electronic Structure and Mechanical Properties of ZrN–Me (Me=Ag, Au, or Pd) Nanocomposite Films." (Jul 2005).

This Article is brought to you for free and open access by the Department of Physics at OpenSIUC. It has been accepted for inclusion in Publications by an authorized administrator of OpenSIUC. For more information, please contact opensiuc@lib.siu.edu.

Correlation between interfacial electronic structure and mechanical properties of ZrN–Me (Me=Ag, Au, or Pd) nanocomposite films

S. M. Aouadi^{a)} and P. K. Shreeman

Department of Physics, Southern Illinois University, Carbondale, Illinois 62901-4401

Q. Ge

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

J. Xu and S. R. Mishra

Department of Physics, University of Memphis, Memphis, Tennessee 38152

(Received 24 March 2005; accepted 23 June 2005; published online 18 July 2005)

Nanocomposite films of ZrN–Me (Me=Ag, Au, or Pd) were prepared using reactive unbalanced magnetron sputtering. The hardness and elastic modulus were measured by nanoindentation and were found to vary differently with composition for the three nanocomposite structures. Young's modulus was found to decrease much more dramatically with the increase in Me content for the ZrN–Ag system. These findings were attributed to the weaker bonding mechanism at the interface between the ceramic and the metallic phases, which is more prone to grain-boundary sliding as shown using first-principles calculations of the electronic structure at the interface for the three systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.2001141]

In the last five years, multiphase thin films have gained a lot of popularity among researchers in the area of protective coatings due to their improved mechanical, chemical, and tribological properties compared to the more traditional single-phase materials.^{1,2} Most of the nanocomposite coatings that have been investigated consist of one or several hard transition metal nanocrystals (TiN, ZrN, DLC, TiB₂, WN₂, etc.) embedded in an amorphous phase matrix (*a*-SiN_x, *a*-BN, *a*-C, *a*-Ag, *a*-Cu, etc.).^{2–4} In most applications, there is a need to increase the resistance to plastic deformation, which requires a nanocomposite coating with both a high hardness and a high toughness.² Most of the work in the literature focused on “explaining” the improved resistance to plastic deformation of these novel materials to be a result of the hindering of the dislocation motions at grain boundaries, the impeding of crack propagation at the interface, and the improved toughness due to grain-boundary sliding.³ Therefore, the interface plays an important role in “shaping” the properties of nanocomposites and its contribution to their overall properties should be investigated.

The goal of the current project is to investigate the effect of the bond at the interface of various novel nitride–metal (ZrN–Me) nanocomposite structures on their mechanical properties. This will entail producing these materials by unbalanced reactive magnetron sputtering, measuring their mechanical properties using nanoindentation, simulating their interfacial electronic/bonding properties using an *ab initio* method based on density functional theory, and correlating the electronic properties at the interface to their mechanical properties.

Nanohardness measurements for the ZrN–Me films were carried out and the mean values and standard deviations of hardness and elastic modulus were estimated. Shown in Fig. 1 are the film hardness and elastic moduli as a function of Me content. The hardness of the films increased gradually with the increase in Me content, reached a maximum value,

and then decreased dramatically. The maximum hardness was found to depend on the additional metal element Me. Young's modulus, on the other hand, decreased with Me content. An increase in hardness and a decrease in Young's modulus translates into an enhancement in the resistance to plastic deformation, usually measured by the ratio H^3/E^2 .² The improved mechanical properties are due to the formation of a nanocomposite structure with an architecture that promotes hindering of dislocation motion and crack development at interfaces and enhances ductility by grain-boundary sliding.⁵ These properties may be tailored by varying the power to Me or other deposition conditions, such as bias voltage, substrate temperature, and ion flux. In addition, the performance of this structure also depends on the intrinsic physical and chemical properties of the component materials, on the degree of miscibility of one phase into the other one, and on the bonds that are created at the interface between the crystallites and the matrix. This leads us to the crucial question about the role of the interface between the two phases that constitute our films and their mechanical properties. By comparing the elastic modulus for the three nanocomposite structures, their values were found to decrease much more dramatically for the ZrN–Ag system than for the other two systems. In contrast, the ZrN–Pd system showed the smallest decrease. The maximum hardness values were found to be in the same range (32–35 GPa). Overall, the ZrN–Ag system showed the best resistance to plastic deformation as measured by the ratio H^3/E^2 .

