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Cyclic nanoindentation studies on TiN and Ti-TiN multilayer coatings deposited on Zr-based metallic glasses

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Résumé :

Des essais de nanoindentation cyclique ont été effectués pour étudier l'influence des revêtements monocouche TiN et multicouche Ti-TiN sur les propriétés mécaniques des verres métalliques à base de zirconium. Les revêtements TiN et Ti-TiN ont été déposés sur verre métallique $Zr_{60}Ni_{10}Cu_{20}Al_{10}$ par pulvérisation cathodique radiofréquence (RF) à température ambiante sous une atmosphère réactive d'azote et en utilisant une cible de titane. L'épaisseur des revêtements déposés est de 300 nm. Des essais de chargement cyclique à différentes vitesses de chargements ont été effectués sur les substrats de verre métallique revêtus avec TiN et Ti-TiN. Nous avons noté une amélioration de propriétés mécaniques telle que la dureté et le module d'élasticité réduit des échantillons revêtus en comparaison avec le substrat non revêtu. De plus, les essais effectués ont montré un changement de comportement en déformation des échantillons, tel que montré à travers l'analyse des courbes charge-déplacement et les images obtenues en utilisant la microscopie à force atomique. L'effet de vitesse de chargement sur le comportement en déformation a été discuté.

Mots clefs : Nanoindentation cyclique, verre métallique, revêtement nanostructuré, multicouche Ti-TiN

Abstract :

Cyclic nanoindentation tests were carried out to investigate the influence of TiN and Ti-TiN multilayer coatings on the mechanical properties of Zr-based metallic glass. TiN and Ti-TiN multilayer coatings have been deposited on $Zr_{60}Ni_{10}Cu_{20}Al_{10}$ metallic glass substrate by RF sputtering. The deposition process was done at room temperature under nitrogen reactive gas using metallic titanium target. The two deposited coating have a thickness of 300 nm. Several cyclic nanoindentation measurements were conducted on TiN, and Ti-TiN coatings deposited on Zr-based metallic glass samples at various loading rates. We have found that the coated metallic samples shows higher mechanical properties such as hardness and reduced elastic modulus compared to the bulk metallic glass substrate. Furthermore, the designed experiments shows a difference in the deformation behaviour of the samples, as being analysed through the obtained load-displacement curves with the atomic force microscopy (AFM) pictures of the residual indentation imprints. The effect of the loading rate on the deformation behaviours of these samples was also discussed in this work.

Key Words : Cyclic nanoindentation, metallic glass, nanostructured coatings, Ti-TiN multilayer

1. Introduction

Bulk metallic glasses (BMGs) are metal alloys with a glassy atomic structure that received an increase interest due to their high physical and mechanical properties, compared with crystalline counterparts, such as high strength up to 5 GPa and large elastic limit that can reach 2% [1,2]. Furthermore, within the region between the glass transition and crystallization temperatures named the supercooled liquid region, their behaviour under compression solicitation is accompanied by high superplasticity reaching 1500% [3]. However, the lack of ductility limits their engineering application. Indeed, in tensile tests at ambient temperature, BMG fail catastrophically on one dominant shear band due to their tendency for shear localization [2]. The initiated shear bands become nucleation sites for the formation of microcracks during loading and contribute towards the catastrophic fracture [4]. Many works has been devoted in order to

enhance the ductility by acting on the BMG matrix composition and varying the chemical composition [5] or via the reinforcement of the matrix by ductile phase dispersion [6]. Other studies have been focused on surface treatment, either by the introduction of surface compressive residual stresses through techniques such as shot peening [7] or by using the nanocrystalline coatings deposited on the surface [8]. In fact, combining different types of multilayer such as hard and soft enhance the resistance to contact damage of coatings [9]. In our approach, we have deposited two types of coatings, TiN monolayer and Ti-TiN multilayer on Zr-based metallic glass to investigate their effect on the mechanical properties. In a previous work, we have used the conventional nanoindentation to compare the apparent mechanical properties of the two deposited coatings [10]. Cyclic nanoindentation is a variation to this conventional test, where the sample is reloaded immediately to even higher loads or depths than the previous loading cycle. It was used in various works to study phase transformations under stress [11,12]. In fact, the unloading-reloading paths do not necessarily overlap in crystalline alloys, resulting in hysteresis loops (strain hardening) or disparities (strain softening) due to sensitive dislocation-microstructure interactions detectable in the unloading-reloading curves [12]. In this study, we have conducted nanoindentation tests with monotone and incremental cyclic modes at various loading rates on TiN and Ti-TiN multilayer coatings deposited on Zr-based BMG in order to study their deformation behaviour.

