Micromechanisms of Mechanical Behavior of Bulk Metallic Glasses

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論文内容要旨

Bulk metallic glasses (BMGs) have aroused a great deal of interest because of their notable properties, such as high strength and excellent elasticity. At room temperature, BMGs tend to form shear bands in which plastic deformation occurs in a highly localized manner. Owing to strain softening, these bands are preferential sites for further plastic flow and generally lead to the final failure that typically breaks a sample along a single shear band. This localized deformation strongly limits the global plasticity of BMGs and restricts their applications as structural materials. In an effort to overcome the problem of limited plasticity of BMG at room temperature, BMG-based composites have been developed by introducing ductile crystalline phases into BMGs, which has been demonstrated to have improved plasticity and toughness over their monolithic counterparts. A number of BMG-based composites have been developed by various techniques such as extrinsically introducing a crystalline phase into the liquid BMGs, *in situ* formation of a crystalline phase from melts, and warm extrusion of gas atomized BMG powders mixed with crystalline particles. Enhanced plasticity has been achieved in these BMG-based composites, which is not normally observed in monolithic BMGs. The presence of crystalline phases is believed to be critical in improving plasticity by effectively preventing continuous strain softening along a single shear band. However, only limited microscopic investigations have been reported in the literature and detailed micromechanisms on the plasticity of BMG-based composites are not well understood, except the fact that crystalline phases can alter the shear band propagation path. More recently, extraordinary plasticity and work hardening were observed in Pt-, Cu-, and Zr-based monolithic BMGs with high strength. A number of explanations have been suggested, including high Poisson's ratio and structural inhomogeneity , work hardening by *in situ* nanocrystallization in shear bands. But all of these explanations are proposed for particular systems, whereas an underlying universal mechanism is still missing. Understanding the mechanisms of plastic deformation and enhancing the plasticity of metallic glasses are therefore of significant importance in this field. In this thesis, a number of issues related to plastic flow in metallic glasses are investigated.

The plastic deformation of BMGs during nanoindentation experiment has been found to be typically associated with serrated flow (pop-in) events, corresponding to the operation of discrete shear bands. By calculating the corresponding plastic strain work and virtual deformation volume of shear band induced pop-in burst during nanoindentation loading, the plastic deformation energy of BMGs can be precisely determined. Seven BMGs with different plasticity were investigated by measuring their plastic deformation energy of the first pop-in events during loading of nanoindentation test. The results indicate that the plastic deformation energy is intrinsically associated with ductility of BMGs, resulting from the formation ability of shear bands. The experimental results show that the ductile BMGs have smaller plastic deformation energy values whereas the brittle ones have the larger values, which paves a new way to determine the intrinsic ductility of BMGs in addition to the traditional mechanical measurements.

A low plastic deformation energy alone will not be enough for a BMG to sustain a large plasticity. TEM characterization reveals that a high density of nanocrystals precipitate exclusively within shear bands produced by uniaxial compression in a ductile $Ni_{50}Pd_{30}P_{20}$ BMG. Electron diffraction analysis and HREM characterization demonstrate that the nanocrystalline phase is an fcc palladium-nickel solid solution. A high density of crystal defects were observed in the *in situ* formed nanocrystals, suggesting that they have experienced severely plastic deformation during the propagation and the arrest of shear bands. The deformability of the precipitated fcc phase appears to be important to the large plasticity of the BMG because it can release the applied stress by plastic deformation rather than cracking. The crystallization in the shear bands within a very short time scale implies that the deformation induced temperature rise may not be the only reason leading to the formation of extensive nanocrystals. The assistance of the high shear strain rate and the large shear strain along the shear bands may be important for the *in situ* nanocrystallization. The obvious strain hardening observed in the homogeneous BMG can be well explained by an exhaustion model in which the critical stress to drive the nucleation of shear bands will gradually increase from easy to difficult nucleation sites during deformation. The applied force is thus required to progressively increase with plastic strain to keep further plastic deformation. The compelling evidence has been provided on the micromechanism of serrated flow in the ductile BMG, the stress drop caused by strain softening and the arrest of shear bands by *in situ* nanocrystallization.