The ground-state energies and electronic structure at the interface of ZrN–Me films were calculated within the density functional theory (DFT) (Ref. 6) formalism using CASTEP (Cambridge Sequential Total Energy Package) software.^{7–9} Zirconium nitride is a diatomic solid which crystallizes in a rock salt structure. The nitride surface was represented by a 1 × 1 supercell three-layers thick on which periodic three-dimensional boundary conditions was applied, allowing a vacuum space of 2 nm between the slabs. In the optimization of both the surface and the surface and Me atoms, only the outermost layer was allowed to relax.¹⁰

^{a)}Electronic mail: saouadi@physics.siu.edu

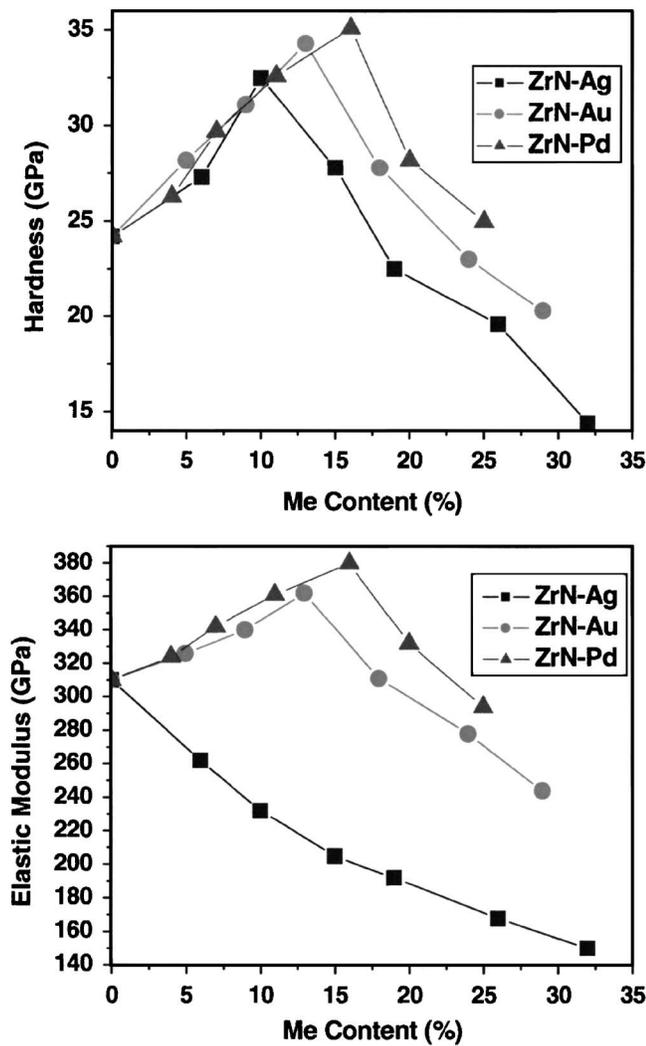


FIG. 1. H and E for ZrN-Me nanocomposite films.

In the next step, we examined the ZrN-Me interface. Three different interfacial geometries were considered and consist of:

- (1) Me on top of the Zr atom (Site A),
- (2) Me on top of the N atom (Site B), and
- (3) Me on top of the four-fold hollow site (Site C).

The adsorption energy per site $E_{\text{ads/site}}$ will be calculated according to equation:

$$E_{\text{ads/site}} = -(E_{\text{ZrN-Me}} - E_{\text{isolated-Me}} - E_{\text{isolated-ZrN}})/n_{\text{sites}}$$

Adsorption energies, E_{ads} , and distances of Me atoms to the surface, d_{int} , computed from the DFT calculations are reported in Table I for the three material combinations at the selected sites. The calculations revealed that A is the preferred site (on top of the Zr atom) for all three nanocomposite combinations, though for ZrN-Pd, the difference between Sites A and B was so small that it could be within the error range of the calculation. The results shown in Table I suggest a significantly weaker binding energy for ZrN-Ag compared to the other two structures.

