Effect of volume fraction on mechanical properties of Zr/ZrN multilayer systems


**A R T I C L E   I N F O**

Article history:
Received 10 June 2016
Received in revised form 1 September 2016
Accepted 3 September 2016
Available online 4 September 2016

Keywords:
Zr/ZrN multilayer
Volumetric fraction
Sputtering
Nanoindentation
Hardness
$H/E^2$ ratio

**A B S T R A C T**

In this paper we study the effect of volumetric fraction and bilayer modulation period ($\Lambda$) on mechanical properties of metal/ceramic multilayer coatings. Two sets of Zr/ZrN multilayer systems with different modulation period and volumetric fraction were synthesized by DC reactive magnetron sputtering. The crystalline structure of the multilayers films was determined by X-ray diffraction and morphology were analyzed by AFM and TEM, which show that crystalline films are formed in all cases. High resolution TEM analysis revealed well-formed multilayer composites with very smooth layers. Nanoindentation tests were carried out to measure the mechanical properties of the multilayer Zr/ZrN coating. Hardness ($H$), elastic modulus ($E$) and elastic recovery ($We$) were determined by using the Oliver and Pharr method, the values are also discussed in terms of $H/E^2$ ratio. The results show that mechanical properties varied according to volumetric fraction Zr/ZrN. However, coatings with metallic volume fraction between 10% and 20% showed a significant improvement in hardness of 16–21% in comparison with monolithic ZrN values. Moreover, the best values for elastic recovery and resistance to plastic deformation ($H/E^2$) also were found in Zr/ZrN multilayer with 10–20% of metallic phase, increasing up to 12% on We and up to 79% on $H/E^2$. These results allowed further understanding of the mechanical behavior of multilayer systems, demonstrating with this the importance of volumetric fraction in a metal/ceramic system.

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1. Introduction

Multilayer thin films composites have been widely studied for their superior mechanical properties such as hardness and wear resistance in comparison to single layer films. This improvement in mechanical properties is mainly due to the creation of interfaces in between the composite. By alternating layers of different materials a number of interfaces parallel to the substrate surface are created, the role of these is to deflect cracks or provide barriers to dislocation motion, increasing the toughness and hardness [1]. Most studies on multilayer coatings have been developed about ceramic/ceramic systems with remarkable improvements in hardness; unfortunately, this increase in hardness makes it prone to brittle fracture. This behavior was studied by Koheler [2] who introduced a method to improving plastic resistance by using alternate layers with different elastic constant. The difference in elastic constants obstructs dislocation movement between layers preventing the system from brittle fracture. Cases of the Koheler method are the multilayer metal/ceramic systems, which are known to have very dissimilar elastic properties. Recent studies have proven that even though metals have a characteristic low hardness, metal/ceramic multilayer composites showed an unexpected enhancement of hardness [3,4]. Combination of ductile metal with a brittle ceramic, offer the potential for attractive combination of strength as well as toughness [5].

One of the first metal/nitride investigations was developed by Shih et al. [3]. They synthesized different multilayer systems of Ti/TiN, Hf/HfN and W/WN and measured hardness and reduced elastic modulus, finding that multilayer films showed superior mechanical properties than monolayer films. Subsequently many investigations were performed, including systems such as, Al/AlN, Al/Al2O3, Ti/TiN, Zr/ZrN and Cr/CrN [6–11]. These investigations found that under some conditions it is possible to improve mechanical properties; furthermore, they have proven that the increase in mechanical properties depends directly on the bilayer microstructure. Moreover, layer thickness and grain size are directly related with hardness and wear resistance; we can describe mechanical properties of laminated composites as a function of materials layer thickness, when bilayer period decreases, hardness and tensile strength increase [12].

Recent theoretical investigations have emerged in order to elucidate the deformation micromechanisms and the effect of
metal/ceramic ratio; e.g., Verma et al. [13] presented a detailed analysis to understand the influence of volumetric fraction for metal/nitride multilayer coatings. They report that volumetric fraction of metal layer play an important role in hardness due to residual stress distribution through the coating. Uniform distribution of residual stress contributes to lower deformation and lower probability of fracture which in consequence yields more resistant materials, highlighting the importance of metallic phase and his contribution to plasticity of the composite. Thicker metallic layers contribute to material deformation while thinner metallic layers restrict deformation and the probability of fracture initiation.

