Evolution of the Mechanical Properties of Ti-Based Metallic Glass During Depth-Sensing Load–Unload Nanoindentation Cycles

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The mechanical behaviour of Ti-based bulk metallic glass during consecutive load–unload nanoindentation cycles, using progressively larger forces, is investigated. Indentation cycles allow evaluating the contact stiffness and, therefore, the hardness and Young’s modulus as a function of the penetration depth. The indentation hardness shows a gradual decrease as the applied load increases, evidencing the occurrence of an indentation size effect. An increase of contact stiffness is also observed during the indentation cycling process, an effect which is accompanied with a slight reduction of the Young’s modulus. These observations are consistent with the presumption that metallic glasses become structurally modified during the course of nanoindentation experiments. In particular, a deformation-induced increase in the amount of free volume occurs within the amorphous structure, leading to a concomitant mechanical softening.

Keywords: Metallic Glass, Mechanical Properties, Nanoindentation, Indentation Size Effect.

Metallic glasses (MGs) are a particular type of metallic materials with no long-range atomic order. Due to their amorphous character, these materials show mechanical properties that are quite different from those of other solid materials. For example, they can exhibit more elasticity and fracture toughness than ceramics and be twice stronger than conventional steels.1,2 However, in spite of their large elasticity, MGs show poor room-temperature macroscopic plasticity. This limited plasticity often precludes the use of macroscopic tensile tests to investigate the mechanical behaviour of these materials. For this reason, nanoindentation has become a versatile technique to assess the mechanical behaviour of MGs.3 This technique is particularly suitable not only to extract some material properties like hardness or elastic modulus but also because the overall mechanical response of the system is recorded during the test. Hence, time dependent phenomena, such as anelasticity or strain rate effects can be investigated in detail.4

From a structural point of view MGs are metastable, in the sense that they tend to crystallize when sufficient energy is provided to the system. Typically, when subject to heat treatments, MGs experience increased atomic mobility and a reduction in the amount of free volume (which is related to local changes in the atomic coordination number associated with structural relaxation). At sufficiently high temperatures, MGs show a glass transition and subsequent crystallization. Remarkably, the structure and properties of metallic glasses can be also modified by means of mechanical procedures.2,5 Surface treatments using shot peening have been reported to drastically enhance the plasticity of MGs.6 In turn, plastic flow typically causes an increase of free volume within the amorphous structure of MGs, hence resulting in mechanical softening.5,7 In some systems, phase separation and even crystallization have been observed when the applied stress is sufficiently high.8,9

In this work, the changes in the mechanical properties of Ti-based metallic glass during nanoindentation tests have been investigated. For this purpose, a specific indentation protocol, consisting of successive load-unload cycles applying progressively larger forces, has been employed. This procedure allows evaluating the contact stiffness and the concomitant mechanical properties (e.g., hardness, Young’s modulus) as a function of applied
indentation load. Our results reveal that once the plastic zone is achieved, the hardness and Young’s modulus exhibit a progressive decrease as the indentation loads are increased. This softening is ascribed to an increase in the amount of free volume as indentation proceeds.

A master alloy with composition Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18} (at.%) was prepared by arc-melting a mixture of high purity (99.9 wt%) elements in an Ar atmosphere. Rods of 3 mm in diameter were obtained from the master alloy by copper mould casting. To confirm their amorphous character, the rods were cut into disk-shaped specimens and structurally characterized by X-ray diffraction. The mechanical properties were evaluated at room temperature using a nanoindenter from Fischer-Cripps Laboratories, operating in the load control mode. The indenter was equipped with a Berkovich pyramidal-shaped diamond tip. Prior to indentation, the samples were carefully polished to mirror-like appearance using diamond paste. The indentation function consisted of fifty load–unload cycles with increasingly higher forces, ranging from 0 to 10 mN [see Fig. 1(a)]. The fifty load–unload cycles are performed exactly at the same position at the surface of the specimen. The loading time was relatively fast (about 2 s for all applied loads) and the unloading response was recorded after application of each load step. Moreover, a load holding segment of 30 s was introduced before each unloading to ensure fully elastic unloading response [see inset in Fig. 1(a) for a detailed view of the load/unload indentation cycles].