To further understand the nature of the ZrN-Me interaction at the interface, an analysis of the density of states (DOS) and the electron density maps for the most stable site was carried out. Figure 2 displays DOS curves for both iso-

TABLE I. Computed adsorption energies and Me-ZrN surface distance.

System	Site	$-E_{\text{ads}}$ (eV)	d_{int} (nm)
ZrN-Ag	A (on Zr)	0.843	0.296
	B (on N)	1.051	0.256
	C (four-fold hollow)	0.943	0.274
ZrN-Au	A (on Zr)	1.556	0.275
	B (on N)	2.090	0.269
	C (four-fold hollow)	1.975	0.272
ZrN-Pd	A (on Zr)	2.682	0.248
	B (on N)	2.756	0.223
	C (four-fold hollow)	2.713	0.233

lated Me and Me at the interface. DOS for isolated Me atoms show the d^{10} configuration for the Pd ground state and the $d^{10}s^1$ configurations for the Ag and Au ground states. When the Me atoms form a bond with ZrN, the gold and palladium d bands show a set of new low-energy states (a broader band in other words) whose energies coincide with those of new peaks appearing in the d components of the DOS projected on the surface ZrN atoms. These new states make the ZrN and Pd or Au overlapping states.

To better analyze the bonding nature of the abrupt metal-ceramic interfaces, we have used the charge density difference¹¹ to study the interfacial electronic structure and bonding. The charge density difference ρ is given by

$$\rho = \rho_{\text{ZrN-Me}} - \rho_{\text{ZrN}} - \rho_{\text{Me}},$$

where $\rho_{\text{ZrN-Me}}$ is the total charge density of the interface system, and ρ_{ZrN} and ρ_{Me} are the charge densities for the isolated ZrN and Me slabs, respectively. Figure 3 shows electron density difference maps, which correspond to the plane (100) containing Zr, N, and Me. There are significant differences in the interfacial bonding characteristics of the ZrN-Me structures for Me=Ag, Au, or Pd. First, the charge depletion around Me is more pronounced for the Pd atom and is the weakest for the Ag atom. There is an electron density increment in the Me-Zr interatomic region indicating that some covalent bond is formed. The charge accumulation in the Me-N direction is much larger for Me=Pd system and is much smaller for Me=Ag system. These results are

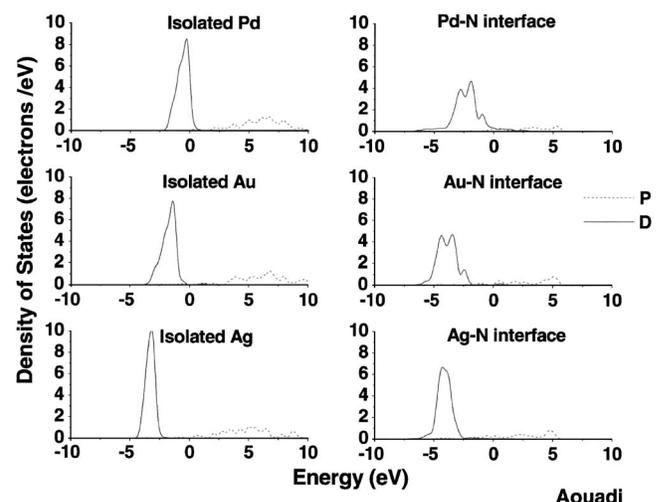


FIG. 2. DOS curve for isolated ZrN.