Although many studies pointed out the importance of metal/ceramic ratio in multilayer system, a deep experimental study of the effect of volumetric fraction in mechanical properties has not been carried out. Following this guideline, the aim of this investigation was to study mechanical properties behavior with variation of volume fraction in a metal/ceramic multilayer thin film. Series of Zr/ZrN multilayer systems with different modulation periods and volumetric fraction were synthesized by DC reactive magnetron sputtering. The structure was studied by XRD and morphological properties were examined by AFM and TEM analysis. Finally, the mechanical properties were determined by nanoindentation test.

2. Experimental details

Monolithic films of Zirconium, Zirconium nitride and Zr/ZrN multilayer thin films were synthesized by DC reactive magnetron sputtering in a high vacuum stainless steel chamber. The growth chamber system was equipped with both rotary vane and turbomolecular pumps that reach a background pressure of 1 × 10⁻⁷ Torr. The gas flow was set by two mass flow-controllers; Nitrogen (99.99%) and argon (99.99%) were used as reactive and sputtering gases, respectively. A high-purity Zirconium disk (99.9%) was used as a target (2 in. diameter) and ultrasonically cleaned silicon substrates (100) were used. Pre-sputtering during 5 min in Ar plasma was performed to clean the Zr target surface before each layer deposition. All samples were grown under work pressure of mTorr with 1.0 sccm constant flow of Ar and 3.0 sccm constant flow of N₂ for ZrN layers. All depositions were made at fixed DC power of 100 W and the substrate temperature was kept at room temperature.

In order to understand the effect of volume fraction on mechanical properties, two different series of Zr/ZrN multilayers thin films were synthesized, labeled as Set 200 and Set 100. Both series differ in the Modular period (Λ), 200 nm and 100 nm for Set 200 and Set 100, respectively. Each series is composed by nine samples varying the volumetric fractions i.e., thickness ratio (tZr/tZrN), where tZr/tZrN=Λ, tZr and tZrN=Zr and ZrN thickness, respectively. In order to avoid substrate influence total thickness was fixed at 1 μm for all samples, Tables 1 and 2 show a summary of synthesis characteristics of Set 200 and Set 100, respectively. In each set modulation period, bilayer number (n) and total thickness were constant in all samples and only volumetric fraction was varied.

The crystallographic structure and grain size of Zr, ZrN and Zr/ZrN coatings were characterized by X-ray diffraction (XRD) in a Panalytical X’pert Pro MRD diffractometer using CuKα radiation operated at 45 kV and 40 mA; scanning angle 2θ was varied between 20° and 80° with a scan step of 0.02°. In order to observe modular periodicity and bilayer arrangement of Zr/ZrN multilayer films we used cross-sectional transmission electron microscopy (TEM) in a Philips CM-200 microscope. Thin films for cross-sectional TEM were prepared on using focused ion beam (FIB) milling technique in a JEM-9320 FIB [14]. Surface morphology and roughness was analyzed by atomic force microscope (AFM) in a XE70 Park Systems in contact mode. Surface roughness (Rq) was obtained by root-mean-square (RMS) roughness analysis, by using the following equation:

\[ Rq = \left( \frac{1}{N} \sum_{i=1}^{N} |Z_i-Z| \right)^{1/2} \]

where N is the number of surface height data, Zi is the surface height data and Z is the mean-height distance. Finally, mechanical properties such as hardness and elastic modulus were evaluated by means of nanoindentation, employing a Nano Indenter G200 coupled with a DCM II head. The equipment was calibrated by using a standard fused silica sample. Tests parameters were the following; the constants of area function were C0=24.06, C1=−177.32, C2=6684.31, C3=−25402.23, and C5=18691.81. The Berkovich diamond indenter with a tip radius of 20 ± 5 nm, maximum load of 1 mN, strain rate of 0.05, s−1, harmonic displacement of 1 nm, frequency of 75 Hz and, Poisson’s coefficient of υ=0.25. The indentation hardness and elastic modulus were calculated using the Oliver and Pharr method [15]. With a continuous measurement of stiffness (S), E and H, a continuous function of surface penetration can be obtained using the Sneddon’s equation [16–18].

\[ \frac{E}{1-\upsilon^2} = \frac{\sqrt{\pi}}{2\beta} \frac{1}{A} S \]

where υ Poisson’s ratio of material, β is 1.085 to Berkovich tip and, A is the area in function of the penetration depth (h).

