Intrinsic and extrinsic size in metallic glasses
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Chapter 2

Preparation and mechanical testing techniques

*This chapter presents a concise overview of the experimental techniques used in this thesis work, e.g. Focused Ion Beam (FIB) for the milling of metallic glass nanopillars, picoindenter installed in Transmission Electron Microscope for the in situ mechanical testing of metallic glass nanopillars. The preparation methods of metallic glasses will be also discussed. Scanning Electron Microscopy and X-ray techniques, which were used for the preparation control and post mortem observation of metallic glasses will be summarized.*

### 2.1 Preparation and characterization techniques

#### 2.1.1 Melt spinning for MG preparation

The method that we have used for the preparation of metallic glassy (MG) ribbons is called melt spinning.\(^1\) A schematic representation and picture of melt spinning technique is shown on Fig. 2.2. The molten material is driven from the nozzle in the form of a jet, which impinges with a rotating wheel. Puddles formed under the counteracting forces of the flow of the material and the surface tension. Because of the low viscosity of the molten metallic alloy, the shear layers extend only a few microns from the surface of the roller into the puddle and stays on the roller surface. Because of a large temperature gradient at the melt-substrate interface, the melt beneath the puddle solidifies into a ribbon. The ribbon remains in contact with the disc surface and then leaves it under the action of the centrifugal force.
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For our experiments we have chosen the compositions $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ and $\text{Al}_{86}\text{Ni}_{9}\text{Y}_{5}$ with low shear modulus over bulk modulus, i.e. $\mu/B$, that according to predictions have higher ductility. The idea was to check whether the ductility of bulk MG alloys may affect the deformation mode of micropillars and the transition of banding events from nucleation control to propagation control. Strips of such MG alloy were prepared by vacuum arc melting and mold-casting with water cooling, SEM micrographs are shown at Fig. 2.3.

Fig. 2.3. SEM micrograph of $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ strip as alloy (a) and melt-spin MG ribbon (b).

2.1.2 Mechanical polishing of MG ribbon

A typical mechanical polishing tool is represented in Fig. 2.4. It consists of a spinning flat plate which is covered by a pad. The ribbon that is being
polished is mounted with special holder. During the process of loading and unloading an oil introduction mechanism deposits the oil on the pad. Both the plate and the holder are then rotated and the holder is kept oscillating as well. A downward manual pressure force is applied to the holder. The manual force depends on the contact area and polishing requirements. The roughness of the ribbon edge that has been achieved by using this technique was equal to 2 to 5 µm, which was suitable for further sample preparation.

Fig. 2.4. Schematic picture of mechanical polishing technique

2.1.3 Surface characterization techniques

Scanning electron microscopy (SEM)

In order to make a link between processing, microstructure and properties in materials science, almost every year new and exciting characterization techniques enter the field. A landmark in the analysis of both bulk materials and surfaces, since its introduction in the 1930s, is the electron microscope. The two most popular electron microscopy techniques probably are the scanning electron microscope (SEM, Fig. 2.5) and the transmission electron microscope (TEM, Fig. 2.8.). The resolving power is defined as the closest
spacing between two points which can be clearly seen by the naked eye to be separate entities. The resolving power in microscopy is limited by diffraction of the source as it passes through a series of apertures. An empirical diffraction limit is given by the Rayleigh criterion

$$\sin \theta = 1.22 \frac{\lambda}{D}$$

(2.1)

where $\theta$ is the opening angle of the ray from the source, $\lambda$ is the wavelength of the incoming electrons or photons and $D$ is the diameter of the lens. It follows therefore that for the best resolving power, $\lambda$ should be as small as possible and/or $D$ should be as large as possible. The electron beam is focused by a system of magnetic lenses to a small spot of around 1-10 nm in diameter. Primary electrons which enter the specimen are scattered elastically or inelastically by the atoms. This can cause electrons to exit the specimen, i.e. backscatter, after traveling through the specimen. Since the material volume in which the electrons are backscattered, can be much larger than for the secondary electrons, the lateral resolution is much smaller.