The interface structure and mechanical properties of a brass-reinforced $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ BMG composite have been studied using TEM and nanoindentation. This study provides an understanding of the microstructure-deformation micromechanism relationship in the composite and has important implications in developing BMG-based composites with improved strength and plasticity. Microstructural examination reveals the formation of an interface layer between the BMG matrix and brass reinforcements, which is composed of nanocrystalline particles embedded in a glassy matrix. The nanoparticles are characterized to be a hexagonal Ni_3Zr (space group $P6_3/mmc$, a=0.531 nm, c=0.430 nm) and an fcc Cu solid solution. Chemical composition analysis shows that the formation of the interface layers is associated with the interdiffusion reaction between the Ni-based BMG and the brass phase. The fast diffusion of Cu into the BMG leads to the loss of the glass forming ability in the interdiffusion zones and causes nanocrystallization. The BMG/brass interfaces in the warm extruded composite are sufficiently strong to withstand high stresses and severe plastic deformation as a result of the formation of an interface layer with a mixed nanocomposite structure. Nanoindentation measurements also show that the interfacial region has a higher hardness than both the BMG matrix and brass, which effectively prevent the deformation and cracking along the interfaces. SEM and TEM observations show that the interface layers suppress the propagation of the shear bands and switch the deformation modes from local shear in the BMG matrix to dislocation sliding and twinning in the crystalline phases, which leads to energy absorption and improved ductility.

In addition, the elegant microcompression method is employed to probe the mechanical behavior of BMGs at micrometer/sub-micrometer scale. The microcompression method has proven itself a viable and reliable way to probe the sub-micrometer-scale mechanical behavior of materials in a scale-down form of conventional uniaxial compression test. In this method, focused ion beam (FIB) is used to fabricate a free-standing micropillar in the area of interest, which is located in the center of a large cavity concurrently milled by FIB. The nanoindentation compression tests were carried out on these pillars using a flat diamond punch. The sample BMGs used were Zr-based ($Zr_{55}Cu_{30}Al_{10}Ni_5$) and Pd-based ($Pd_{40}Ni_{40}P_{20}$), provided in the form of rods several millimeters in diameter. The micro-pillars with nominal diameters ranging from ~1 μm to 40 μm and an aspect ratio ranging from 2:1 to 4:1 were prepared by a Hitachi FB-2100 FIB system for micro-compression tests. Size effects on fracture stresses of two distinct monolithic BMGs have been observed when compressed in a form of micro-pillars with micrometer-scale diameters. Strikingly, a 'threshold' sample size is observed for both BMGs, above which a strengthening effect arises with decreasing sample size probably caused by the crack-like behavior of shear bands during their propagation, whereas below which the fracture stresses decrease with sample diameters, stemming from the fact that the sample size is less than the critical size of shear band nucleation.

論文審査結果の要旨

バルク金属ガラスの機械的性質に関する研究の博士論文について、審査が行われた。博士論文の概要は次の通りである。

１，ナノインデンテーション試験による弾性変形エネルギーの評価

ナノインデンデンデーション法によって正確な弾性変形エネルギーを評価することで、脆性金属ガラスと延性金属ガラスとを明確に区別できる評価方法を確立した。

２，電子顕微鏡による延性金属ガラスのせん断帯近傍のナノ結晶化領域の解析

単相Ｐｄ基金属ガラスの圧縮変形後のせん断帯領域を高分解能電子顕微鏡によって解析した。せん断帯に沿って明瞭なナノ結晶が形成されており、ナノ結晶内部に大きな応力が生じたことによる多数のキンクが観察されたことを示した。この観察により、せん断帯のナノ結晶による“セルフロック”メカニズムによる金属ガラス延性の起源を明瞭に示した。

３，複合金属ガラスの変形組織解析

Ni 基バルク金属ガラスに Cu 金属相を複合することで延性が改善された。それは、金属ガラスと金属相との界面に中間相が生成しているからであり、電子顕微鏡を用いて詳細に中間相を解析し、ナノ結晶を呈していることを明らかにした。ナノインデンテーションと FIB 法で中間相へ変形を付加し、その部分を電子顕微鏡観察する工夫をしめした。それにより、中間層がせん断帯の応力集中を緩和している機構を明らかにし、延性の起源を明確にした。

４，金属ガラスのマイクロ圧縮テスト

FIB 法で種々の金属ガラスのマイクロ圧縮試験片を作製し、ナノインデンテーションを使用してマイクロ圧縮機械特性を評価した。変形メカニズムが直径 5μm を境に変わることを示し、これにはせん断形成の活性化体積が密接に関わっていることを示した。

いずれの研究トピックは、金属ガラス研究に新たな知見をもたらすものであり、王科氏の独創性、計画性、実行性を示し、研究者としての素質を示す上で十分である。

よって，本論文は博士(工学)の学位論文として合格と認める。