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Zr</th>
<th>% ZrN</th>
<th>tZr (nm)</th>
<th>tZrN (nm)</th>
<th>Modular period, Λ (nm)</th>
<th>Zr/ZrN Bilayers (n)</th>
<th>Total thickness (nm)</th>
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<td>–</td>
<td>–</td>
<td>–</td>
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<td>180</td>
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<td>1000</td>
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<td>30</td>
<td>140</td>
<td>60</td>
<td>200</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>M200-60/40</td>
<td>60</td>
<td>40</td>
<td>120</td>
<td>80</td>
<td>200</td>
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<td>40</td>
<td>60</td>
<td>80</td>
<td>120</td>
<td>200</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
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<td>30</td>
<td>70</td>
<td>60</td>
<td>140</td>
<td>200</td>
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<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>ZrN</td>
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<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>1000</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Morphological and structural properties

X-ray diffraction analysis were performed on Zr, ZrN and Zr/ZrN thin film systems in order to identify crystallographic structure, resident phases and determine grain size. Fig. 1(a) and (b) shows the diffraction pattern of representative Zr/ZrN multilayer thin films; (a) Set 200 and (b) Set 100, in graphics multilayers Zr/ZrN are compared with Zr and ZrN monolayer films, in order to verify the presence of the Zr and ZrN phases. ZrN thin film presented (111), (200) and (222) crystallographic reflections, however the results indicate that (111) is the dominant preferred orientation for all samples, just as has been previously reported [19–24]. While, XRD pattern of Zr thin film shows hcp-α phase with (002) and (004) reflections with a dominant (002) preferred orientation [24,25]. Whereas multilayer films spectra show both Zr and ZrN phases, no diffraction peaks from oxide phases were observed. However, in multilayers coatings the (200) ZrN reflection is not observed due to ZrN layer thickness [26]. An obvious change of peak intensity with volume fraction is observed; when volume fraction increase the intensity of the reflections peaks also increase has a consequence.

The grain size of the films were calculated using the Debye-Scherrer’s formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where $D$ is the diameter of the crystallites forming the film, $\lambda$ is the wavelength of Cu-Kα line, $\beta$ is FWHM in radians and $\theta$ is the Bragg angle.

The grain size of Zr and ZrN monolayers films were 27 nm for both, while in multilayers films the dimensions of grain size were...
in the range of 9–25 nm and 8–26 nm for the ZrN and Zr phases, respectively. The calculated values are listed in Tables 3 and 4. With decreased layer thickness there is a decrease in the grain size. The smallest grain size belong to thinner thickness layers, what is clearly predictable because the grain size will roughly scale with the individual layer thickness [6].

The grain size was confirmed by AFM examination being similar to that determined by XRD. Fig. 2 shows AFM representative images of Zr/ZrN multilayer films, the surface was analyzed in contact mode over a scan area of 500 nm². The images revealed a smooth and uniform surface with an average grain size varying from 20 to 30 nm. On the other hand, AFM data used for roughness measurement reveals quite smooth surface for all the multilayers, with roughness values in the range of 2–6 nm.

The results indicated that both roughness and grain size were similar for all samples, which suggest that period, bilayer number and Zr: ZrN ratio thickness do not affect the surface morphology of Zr/ZrN composites.

Fig. 3 shows cross-sectional transmission electron microscope images obtained from representative Zr/ZrN multilayers with bilayer period of 100 nm (taken at edge and in the middle region of Set 100). It can be seen that a well-formed layered structure of ten bilayers was obtained and the layer thickness was confirmed from the magnified view in the inset. Zr layers are visible as bright bands and ZrN layers as dark ones, the uniform contrast of the images indicates a homogeneous and smooth Zr and ZrN layers.

### 3.2. Mechanical properties

Fig. 4 shows variations on (a) hardness and (b) elastic modulus as a function of volumetric fraction of Zr/ZrN multilayer coatings. For comparison, both series are plotted in the same graph. In both cases values of Set 100 were better than those of Set 200. In general, the mechanical properties were improved with decrease on modular period, in good agreement with other reports [3–12]. It can be observed that hardness values are closely related with volume fraction of metallic and ceramic phases. With high volume fraction of metallic phase Zr-90% the hardness tends to be like pure Zr; on the other hand, with high volume fraction of ceramic phase ZrN-90% the hardness tends to be similar to ZrN. However, coatings with metallic volume fraction between 10% and 20% showed a significant improvement in hardness of 16–21% in comparison with monolithic ZrN coating. Results of mechanical properties of Set 200 and Set 100 are summarized in Tables 3 and 4, respectively.