Fig. 2.5. left: Schematic representation of a SEM; right: picture of one of the SEMs (Phillips XL30 SEM FEG) of the Materials Science group.
If the microscope is operating in the backscattered mode, the result is a lateral resolution of the order of micrometers. The penetration depth of the high energy electrons will cause the electrons to be trapped in the material. When studying conducting materials, the electrons will be transported away from the point of incidence. If the specimen is a non-conducting material, the excess electrons will cause charging of the surface. The electrostatic charge on the surface deflects the incoming electrons, giving rise to distortion of the image. In order to reduce surface charging effects, a conducting layer of metal, with typical thickness of 5-10 nm, can be sputtered onto the surface.

Charging of the surface is not the only factor determining the resolution of a scanning electron microscope. The width of the electron beam is also an important factor for the lateral resolution. A narrow electron beam results in high resolution. The broadening of the spot size is the sum of broadening effects due to several processes. The first contributor is the beam itself and the second part is the contribution due to diffraction of the electrons of wavelength $\lambda$ by the size of the final aperture. The latter parts are the broadening caused by chromatic and spherical aberrations. To achieve the smallest spot size, all contributions should be as small as possible. Decreasing the accelerating voltage will not only cause the wavelength of the electrons to increase, but also the chromatic aberration increases as well, resulting in increasing of the spot size and, as a consequence, a decrease in resolving power of the microscope.

**X-ray characterization technique**

The principle of this technique is based on the detection of a diffracted beam when the Bragg diffraction condition $n\lambda = 2d\sin\theta$ is fulfilled, where $d$ is the space between the planes, $\theta$ is the diffraction angle, $n$ is the order of the diffraction peak and $\lambda$ is the wavelength of the X-rays.\(^4\)

During the collection of the diffraction spectrum, only the detector rotates through the angular range, thus keeping the incident angle, the beam path length, and the irradiated area constant. The long slit on the receiving side allows only those beams that are nearly parallel to arrive at the detector. This has an added advantage of reducing the sensitivity to sample displacement from the rotation axis.
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Fig. 2.6. X-ray diffraction (XRD) spectra of Al\textsubscript{86}Ni\textsubscript{9}Y\textsubscript{5}MG

A single circle diffractometer was used with an grazing angle of 1.5°, with a CuK\textsubscript{α} radiation (\(\lambda=1.540\) Å) generator operated at 40kV and 40mA. Fig. 2.6 shows a XRD spectra of the amorphous Al\textsubscript{86}Ni\textsubscript{9}Y\textsubscript{5} ribbon. Two homogeneous rings are indicating on the amorphous nature of the investigated metallic ribbon.

2.1.4 FIB technique

The Focused Ion Beam technique was used for the fine stage in the preparation of the samples for mechanical testing in TEM. A FIB instrument represents an ion gun installed in a SEM. Both instruments operate with focused beam to image the specimen, i.e. an ion beam for the FIB and an electron beam for the SEM. In the FIB, secondary ions are used to image and to mill the sample.
The operation of a FIB begins with a liquid metal ion source. A reservoir of gallium (Ga) is positioned in contact with a sharp W needle. Ions are emitted as a result of field ionization and post-ionization and then accelerated down the FIB column towards the sample (Fig. 2.7.a). When Ga ions are accelerated toward the target sample, they enter the sample and create a cascade of events which results in the ejection of a sputtered particle (Fig.2.7.b)

2.2 Picoindentation tests in TEM

2.2.1 Introduction of TEM

The optical microscope has a limited spatial resolution because it uses as source visible light, which has a relatively long wavelength. The electron microscope has the best possible source to overcome this limitation because of the wave-like character with short wavelength of accelerated electrons. The first Transmission Electron Microscope (TEM) was built by Max Knoll and Ernst Ruska in 1932. The famous DeBroglie equation relates the momentum of the particle, and the wavelength through Planck’s constant

\[ \lambda = \frac{h}{p} \]  

When electrons are accelerated to a high energy of 200 keV by the accelerating voltage, the corresponding wavelength of the electrons is 2.51 pm, which is a very small value compared to the diameter of the atoms. However, the resolution of a TEM is not equal to the wavelength, because is limited by the aberrations of the electro-magnetic lenses used in the
microscope. A reduction in the spherical aberration of the objective lens is a first step to increase the resolution limits in high resolution microscopy.

