

IN-SITU MEASUREMENTS IN METALLIC GLASSES BY SMALL-ANGLE SCATTERING OF X-RAYS

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*Laboratoire de Métallurgie Physique, 40, avenue du Recteur Pineau, 86022 Poitiers, France.*INTRODUCTION

Up to date much effort has been devoted to determine the structure of amorphous materials by means of diffraction techniques which give informations on the short-range order. Sometimes no difference can be detected in the structure of a metallic glass, liquid-quenched or sputtered, but obvious differences exist in their mechanical properties, namely brittleness versus ductility (1). Consequently, such differences must be linked to another range of order (middle-range order or mean-range structure). Such an order or structure is relevant to scattering techniques in the small-angles region. This technique provides also information on impurities; pollution of the samples such as oxidation during their heating, fluctuations in composition or density. Surprisingly, small-angle scattering has not much been used in the past on amorphous materials. So we chose this technique in the present study.

Our investigation in metallic glass is twofold. Firstly we are interested in their structure after elaboration, a structure which depends on their way of preparation and their nominal composition. Secondly, we have studied "in situ" their evolution with time and temperature when approaching the glass transition temperature.

We shall begin with some results on Cu-Zr alloys prepared by two different techniques, i.e. rapid quenching from the liquid state and sputtering. These results will show that highly significant differences appear on the scattering patterns. Then we shall continue with an investigation of the initial states of different compositions of Cu-Ho, Cu-Y and Ni-Y amorphous alloys prepared by the sputtering technique alone, in which spatial corre-

lations are observed. Finally, the evolution of Cu-Y and Ni-Y with temperature and time will be followed and analyzed.

EXPERIMENTAL TECHNIQUE

Small-angle scattering of X-rays is a suitable technique when emphasis in a study is put on mean-range order or mean-range structure (domains of some ten Å or less) in small and thick samples. But in an amorphous material it is also worthwhile to get information on heterogeneities and variations in first atomic distances. This is the reason why a specific camera has been realized for X-ray scattering measurements between the angular origin and $q = \frac{4\pi \sin \theta}{\lambda} = 6.25 \text{ \AA}^{-1}$ including the small-angles region and the first diffraction halo characteristic of an amorphous material. The heating of the sample is carried out "in situ" with a small electrical furnace on the axis of the X-ray beam and in the middle of the vacuum chamber (up to 10^{-6} torr.) The camera works in punctual collimation, this means that intensities are lower in the small-angle region than with linear collimation generally used by workers in this field. This is the reason why our camera is adapted for an alignment on the very powerful beam given by the synchrotron radiation of L.U.R.E.* at Orsay. Furthermore the scattered intensities are recorded by means of a position-sensitive proportional counter. The high sensitivity of this technique allows "in situ" measurements when heating the sample and provides in a short time informations concerning the 3 regions indicated on figure 1. The counter can be rotated around an axis centered on the sample.

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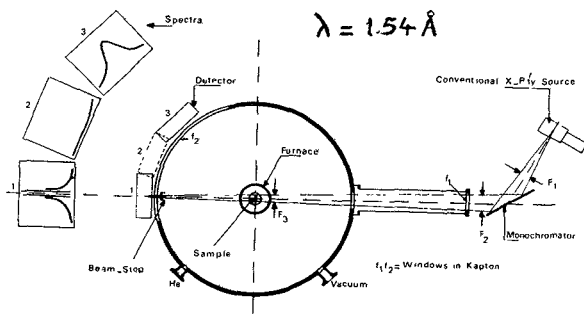


Fig. 1 : Scheme of the S.A.S. set up.

S.A.S. RESULTS ON Cu-Zr

We studied amorphous $\text{Cu}_{66}\text{Zr}_{34}$ alloy prepared by two different techniques, i.e. sputtering and rapid quenching from the melt (melt spinning). We used calorimetric measurements and the scattering of X-rays. Our results are to appear soon (3), but, as this alloy behaves differently from the others studied in this paper, it is interesting to give here some results obtained with X-rays only, as shown on figure 2 where differences occur in the three angular regions.

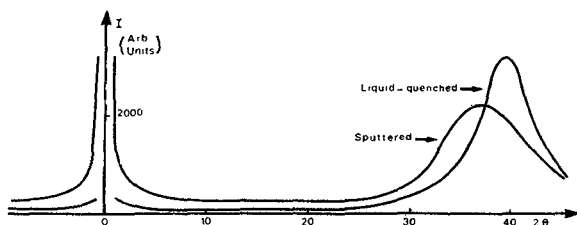


Fig. 2 : Scattered intensities of the two $\text{Cu}_{66}\text{Zr}_{34}$ alloys just prepared by sputtering or quench from the liquid state.