In addition, the graphs in Fig. 4 show a linear relationship of hardness and elastic modulus in regard to Zr/ZrN volumetric fraction percent. However, in samples with Zr/ZrN volumetric fraction percent of ZrN-10% and Zr-10% there is an increase on hardness respect to Zr and ZrN monolayer films. This increase on hardness can be attributable to layered structure, the introduction of Zr/ZrN interfaces and having smaller Zr and ZrN grain size in multilayers systems increasing hardness and toughness. Therefore, mechanisms of the hardness enhancement observed for compositionally modulated Zr/ZrN multilayer films could be considered on the basis of Koehler’s theory. In monolayer coatings, the cracks can run from the coating surface to the substrate. However, in multilayer coatings the interface Zr/ZrN can deflect cracks or provide barriers to dislocation motion, increasing the toughness and hardness of coating [2]. On the other hand, the grain size also has an important effect in hardness, has been demonstrated that hardness increases with grain size. This has been attributed to the increased area fraction of grain boundaries, which acts as strong barrier to dislocation motion [27]. In Tables 3 and 4 the calculated grain sizes for all the multilayer coatings are given. The grain sizes of Zr and ZrN were bigger in monolithic films than in multilayer. However, according to tendency thinner layers have smaller grain size, contributing to increase hardness and resistance of layered systems.

It is important to optimize the volume fraction of the metal in order to maximize toughening and keep the maximum hardness possible. These results suggest that adding 10–20% volumetric

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### Table 3
Summary of mechanical properties of monolithic films and Zr/ZrN set 200.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr grain size (nm)</th>
<th>ZrN grain size (nm)</th>
<th>Hardness H (Gpa)</th>
<th>Elastic modulus E (Gpa)</th>
<th>$H^2/E^2$ (Gpa)</th>
<th>We (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>27</td>
<td>–</td>
<td>6.1</td>
<td>112.1</td>
<td>0.018</td>
<td>29.2</td>
</tr>
<tr>
<td>M200-90/10</td>
<td>25</td>
<td>14</td>
<td>10.2</td>
<td>186.5</td>
<td>0.031</td>
<td>31.5</td>
</tr>
<tr>
<td>M200-80/20</td>
<td>24</td>
<td>14</td>
<td>11.1</td>
<td>204.3</td>
<td>0.033</td>
<td>30.7</td>
</tr>
<tr>
<td>M200-70/30</td>
<td>23</td>
<td>19</td>
<td>11.6</td>
<td>213.8</td>
<td>0.034</td>
<td>32.4</td>
</tr>
<tr>
<td>M200-60/40</td>
<td>22</td>
<td>19</td>
<td>12.9</td>
<td>221.0</td>
<td>0.044</td>
<td>34.4</td>
</tr>
<tr>
<td>M200-50/50</td>
<td>19</td>
<td>22</td>
<td>14.9</td>
<td>228.2</td>
<td>0.064</td>
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</tr>
<tr>
<td>M200-40/60</td>
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<td>23</td>
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<td>38.7</td>
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<tr>
<td>M200-30/70</td>
<td>19</td>
<td>26</td>
<td>18.4</td>
<td>265.7</td>
<td>0.088</td>
<td>43.7</td>
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<tr>
<td>M200-20/80</td>
<td>16</td>
<td>26</td>
<td>21.3</td>
<td>278.7</td>
<td>0.124</td>
<td>44.8</td>
</tr>
<tr>
<td>M200-10/90</td>
<td>11</td>
<td>26</td>
<td>24.5</td>
<td>321.8</td>
<td>0.142</td>
<td>47.2</td>
</tr>
<tr>
<td>ZrN</td>
<td>–</td>
<td>27</td>
<td>21.1</td>
<td>336.6</td>
<td>0.083</td>
<td>42.8</td>
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### Table 4
Summary of mechanical properties of monolithic films and Zr/ZrN set 100.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr grain size (nm)</th>
<th>ZrN grain size (nm)</th>
<th>Hardness H (Gpa)</th>
<th>Elastic modulus E (Gpa)</th>
<th>$H^2/E^2$ (Gpa)</th>
<th>We (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>27</td>
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<td>6.1</td>
<td>112.1</td>
<td>0.018</td>
<td>29.2</td>
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<td>M100-90/10</td>
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<td>36.0</td>
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<td>M100-60/40</td>
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<td>228.5</td>
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<td>38.8</td>
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<tr>
<td>M100-50/50</td>
<td>19</td>
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<td>16.0</td>
<td>247.5</td>
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<td>39.6</td>
</tr>
<tr>
<td>M100-40/60</td>
<td>17</td>
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<td>19.3</td>
<td>273.6</td>
<td>0.096</td>
<td>43.3</td>
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<td>M100-30/70</td>
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<td>19.9</td>
<td>277.3</td>
<td>0.101</td>
<td>44.4</td>
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<tr>
<td>M100-20/80</td>
<td>13</td>
<td>21</td>
<td>25.1</td>
<td>328.0</td>
<td>0.147</td>
<td>47.3</td>
</tr>
<tr>
<td>M100-10/90</td>
<td>8</td>
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<td>334.0</td>
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<td>48.1</td>
</tr>
<tr>
<td>ZrN</td>
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<td>21.1</td>
<td>336.6</td>
<td>0.083</td>
<td>42.8</td>
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</table>
fraction of metallic material is a good way to optimize hardness of multilayer composites, obtaining better results with 10% of volumetric fraction. A high hardness of a material is only one parameter which ensures scratch and abrasion resistance. Protective overcoat films must be highly resistant also to plastic deformation during contact events [28]. In order to evaluate resistance and toughness of coatings it is important to consider other parameters that characterize mechanical behavior of materials such as elastic recovery (We) [15] and resistance to plastic deformation (H/E) [29]. A more elastic material will allow the applied load to be distributed over a greater surface area, thus reducing the contact stress and requiring application of a higher contact force to initiate yielding. The resistance of the film against its cracking increases with increasing ratio H/E [30]. For these reasons, results coming from nanoindentation testing have been analyzed also in terms of H/E and We of the Zr/ZrN multilayer coatings.