2. Experimental details

Monolithic TiN and Ti-TiN multilayer nanocoatings were deposited on $Zr_{60}Ni_{10}Cu_{20}Al_{10}$ bulk metallic glass substrate by means of RF sputtering technique in nitrogen and argon atmosphere at room temperature using a 99.9% pure titanium target. The typical base pressure in the deposition chamber was about 1.33×10^{-6} Pa and the total working pressure was 0.66 Pa. Typical deposition rates of about $3 \text{ nm} \cdot \text{min}^{-1}$ for Ti and $0.9 \text{ nm} \cdot \text{min}^{-1}$ for TiN were obtained. Ti-TiN multilayer coatings were elaborated with a period thickness $\Lambda = 5 \text{ nm}$. The samples were previously cleaned with acetone and alcohol ultrasonic baths before the deposition process. The obtained thickness is about 300 nm. Nanoindentation tests were conducted using the triboscope system (Hysitron Inc.) coupled with an atomic force microscope. This allows us to visualize the surface before and after the mechanical testing and thus for the determination of the size of the imprints. The hardness H and the reduced Young's modulus E_r were measured using a Berkovich tip with a total included angle of 142.3° and a radius of curvature of approximately 100 nm. In order to test the reproducibility, each test was repeated at least five times.

3. Results and discussion

In previous work, we have conducted conventional nanoindentation tests on TiN monolayer and Ti-TiN multilayer coatings deposited on $Zr_{60}Ni_{10}Cu_{20}Al_{10}$ metallic glass substrate to assess nanomechanical film properties such as hardness and reduced elastic modulus values [10]. The obtained values of hardness H and reduced Young's Modulus E_r , evaluated using the model of Oliver and Pharr [13] are given in table 1. It is obvious that Zr-based metallic glass sample coated with TiN coating show higher values of hardness and elastic modulus than the uncoated samples and the coated one with Ti-TiN multilayer coating. The difference between the obtained values and those found in the case of the same coatings deposited on the Silicon substrate is due to the effect of the substrate. Moreover, the H/E ratio parameter could be used to evaluate the resistance of the film to plastic deformation [14]. As shown in table 1, H/E ratio was found to reach higher values in the case of coated systems compared with the uncoated bulk metallic glass. The main goal here is to enhance the apparent mechanical properties of coated metallic glass substrate in order to prevent the initiation of shear bands from the substrate surface under applied stress.

TABLE. 1 – Experimental values of hardness and elastic modulus [10]

Samples	H (GPa)	Er(GPa)	H/E
$Zr_{60}Ni_{10}Cu_{20}Al_{10}$	6.87 ± 0.73	104.1 ± 5.2	0.06
TiN/ $Zr_{60}Ni_{10}Cu_{20}Al_{10}$	22.42 ± 1.8	199.4 ± 13	0.11
TiN/Si	23.19 ± 2.1	253.58 ± 6.2	0.09
Ti-TiN/ $Zr_{60}Ni_{10}Cu_{20}Al_{10}$	11.14 ± 0.96	125.2 ± 7.7	0.09
Ti-TiN/Si	32.2 ± 2.5	262.9 ± 6.4	0.12

In order to study the deformation behaviour when reloading-unloading many times the two coated systems, we have conducted incremental cyclic nanoindentation tests. In fact, cyclic nanoindentation tests could be very effective to extract sensitive information about coated Zr-based BMG such as possible shifts in nanoindentation curves or in the yield point that may arise due to local structural changes. Figure 1-a shows load versus time function used in the nanoindentation process. The cyclic nanoindentation tests have been conducted at a loading rate of 1000 $\mu\text{N/s}$.