The load holding segment is particularly necessary in metallic glasses since time-dependent (i.e., anelastic effects) can play an important role in the measured mechanical properties.\(^4\) The cyclic load–unload method renders the values of contact stiffness as a function of the penetration depth. In all cases, the thermal drift was kept below ±0.05 nm s\(^{-1}\) (as estimated from the load-holding segments). From the load–displacement curves, the hardness, \(H\), and reduced elastic modulus, \(E_r\), values were evaluated at the beginning of each unloading segment. The presented results are the average of a total amount of ten tests for each indentation condition. From the unloading slope, the contact stiffness is determined as:\(^{10}\)

\[
S = \frac{dP}{dh}
\]  

(1)

where \(P\) denotes the applied load and \(h\) the penetration depth. Evaluation of the elastic modulus follows from its relationship with the contact area, \(A\), and the contact stiffness:

\[
S = \beta \frac{2}{\sqrt{\pi}} E_i \sqrt{A}
\]  

(2)

where \(\beta\) is the so-called King’s factor, that depends on the geometry of the indenter, and \(E_i\) is the reduced Young’s modulus, defined by:

\[
\frac{1}{E_i} = \frac{1 - \nu_i^2}{E} + \frac{1 - \nu^2}{E_i}
\]  

(3)

The reduced modulus takes into account the elastic displacements that occur in both the specimen, with Young’s modulus \(E\) and Poisson’s ratio \(\nu\), and the indenter, with elastic constants \(E_i\) and \(\nu_i\). Note that for diamond \(E_i = 1141\) GPa and \(\nu_i = 0.07\). The Poisson’s ratio of the Ti-based MG was measured by acoustic measurements and a value \(\nu = 0.37\) was obtained.\(^{11}\)

The contact area was estimated using the method of Oliver and Pharr.\(^{10}\) For a Berkovich indenter, \(A\) depends on the so-called contact depth, \(h_c\), as follows:

\[
A = 24.56h_c^2 + f(h_c)
\]  

(4)

where the first term corresponds to an ideal pyramidal Berkovich-type indenter tip and the second term is determined using proper corrections for the blunting of the tip (calibrated using a fused quartz specimen). The contact
depth is related to the maximum penetration depth, \( h_{\text{max}} \), using the following expression:

\[
h_c = h_{\text{max}} - 0.75 \frac{P_{\text{max}}}{S} \tag{5}
\]

Corrections for the instrument compliance and initial penetration depth were also applied. The hardness is calculated using the following expression:

\[
H = \frac{P_{\text{max}}}{A} \tag{6}
\]

As shown in Figure 1(b), the slope of the unloading segments of the indentation cycles (i.e., the contact stiffness) tends to progressively increase as the maximum applied load increases. According to Eq. (1) this means that the product \( E_r \sqrt{A} \) becomes larger as the indentation proceeds. Careful analysis of the contact area using the method of Oliver and Pharr, allows evaluating the dependence of hardness and Young’s modulus as a function of the penetration depth. Remarkably, both \( H \) and \( E \) tend to gradually decrease when the applied indentation load is increased (see Fig. 2). This indicates that the Ti-based MG exhibits a so-called indentation size effect (ISE). Note that a moderate reduction in both \( H \) and \( E \) is observed for maximum applied loads lower than 1 mN, probably because for such small loads the plastic zone underneath the indented region is not yet fully developed.

The decrease of \( H \) and \( E \) with the applied load could be, to some extent, an artifact arising from improper calibration of the indenter for the tip geometry. To rule out this possibility, the same cyclic load/unload indentation experiments were performed on fused silica. In this case, as shown in Figure 3, both \( H \) and \( E \) remain virtually independent of the maximum penetration depth, thus confirming that the ISE observed in the Ti-based glass is a consequence of a change in the material properties during the course of the nanoindentation experiments.