Fig. 5 shows variation on (a) resistance to plastic deformation and (b) elastic recovery as functions of volumetric fraction of Zr/ZrN multilayer coatings. As can be seen on graphs, both We and H/E of multilayer coatings shows higher values than those of monolithic ZrN, increasing up to 12% on elastic recovery and up to 79% on resistance to plastic deformation. The best values for H/E and We were found in Zr/ZrN multilayer with 10–20% of metallic phase, just like those of E and H.

Indentation tests produce deformation of contact area due to residual stress accumulation and if plastic limit is exceeded microcracking developing begins. Stress distribution is direct related to mechanical behavior of materials. If the material is capable to absorb energy and distribute it uniformly, it will resist heavier loads before a fail occurs due to residual stress accumulation, this behavior delays cracking and increases the toughness of the material. In metal/ceramic multilayer systems with thick metallic layers the metallic phase tends to suffer deformation because of its high plasticity, while the ceramic phase is prone to stress accumulation and developing micro-cracking because of its high fragility. On the opposite side, in multilayer systems with thin metallic layers the metallic phase contributes to concentrate stress at the metal/ceramic interface producing interface delamination instead of micro-cracking which contributes to cracking delay. The presence of metallic layers promotes micro-cracking through metal/ceramic interface, instead of through layers, toughening the composite [31].

4. Conclusions

The effects of volumetric fraction and bilayer period on the mechanical properties of Zr/ZrN multilayer films were investigated. Two sets of Zr/ZrN multilayer systems with different modulation period and volumetric fraction were fabricated by DC reactive magnetron sputtering. The crystallinity of the multilayered films was verified by X-ray diffraction and high resolution transmission electron microscopy (HRTEM) analysis revealed uniform well-formed multilayer composites. Nanoindentation tests indicated that the H, E and We increased when period decreased. Also, the results
Fig. 3. Cross-sectional TEM micrographs of (a) M100-90/10, (b) M100-50/50 and (c) M100-10/90.

Fig. 4. Variations on (a) hardness and (b) elastic modulus as functions of volumetric fraction of Zr/ZrN multilayer coatings.
show that mechanical properties varied according to volumetric fraction Zr/ZrN. However, coatings with metallic volume fraction between 10% and 20% showed a significant improvement in hardness of 16–21% in comparison with monolithic ZrN values. Moreover, the best values for elastic recovery and resistance to plastic deformation also were found in Zr/ZrN multilayer with 10–20% of metallic phase, increasing up to 12% on We and up to 79% on H/E². These results allowed further understanding of the mechanical behavior of multilayer systems, demonstrating with this the importance of volumetric fraction in a metal/ceramic system.

Acknowledgments

The author would like to thank to P. Casillas, E. Aparicio, I. Gradilla, I. Ponce and E. Murillo from CINyN-UNAM for invaluable technical assistance. Special thanks to C. Ornelas and O. Solis from CIMAV-Chihuahua for performing FIB and TEM experiments. S. Payán-Díaz would like to thank the scholarship from Consejo Nacional de Ciencia y Tecnología (CONACYT), México.

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