From the designed cyclic nanoindentation tests performed on Zr-based metallic glass, the obtained load-displacement curve shows that the unloading and reloading curves overlap. Furthermore, the onset of yielding upon each reloading is always noted to take place at a higher load than the load reached in the previous cycle. This phenomenon called “hardening and recovery” mechanisms is reported in our previous work [15]. However, for the coated systems, the reloading path is displaced relative to the unloading path of the previous cycle. When sections of the curve containing the unloading-reloading path are magnified, it is obvious that they do not overlap and show two different phenomena relative to the behaviour of loaded coated samples. In the case of TiN coated Zr-based metallic glass, the unloading-reloading paths form an open jaw as shown in figure 1. The open jaw signifies that the coated sample behaviour was softer in reloading compared to the previous unloading path. The disparity between the unloading and reloading paths increases as the indentation force/depth of cycling increases. Although, in the case of Ti-TiN coated Zr-based BMG, the magnified unloading-reloading paths illustrate hysteresis loops produced when performing cyclic loading. The coating resistance to deformation becomes greater during reloading than that presented by the unloading path. This result can be explained by the increased ductility of Ti-TiN multilayer structure due to the presence of Ti layer. Furthermore, it is clear that the obtained load-displacement curve for Ti-TiN multilayer coated metallic glass substrate reproduces the increase of the onset of yielding seen in the case of uncoated one. This is can be explained by the combination of the multilayer types of coating and the effect of the softer substrate type, when reaches depth more than 10% of the deposited coating.