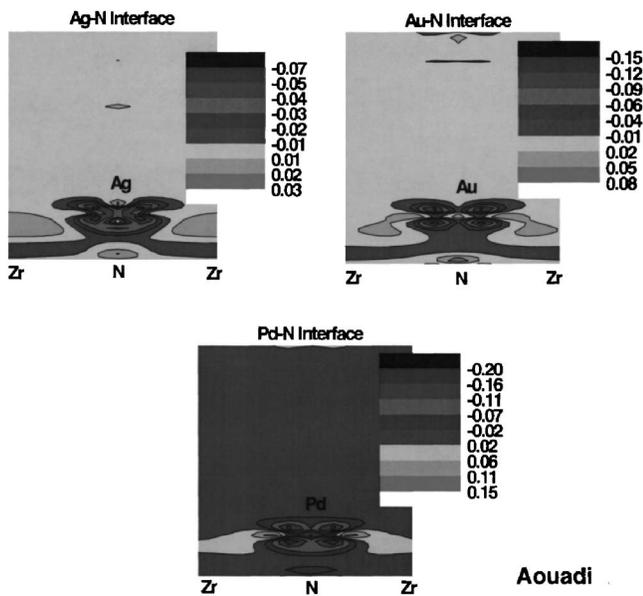


FIG. 3. Electron density difference map.

in agreement with the results obtained from the adsorption energy and DOS calculations, which consistently show that the ZrN-Pd bond is the strongest and the ZrN-Ag is the weakest.

The present investigation is a preliminary study to understand the correlation between the electronic structure at the interface of three combinations of ZrN-Me films and the mechanical properties of the aggregate. A correlation seems to exist between the experimental and the computational results. The elastic modulus decreases more dramatically for Ag and this could be explained by the fact that the ZrN-Me system is more prone to grain-boundary sliding as a result of the weaker interfacial bond in comparison to ZrN-Au or ZrN-Pd. As a result, ZrN-Ag displays the best resistance to plastic deformation, as measured by the ratio H^3/E^2 . 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).¹² Grain-boundary sliding was suggested by many workers as a mechanism for improving ductility and providing superplasticity of single phase ceramic nanocrystalline materials.¹³⁻¹⁵ The more recent work on nanocomposite structures indicate that grain-boundary sliding can be a primary mechanism of superplasticity.^{4,16,17} The results obtained by DFT (potentials, electronic structures, etc.) may be incorporated into a more complex multiscale program to simulate more quantitatively the mechanical properties of these nanocomposite structures with specific architectures.

This research was supported by the Center for Advanced Friction Studies and the Materials Technology Center of Southern Illinois University.

¹S. Vepek, M. G. J. Vepek-Heijman, P. Karvankova, and J. Prochazka, *Thin Solid Films* **476**, 1 (2005).

²J. Musil, P. Karvankova, and J. Kasl, *Surf. Coat. Technol.* **139**, 101 (2001).

³A. A. Voevodin and J. S. Zabinski, *Compos. Sci. Technol.* **65**, 741 (2005).

⁴N. Crainic and A. T. Marques, *Key Eng. Mater.* **230**, 656 (2002).

⁵S. Zhang, D. Sun, Y. Fu, and H. Du, *Surf. Coat. Technol.* **167**, 113 (2003).

⁶R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).

⁷V. Milman, V. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, *Int. J. Quantum Chem.* **77**, 895 (2000).

⁸M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).

⁹M. 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).

¹⁰N.-C. Hernández, J.-F. Sanz, *Int. J. Mol. Sci.* **2**, 263 (2002).

¹¹L. M. Liu, S. Q. Wang, and H. Q. Ye, *J. Phys.: Condens. Matter* **15**, 8103 (2003).

¹²G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants*, 15th ed. (Longman, London, UK, 1993).

¹³F. Wakai, *Ceram. Int.* **17**, 153 (1991).

¹⁴T. G. Nieh, J. Wadsworth, and F. Wakai, *Int. Mater. Rev.* **36**, 146 (1991).

¹⁵T. G. Langdon, *Mater. Sci. Eng., A* **166**, 67 (1993).

¹⁶J. Schiotz, F. D. Di Tolla, and K. W. Jacobsen, *Nature (London)* **391**, 561 (1998).

¹⁷C. C. Koch, D. G. Morris, and K. Lu, *A. Inoue, Mater. Res. Bull.* **24**, 54 (1999).