Quasicrystalline Phase Formation on Glassy ZrAlNiCuPd Alloys by Linear Varying Joule Heating

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Abstract. Linear varying current Joule heating was employed to perform thermal treatments on bulk amorphous samples. Using this method it is possible to monitor the evolution of the materials structure through the on-line measurement of the sample’s electrical resistance. Therefore, it is possible to interrupt the treatment at any desired point. Using this method, we have succeeded to obtain icosahedral phases in some glassy alloys. The quasicrystallization results in an increase of the sample’s resistance, which is visible in the Joule heating curves.

Introduction

It is well known that suitable thermal treatments can improve and stabilize the physical properties of amorphous materials produced by rapid solidification techniques. The soft magnetic properties of ferromagnetic amorphous materials (both ribbons and wires) are further improved either by low-temperature anneals which induce structural relaxation or by high temperature thermal treatments, leading to surface crystallization [1] and/or nanocrystallization [2,3]. Besides an enhancement of the magnetic properties, fast-heating treatments can lead to materials with better mechanical properties [4]. In particular, techniques that explore the heat released by an electrical current flowing through the sample (Joule heating) have emerged as one of the most promising methods to obtain materials with optimized physical properties. Joule heating is conceptually simple and experimentally versatile, allowing one to follow the structural transformation of the samples through on-line monitoring the materials resistance during annealing [5].

On the other hand, several Zr-based alloys display high glass-forming ability that allows one to produce relatively thick amorphous materials [6]. Besides their promising properties, these glassy alloys can also be precursors of novel nanocrystalline and quasicrystalline materials. In particular, the possibility of controlled formation of icosahedral phases during crystallisation of amorphous Zr-based alloy system opens attractive perspectives on new system with improved mechanical properties.

Addition of Pd, Au or Pt into melt-spun Zr-Al-Cu amorphous alloy induces the formation of a nanostructure consisting of Zr₂(Cu,M) (M=Pd, Au or Pt) and remaining amorphous phase, with the nanostructured alloys showing better mechanical properties than the corresponding amorphous alloy [7]. Recently, the formation of an icosahedral phase in a wide annealing temperature range, induced by Ag addition, was reported in amorphous Zr-Al-Ni-Cu-Ag [8]. The addition of Pd also lead to the formation of icosahedral phases after specific annealing [9].
In this work we apply a novel method called linear varying current Joule heating (LVC-JH) on glassy Zr65Al7.5Ni10Cu7.5Pd10. Each different sample displays a typical resistance versus current curve, with different discontinuities that mark the different crystallization stages. It was possible to stop the annealing at different points of the crystallization process, and samples with different phases were thus produced. These samples were studied at room temperature by means of X-ray diffractometry and transmission electron microscopy.

**Experimental methods**

The experimental setup of the LVC-JH is identical to the one of dc Joule heating [5], i.e., composed of two pairs of U-shaped contacts used for clamping the ends of the sample, kept under vacuum, to minimize thermal losses by conduction and convection. The annealing current, $I$, is varied step-by-step with a waiting time interval $\Delta t$ before each further step, from zero up to a final value. The heating rate $\Delta I/\Delta t$ can be properly adjusted according to the purpose of the experiment. The resistance is monitored during the treatment, and the on-line analysis of the $R$ vs. $I$ and $dR/dt$ vs. $I$ curves allows one to select the appropriate point to interrupt the annealing [10,11]. It is also possible to specify the way the annealing current is decreased down to zero, either by slowly decreasing the current amplitude or by abrupt interruption of the applied current [10,11].

It is worth noting that it is extremely easy to modify the heating and cooling rates of the treatment, by simply modifying either the current step $\Delta I$ (from few mA to A) or the waiting time $\Delta t$ after the current change (from some ms to several minutes). In this way it is possible to perform treatments that reach the same temperature in few seconds or hours, thus covering a wide range of heating rates. The same occurs for the cooling rate, which in the present configuration is maximum when the current is simply switched off (and the temperature reaches room temperature in few seconds [4]), or it can be slowly decreased with chosen current steps and waiting times [11]. The cooling rate can be further increased if some cooling gas is inserted into the system, but it was found that the natural cooling process is rapid enough even to quench high temperature metastable phases down to room temperature [11]. Although some calibration work must still be done to effectively use of Joule heating techniques in novel amorphous materials, it is clear that LVC-JH represents a simple, reliable and versatile alternative to rapid thermal annealing.

X-ray diffraction (XRD) was performed in the samples after Joule heating to different currents (temperatures), using a Siemens D5000 apparatus with CuKα radiation. Transmission electron microscopy (TEM) were also performed at the same treated samples, using a Philips CM120 microscope operating at 120kV.

**Experimental Results**

In the present work, we have applied linear varying current Joule heating to Zr-based metallic glasses, which belong to the family of the bulk metallic forming alloys that display wide supercooled liquid regions [12,13]. Such glasses have been extensively investigated in recent years,
because they show a wide supercooling range, lower critical cooling rates for glass formation, high dense packing and excellent thermal stability, besides other unique properties [6]. Upon annealing, depending on the alloy’s composition one can obtain nanocrystalline [14] and/or quasicrystalline [12,15] structures [16].