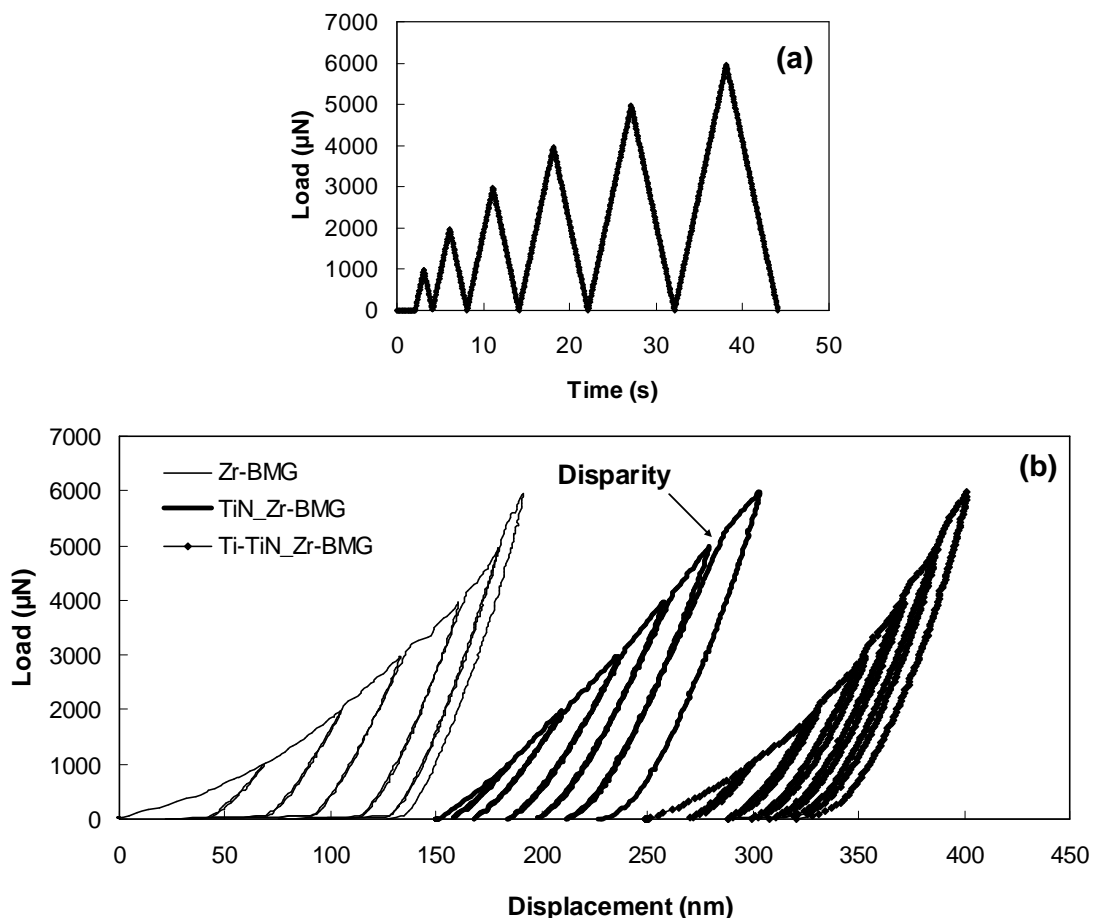


FIG. 1 – (a) Load versus time function used in cyclic nanoindentation conducted on Zr-BMG and Zr-BMG coated with monolayer TiN and Ti-TiN multilayer thin films at loading rate of 1000 $\mu\text{N/s}$ (b) obtained load displacement curves

In order to analyse the deformation of the surface after cyclic nanoindentation tests, the obtained imprints were scanned by atomic force microscopy. Figure 2 shows section analyses of the permanent imprints after cyclic loading conducted on Zr-BMG uncoated and coated with TiN monolayer and Ti-TiN multilayer at a loading rate of 1000 $\mu\text{N/s}$.

As shown in Figure 2-a, the plastic deformation of the uncoated Zr-based metallic glass substrate was illustrated by the pile-up around the indent which was not the case of TiN coated Zr-BMG. The imprint obtained in the case of Ti-TiN multilayer coating shows more ductile behaviour compared with that obtained in the case of TiN coating shown by the surface of the indentation imprint. We can conclude from the obtained sections the elastic behaviour of TiN coated Zr-BMG. This is illustrated by the lower value of indentation depth and impression size in figure 2-b.

