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Thermal transport properties in amorphous/nanocrystalline metallic composites: A microscopic insight

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ABSTRACT

In the last years new composite materials made of a metallic glass matrix with embedded nanocrystals have arisen as a promising alternative to the metallic glasses, due to their higher hardness. Although the effects of a partial nano-crystallization onto mechanical and magnetic properties have been widely investigated, nothing is known about thermal transport properties, interesting for recently proposed novel applications. Here we investigate how thermal transport is modified in presence of nanocrystalline inclusions in a Zr-based bulk metallic glass. By means of electric measurements and inelastic x ray scattering we are able to disentangle the effects of a partial nanocrystallization onto the two different contributions to heat transport, the electronic and the vibrational one. We show that no enhanced electrons or phonons scattering from the interfaces is observed, while the presence of crystalline nanoinclusions leads to an increase of both contributions, via an increased electric conductivity and transverse acoustic speed of sound. Surprisingly, while a gradual modification of the electric conductivity with the crystalline fraction is observed, even a low crystalline fraction is sufficient to modify elastic and vibrational properties. Our results indicate that low crystallinity composites are indeed promising alternative to both amorphous and crystalline alloys, thanks to their unique combination of high ductility, polycrystal-like vibrational properties and amorphous-like electric transport.

1. Introduction

In the last decades, Metallic Glasses (MG) have aroused as revolutionary materials in a number of structural applications, due to their excellent mechanical properties, intimately related to their disordered atomic structure [1–3]. Despite their great potential, however, their widespread use has long been hindered by their inherent brittleness, displayed under plastic deformation below the glass transition temperature, and related to shear bands instability [1,4].

Several ways have been explored to overcome the MG macroscopic brittlelike behavior, among which material size reduction, for playing on the surface to volume ratio to increase the ductility, chemical composition tuning, for playing on the kind of atomic bonding, or partial nanocrystallization. This latter appears as a simple and most promising way, as it can be realized very easily, by means of a variety of procedures, from compression to nano-indentation to controlled thermal protocols [5,6].

Whatever the method, a microstructure with a variable density of nanometer-sized crystalline particles embedded in an amorphous matrix is obtained, which has been found to display a higher hardness and in some cases an improved ductility with respect to the parent glassy phase, both under compression and tensile strength [7–11]. Such improvement has been understood in terms of an active role of the precipitates in changing the shear bands propagation, thus confining the deformation [12]. Starting from this, partially crystallized MG have been the subject of intense studies, with the aim of identifying the conditions for which the

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functional properties are not lessened by the partial crystallization while the mechanical resistance is increased.

At this day, investigations have mainly focused on the effect of nanocrystallites on mechanical [13–15] and magnetic [16,17] properties. However, a more global understanding of their influence on all different properties is needed for allowing to expand the application fields of metallic glasses composites. Indeed, many novel applications have been recently proposed for MG, exploiting the combination of their excellent mechanical properties with other functional properties, such as thermal and electronic transport. A recent example is the investigation of the potential of MG as alternative thermal barrier coating materials (TBC), on substrates where classical ceramic coatings are not appropriate [18–20], which takes advantage of their unusual combination of a relatively low thermal conductivity with a metallic electric character, together with a reduced thermal expansion.

So far, only data on thermal conductivity of fully amorphous or crystalline phases [21–24] have been reported, giving indication of an important increase of the thermal conductivity upon crystallization. Still, the information on a partial nanocrystallization effect is dramatically lacking. Some insight can be obtained from the electric transport properties, as in a metallic system electrons are the dominating heat carriers and their contribution to the thermal conductivity is proportional to the electric one.

It is largely known that electrical resistivity decreases upon crystallization [25–27], reaching values typical for a metallic polycrystal, and it has been observed that such a decrease can be accompanied by a change in the temperature behavior: in the polycrystal, the resistivity increases with temperature, as typically for metals [28], while in glasses the behavior depends on the specific alloy composition [29,30]. During crystallization, the resistivity decrease is generally assumed to be linear with the crystalline fraction, and, as such, it has often been used to monitor crystallization [31–34]. However, a non monotonic evolution has been reported in a $Cu_{46}Zr_{46}Al_8$ MG [35], with an increase in the early stages of crystallization, followed by the usual decrease. Such behavior has been explained in terms of a strong electron scattering at the amorphous/crystalline interfaces, due to the precipitation of a high density of very small ($\approx 1-2$ nm) nanocrystals at the beginning, which decreases with the proceeding of crystallization when nuclei start to grow.