Figure 1 shows typical resistance vs. applied current curves, obtained during annealing of the initially amorphous Zr₆₅Al₇.₅Ni₁₀Cu₇.₅Pd₁₀ ribbon. This alloy has received much attention lately due to the discovery of quasicrystalline phases when the sample is annealed in the supercooled liquid range. Several samples were produced, stopping the treatment at different currents I, chosen properly before or after the well-marked steps found in the R vs. I characteristic curve. The resistance curves were normalized to the value of resistance when a current of 0.2 A is flowing through the sample. As can be seen in Fig. 1, the curves have always the same profile, a small bump, followed by a steep decrease of resistance owing to crystallization (at about 1.7 A, which should correspond to 435°C [8]). Upon crystallization the resistance of the sample drops sharply, a feature which is clearly observed in Fig. 1 from 1.7 to 2.2 A. After massive crystallization, the resistance stabilizes, or decreases at a slower rate with increasing of current intensity. Notice that sample 1 reaches the final current value of about 4.2 A, that corresponds to the melting temperature of the sample. After reaching the final current value the current was suddenly switched off, and each sample was subsequently analyzed by means of X-ray diffraction and electron microscopy. The results are presently being analyzed.

Notice that LVC-JH allows one to precisely stop the treatment at any desired point, where the current is abruptly interrupted, and the sample returns rapidly (few seconds) to room-temperature. Figure 2 shows the x-ray diffraction patterns of the Joule-heated samples (annealed up to different final current values). Although the intensities are rather low, it is possible to clearly follow the evolution of the structure after the thermal treatments.

Sample 7 is still in the glassy state after a treatment up to 1.15 A, whereas a metastable phase evolves in the samples submitted to Joule heating with increasing current values. Sample 6 shows clear Bragg peaks of the icosahedral quasicrystalline phase (see Fig. 3), as reported for this composition elsewhere [17] and also during fast heating of our sample in a synchrotron beam [18]. In Figure 3, we could index the peaks that appear for sample 6 as (100000), (110000) and (101000), respectively. The appearance of the i-phase peaks in sample 6 occurs for final current annealing values corresponding to a small maximum in R observed before the sharp drop in Fig. 6. This fact suggests that the i-phase has a higher electrical resistivity than the amorphous phase for this composition. Others have also reported resistivity increases during the amorphous→i-phase transformation [19,20]. The increase in resistivity observed in an amorphous-icosahedral phase transformation is probably related to the quasiperiodicity of the lattice, and increases with the degree of quasiperiodic order [21], indicating that the quasicrystals can present features analogous to crystalline semi-insulators [20,21]. In the case of Joule heating, an increase of electrical resistivity implies an increase of the Joule power, and subsequently in a rapid increase of the temperature of the sample. The kinetics of the process must be further studied in order to precisely control the transformation in order to easily obtain quasicrystalline materials.
Fig. 4 shows the microstructure and corresponding selected area diffraction pattern (SAEDP) for a Zr_{65}Al_{17.5}Ni_{10}Cu_{7.5}Pd_{10} sample after Joule heating up to 3.6 A (sample 5). The observed microstructure is completely different from the one observed during in-situ heating in the TEM, resembling a highly twinned microstructure observed after induction heating during synchrotron in-situ experiments of Zr_{55}Ti_{10}Cu_{25}Al_{10}Ni_{6} and suggesting an important effect, not yet completely clarified, of the heating rate during crystallisation of Zr-based alloys [22].

Figure 2. X-ray diffraction patterns of Zr_{65}Al_{17.5}Ni_{10}Cu_{7.5}Pd_{10} samples after the Joule heating treatments displayed in Fig. 1.

Figure 3. X-ray diffraction pattern of Zr_{65}Al_{17.5}Ni_{10}Cu_{7.5}Pd_{10} ribbon annealed up to 1.7 A (sample 6). The displayed index are related to a quasicrystalline phase.

Conclusions

In conclusion, exploring the Joule heat generated by a flowing electrical current, it is possible to obtain application-oriented materials with potentially improved physical properties when compared to conventionally annealed ones. In addition, Joule heating allows one to directly monitor the structural transformation that occurs within the sample.

A novel variation of the Joule heating technique was employed to follow the structural transformations in bulk amorphous alloy compositions. The results indicate that it is possible to establish precise criteria to perform optimal thermal treatments. The reproducibility of the experimental results suggests that some other properties related to the structure of the material, specially those of technological interest can be controlled by this method.
Figure 4. Zr$_{65}$Al$_{11.5}$Ni$_{10.3}$Cu$_7$.5Pd$_{10}$ alloy annealed up to 3.6 A, (a) bright field electron micrograph (b) corresponding SAED pattern.

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References