Generally the chemical composition of the material can also be obtained with a resolution of a few nanometers. Electron microscopy is not just a single technique, but a diversity of electron-matter interactions with unique properties are used to gain insight in structure, morphology and chemical composition, where the latter is obtained via spectroscopic techniques (Fig. 2.8).

During elastic interaction no energy is transferred from the electron to the sample, as a result the electron leaving the sample has its original energy and contributes to the direct and diffracted beams. In contrast, inelastically scattered electrons reduce the quality of the images and diffraction patterns. Most of the signals other than elastic scattering are used in analytical microscopy to obtain chemical and other spectroscopic information from the specimen. JEOL 2010F TEM (Fig. 2.8.) was used for the research work presented in this thesis.

![Fig. 2.8. Left: schematic of lenses, apertures, stigmators, and deflectors of TEM column; right: picture of one of the TEMs (JEOL 2010F) of the Materials Science group.](image)

The electron beam of a JEOL 2010F is operated at an acceleration voltage of 200 keV. A Gatan digital micrograph software and CCD cameras were used to record and analyze the TEM images. In-situ TEM compression
experiments were performed using a Hysitron picoindenter TEM holder (Hysitron Inc., Minneapolis, MN, USA) implemented on the JEOL 2010F TEM.

### 2.2.2 In situ compression, tension and cyclic tests in TEM

Testing the mechanical properties of nanoscale materials faces a number of inherent challenges. As the size of the “target” decreases, the inability to actually see what occurs during testing can be troublesome. Here we present a compression, tension and cyclic experiments of the *in situ* mechanical testing. With the picoindenter TEM holder (Hysitron Inc., Minneapolis, MN, USA) equipped on JEOL 2010F TEM it is possible to acquire quantitative mechanical data while simultaneously monitoring the microstructural evolution of the sample with the TEM (Fig. 2.9).

![Fig. 2.9. Scheme of quantitative in-situ compression test in TEM (a) specimen diameters are at a submicrometer range, length of specimen base is mm range and total with sub-mm range, Hysitron picoindenter (b)](image)

In-situ TEM compression experiments were performed using a picoindenter with a diamond flat punch of 2 mm in diameter. The indenter has several unique features, which are particularly critical to the present study. First, it is integrated with a miniature capacitive load–displacement transducer permitting high resolution load and displacement measurements (resolution of ~0.3 μN in load, ~1 nm in displacement). In addition, a rapid instrument response and data acquisition rate (the controller is operating in a continuous loop and samples data at 20 kHz) allows discrete flow events to be well-resolved. The experiments were run in two typical control modes:
displacement control, which shows a great sensitivity, and load control, which has an advantage when evaluating sudden displacement jumps. The displacement and/or load rate are programmed in such a way that a nominal strain rate of $\sim 10^{-2}$ s$^{-1}$ is applied. Together with the high data acquisition rate, this all makes it possible to evaluate the development of a single SB event.$^{6,7}$

Tensile experiments allow circumventing some artifacts (tapering, shear band formation due to friction) and increased purity of MG testing at the nanoscale. In-situ TEM tension experiments were performed by using a Hysitron picoindenteter TEM holder with an in house –made Al tip sample holder and W indenter tip.

Fig. 2.10. (a) TEM picture of compression testing; (b) FIB milled W tensile tip and mushroom-like nanopillar.

Al holder was designed and developed in order to achieve good calibration and to avoid undesirable mechanical noise during tensile experiments. Tungsten tip was designed and made first by electrochemical polishing and later on milled by Focused ion beam (FIB) to a desired shape.

References

1. The Institute of Solid State Physics, Materials Science and Technology in Kharkiv Institute of Physics and Technology (KIPT)