To our knowledge, nothing exists yet in the literature on how the vibrational contribution to the thermal conductivity can be affected by the nanocrystalline inclusions. For understanding it, a microscopic investigation of the properties of the quasi-particles responsible for this contribution, the phonons, is required.

Here we tackle this problem, using a combined macroscopic/microscopic approach to disentangle the effect of a partial nanocrystallization on the electronic and vibrational contributions to heat transport in a Zr-based MG, chosen because of its good combination of strength, ductility, corrosion resistance and large glass forming ability, which make it suitable for massive industrial production and applicability.

We find that the electronic contribution to the thermal conductivity gradually and weakly increases with the crystalline fraction, as can be predicted using an effective medium theory, where interfaces don't play any major role in the range of crystalline fractions investigated. No interface-related enhanced phonons scattering can be detected neither on the vibrational contribution, the partial nanocrystallization causing only a slight increase of the transverse sound velocity, and thus of the macroscopic shear modulus, towards the crystalline value. The global effect is an increased total thermal conductivity, mostly due to the electronic contribution.

The paper is structured as follows: in section 2, we give details on the experimental methods used for this investigation, then in section 3 we report on sample preparation and focus on the different contributions to the thermal conductivity: the electric one (section 3.3) and the vibrational one (section 3.4). All results are thus globally discussed in the last section.

2. Experimental methods

$Zr_{52.5}Cu_{27}Al_{10}Ni_8Ti_{2.5}$ metallic glass rods (3 mm diameter, 8 cm length) were prepared by arc-melting the pure elements in stoichiometric concentration under argon atmosphere and quenching the master alloy in a water-cooled copper mold. The fully amorphous character of the alloy was confirmed by x-ray diffraction (XRD) at T = 300 K prior to any processing. Discs 300 μm to 2 mm thick were then cut from the rod for further analysis and amorphous/crystalline composites preparation.

The crystallization process was monitored by differential scanning calorimetry (DSC) using the Diamond apparatus from Perkin Elmer. Structural characterization, aiming to confirm the predicted crystalline fraction, and measure the crystalline grains size distribution was done by means of XRD and transmission electron microscopy (TEM). XRD was performed at the X-ray diffraction center Henry Lonchambon, Lyon, using a D8 Advanced diffractometer in Bragg-Brentano geometry with $\lambda = 1.541$Å, while TEM was performed using a JEOL JEM2100 equipped with a LaB6 thermionic electron gun and a High Tilt objective pole piece. The microscope was operated at 200 keV with a point-to-point resolution of 0.25 nm. The samples were mounted on a double-tilt beryllium sample holder and the images were recorded on a Gatan Orius SC1000 bottom mount CCD camera, 4008 × 2672 pixels with a physical size of 9 μm each. For TEM measurements, samples were prepared by using a precision ion polishing system (PIPS, Gatan 691 model) in top-bottom mode at 2.5 kV with a milling angle of ±4°, the instrumental parameters having been chosen in order to hinder any ion beam induced crystallization [12,36,37].

Electric transport measurements were performed by means of the Van Der Pauw technique using a home-made apparatus working between 50 and 300 K. Room temperature absolute values were counter-checked using a commercial 4 points probe. Thermal conductivity was measured by means of the Thermal Scanning Microscopy technique (SThM) at the Cethil, in Lyon [38,39], on samples polished with a 0.5 μm diamond powder.

In order to get insight into the vibrational contribution to thermal transport, phonon dispersions were measured by inelastic X-ray scattering (IXS) at the ID28 beamline of the ESRF, Grenoble. A high energy resolution of ≈2.8 meV was reached using the (9,9,9) reflection of the silicon crystal monochromator, corresponding to an incident x-ray energy of 17.794 keV (wavelength $\lambda_0 = 0.6968$Å). The beam was focused into a spot of $150(H) \times 90(V)\mu$m (FWHM) on the sample, which was hosted in a vacuum chamber for avoiding any small angle scattering from the air. Spectra were collected in a fixed-q scanning-energy mode at a given position of the analyser chamber, hosting 9 analysers at different scattering angles 2θ, thus allowing for simultaneously collecting 9 different momentum transfers $q = \frac{4\pi}{\lambda_0}\sin(\theta)$. Details on the IXS setup can be found elsewhere [40–42].

3. Results and discussion

3.1. Samples preparation

Amorphous/crystalline composites were prepared by isothermally annealing the glass at a temperature lying between the glass transition and the crystallization temperature, monitoring the