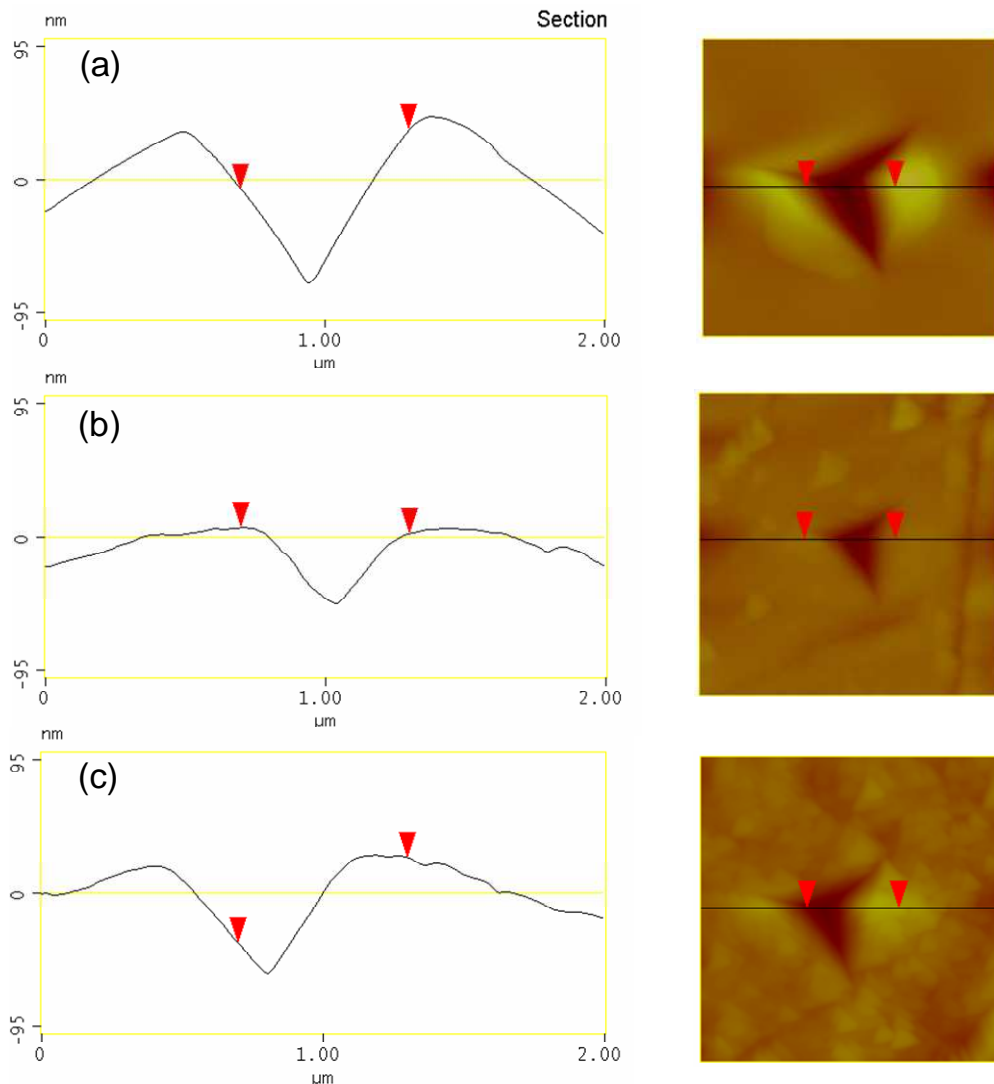


FIG. 2 – AFM images and corresponding height profiles of the indents formed on (a) Zr-BMG (b) TiN/Zr-BMG (c) Ti-TiN/Zr-BMG obtained under incremental cyclic loading at a loading rate of 1000 $\mu\text{N/s}$

As reported in our previous work [15], Zr-based metallic glass shows loading rate dependant plastic deformation behaviour under quasi-static cyclic loading. However, they shown a loading rate independent behaviour when performing incremental cyclic loading. This was associated with the shear bands nucleation and propagation mechanisms feature of the heterogeneous deformation of metallic glasses at temperature well below the glass transition temperature. To extract sensitive information about the deformation behaviour of deposited coatings under different loading rates, incremental cyclic loading at various loading rate was performed at loading rates of 500, 1000 and 2500 $\mu\text{N/s}$. The open jaw or “disparity” between unloading and reloading path phenomenon, found in the case of TiN coated bulk metallic glass shown in figure 1, increases when increasing the applied load and decrease with increasing the loading rate. Whereas,

TiN coating is characterized by the hardness, which means that we expect a hardening phenomenon and the appearance of hysteresis loop when performing cyclic loading. However, the least phenomenon is found in the case of Ti-TiN multilayer coated Zr-based metallic glass showing of hysteresis loops that decrease with the increase of loading rate. This difference can be explained by the effect of the dislocations-microstructure interactions in the coatings beneath the indenter and the type of substrate when the indentation depths exceed more than 10% of the coating thickness. In the case of Ti-TiN coatings, there is a tendency to have an elastic recovery due to multilayer structure consisting of alternating thin layers of a hard material and a softer more ductile material. The dependency of hysteresis loop width on loading rates has been found also by Bhushan et al. for $Ti_{1-x}Al_xN$ thin films. This has been explained by the fact that the change of the hysteresis loop area indicates the onset of plastic deformation and this depends on the substrate [16]. Furthermore, Dharma et al. noticed that the existence of large compressive stress in the film and the continuous plastic deformation are the main reasons behind the formation of the hysteresis loop in the repeated loading-unloading tests [17]. In other work, we have used a numerical simulation to compare TiN monolayer and Ti-TiN multilayer deposited coatings. The obtained simulation shows the transfer of charge to the substrate [18]. This may explain the dependency of the response of the deposited coatings on the type of substrate. It is important to mention that the obtained results are similar for all the tests performed and this proves that showed curves really reflect the material behaviour and are not artefacts of the test procedure or equipment.