The ISE is often observed in crystalline materials and is commonly ascribed to strain gradient hardening occurring in small indentations.\(^{12,13}\) This effect originates from the need to create the so-called “geometrically necessary dislocations” in order to form the residual indentation impressions in the case of very low applied loads (when the amount of pre-existing dislocations is exceedingly small). For large indentations, the strain variation between two extremes is more gradual and the dislocations statistically stored in the material can easily accommodate the shear stress without need of the geometrically necessary dislocations, thus reducing strain gradient effects. In spite of the lack of dislocations in MGs, these materials also occasionally show an ISE.\(^{11,14}\) In this case, the ISE is explained as a consequence of strain softening associated with a net production of free volume caused by the applied stress.\(^{11}\) In this work, we have fitted the ISE using surface energy considerations, as previously reported by Zhang et al.\(^{15,16}\)

According to these authors, the ISE effect when using a Berkovich indenter can be adjusted using the equation \( H = \sigma + 1.1827 f/h \), where \( \sigma \) is the pressure average over the contact area and \( f \) is a constant.\(^{13}\) From the result of our fit [see Fig. 2(a)], we obtain \( \sigma = 5.64 \text{ GPa} \) and \( f = 150.3 \text{ J/m}^2 \). These results are similar to those obtained by Zhang et al. in polycrystalline Cu and, as expected, much larger than the ones corresponding to polymeric materials.\(^{15}\)

A quantitative evaluation of the amount of generated free volume during indentation is difficult since it depends on the strain rate, the already existing amount of free volume and, furthermore, creation of free volume competes with its thermally-induced annihilation.\(^{16,17}\) It should be noted that strain softening has been investigated in several families of MGs subject to macroscopic compression tests.\(^{7}\) However, reports on indentation-induced mechanical softening are more scarce.
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Fig. 3. Dependence of (a) hardness, $H$, and (b) elastic modulus, $E$, on the maximum penetration depth, corresponding to the indentation cycles performed on fused silica.

Fig. 4. Dependence of (a) $S^2$ on $P$ and (b) $H$ on $E^2$, corresponding to the indentation measurements performed on the Ti-based metallic glass.

It is worth mentioning that by combining Eqs. (2) and (6), an interesting relationship (which does not contain the contact area) can be derived between the hardness and the reduced elastic modulus:

$$\frac{P}{S^2} = \pi \frac{H}{4\rho^2 E^2}$$

(7)

The validity of Eq. (7) has been checked for the Ti-based metallic glass. As shown in Figure 4, $S^2$ increases linearly with $P$. Since $\beta$ is a constant, this means that $H$ should linearly increase with $E^2$, as it is indeed observed experimentally [Fig. 4(b)]. Remarkably, from the ratio between $P/S^2$ and $H/E^2$ an average value of 0.71 is obtained, which is consistent with Eq. (7) provided that $\beta$ is approximately equal to 1.05. The value of $\beta$ has been an issue of discussion in the literature recently since an exceedingly small value for $\beta$ can result in an overestimation of the reduced Young’s modulus. A numerical analysis that modeled indentation on an elastic half-space using a flat triangular punch yielded $\beta = 1.034$. It has

and the cyclic loading indentation experiments presented here constitute an easy way of studying this effect. In this work, no evidence for crystallization or phase separation was observed by electron microscopy in the indented Ti-based metallic glass. In certain MGs (e.g., Zr-based ones), where crystallization is indeed induced by application of mechanical stress, an increase of hardness is observed, which competes with the mechanical softening, resulting in a non-monotonic dependence of hardness as a function of the penetration depth.18

In crystalline materials the ISE typically affects only $H$ while $E$ remains independent of the maximum load. Conversely, in MGs, the ISE affects both $H$ and $E$.19 Indeed, in our experiments, the decrease of $H$ is accompanied with a reduction of $E$. It can be argued that such a reduction of $E$ is the consequence of a reduced atomic packing and enhanced atomic mobility, due to the deformation-induced increase of free volume in the region of material affected by the indentation impression.

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been later shown that $\beta$ depends on the geometry of the indenter and values as high as $\beta = 1.2$ can be encountered for sufficiently small indenter angles.\(^{21}\) Hence, our result agrees rather well with the values for $\beta$ reported in the literature.

In summary, indentation experiments using load–unload cycles with increasingly large forces reveal that Ti-based metallic glass exhibits deformation-induced strain softening. The decrease of hardness and Young’s modulus with the maximum applied load can be ascribed to a net production of free volume in the amorphous structure, similar to what has been reported in the literature for metallic glasses subject to macroscopic compression tests. Our results indicate that certain care needs to be taken when evaluating the mechanical properties of metallic glasses by means of nanoindentation, since the indentation stresses can induce structural effects in the glassy nature of amorphous metallic alloys, which in turn can affect their concomitant mechanical response.

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References and Notes


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