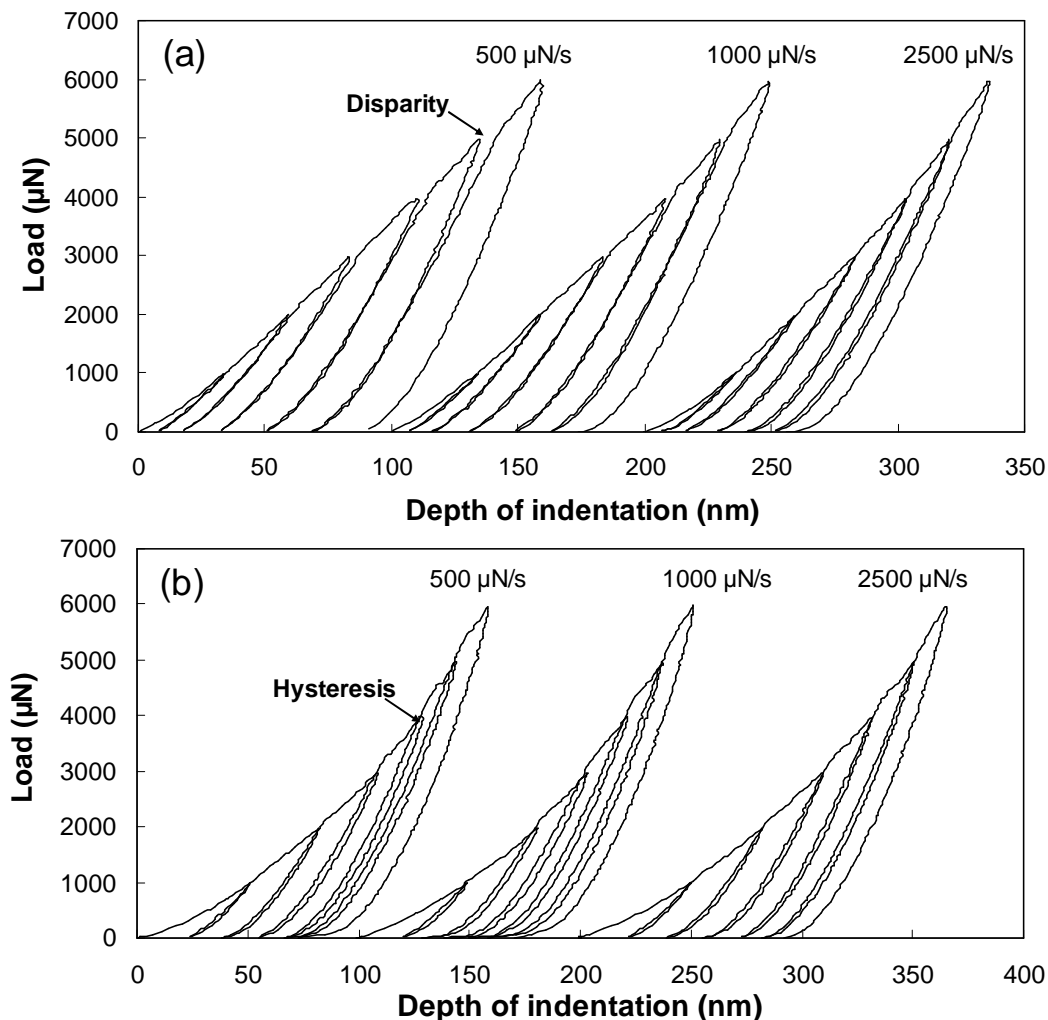


FIG. 3 – Load-displacement curves of incremental cyclic loading for (a) TiN/Zr₆₀Ni₁₀Cu₂₀Al₁₀ (b) Ti-TiN/Zr₆₀Ni₁₀Cu₂₀Al₁₀ under different loading rates

4. Conclusion

Incremental cyclic nanoindentation tests were carried on TiN and Ti-TiN multilayer coatings deposited on Zr-based metallic glass. An enhancement of mechanical properties was noted compared to the uncoated Zr-BMG. The cyclic incremental nanoindentation tests performed under different loading rates have shown two

different phenomena for TiN and Ti-TiN multilayer coated systems; open jaw and hysteresis, respectively. Despite the lack of quantitative characterization of the origin of the so called hysteresis loop and disparity, it is presumed that those phenomena are due to sensitive dislocation-microstructure interactions.

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