First of all the liquid-quenched alloy has a very small scattered intensity near the angular origin, in opposition to the sputtered alloy where its scattering increases very strongly and corresponds to large defects. The differences are also important for the first diffraction halo, concerning its angular position, amplitude and width. At least in the middle angular region the scattered intensity is 4 or 5 times higher for the sputtered alloy than for the other.

Our interpretation of these differences is based on the fact that the sputtering technique, when projecting the atoms on a target, build a different sample from the one obtained by melt spinning which has a memory of the liquid state. Thus the sputtered alloy retains Argon atoms which create voids filled with Argon and density fluctuations. Furthermore, the macroscopic densities of the two alloys are different. These observations lead us to the conclusion that the sput-tered alloy is a more homogeneous material than the sput-tered one.

During heating, they behave also differently, the crystallisation temperature being higher for the sputtered alloy. But during the heating, some oxidation occurs (even in a vacuum of 10^{-6} Torr) near the glass transition temperature located at 476°C for the liquid-quenched alloy and 532°C for the sputtered one. This is the reason why we choose other alloys in which the structural evolutions occur at lower temperatures and are different from those observed with the Cu-Zr system as shown on figure 2, where differences occur in the three angular regions.

INITIAL STATES OF Cu-Ho, Cu-Y and Ni-Y ALLOYS.

These amorphous alloys have been prepared by sputtering method which makes it possible to obtain a larger range in composition than the quench from the liquid state. The thickness of the samples is sometimes different, but the accumulation times vary accordingly.

The recorded intensities of three amorphous Cu-Ho alloys are shown on figure 3.

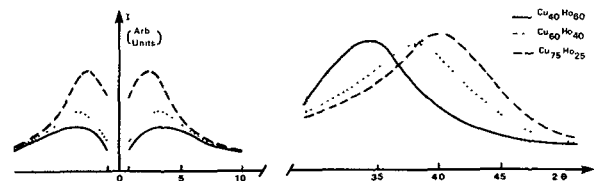


Fig. 3 : Scattered intensities of Cu-Ho alloys.

Concerning the angular position of the diffraction halo, we note a classical result : the higher the composition in large Ho atoms, the more important the shift towards the primary beam. But the new fact with this amorphous system is the presence of a small-angle scattering ring.

There are two explanations for such a ring in a S.A.S. pattern: the depleted shell model (4) and the interference effect which can be linked with spinodal decomposition (5) as it occurs in pre-precipitated Al-Zn alloys for example (6). The first model seems unlikely for us because an embryo must exist or be created and an important diffusion is needed to build the concentration gradient. On the contrary, fluctuations in composition, linked with fluctuations in density can form small domains enriched in electrons, while other domains are impoverished, and consequently account for the observed S.A.S. pattern. If the second model is retained, the angular position of the ring indicates a spatial correlation of $\sim 25 \text{ \AA}$ between domains.

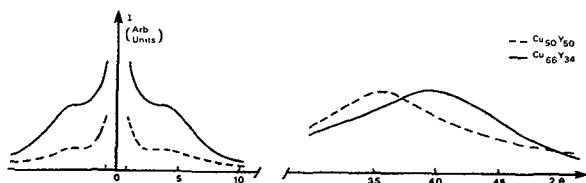


Fig. 4 : Scattered intensities of Cu-Y alloys.

The spectra concerning two compositions of the amorphous Cu-Y system, prepared by another sputtering apparatus, are shown on figure 4. There is also a spatial correlation between density fluctuations with a wavelength of $\sim 20 \text{ \AA}$ in these freshly-prepared samples. The intensity which increases near the primary beam could be due to a small degree of oxidation of these samples.

Other experiments upon amorphous Ni-Y alloys prepared by another again sputtering device were carried out. Their scattering curves, most of the time, display also a ring.

So, the S.A.S. pattern of metallic glasses, corresponding to three systems, each prepared with a different sputtering apparatus, do present similarities : a ring. Emphasis has been made on the initial state of these alloys because it will certainly play a major part during their evolution with temperature and time.

EVOLUTION WITH TEMPERATURE AND TIME

We start with the amorphous $\text{Cu}_{66}\text{-Y}_{34}$ alloy (figure 5).

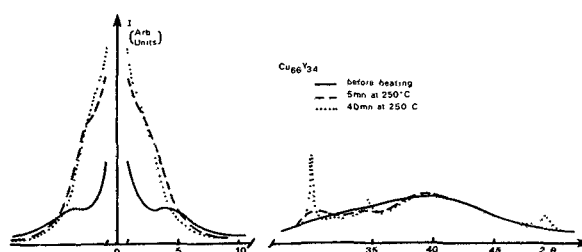


Fig. 5 : Scattered intensities of $\text{Cu}_{66}\text{-Y}_{34}$

During the heating, there is a gradual evolution of the ring which amplitude increases and angular position shifts towards the primary beam. Such a behaviour is in fully agreement with Langer's theory of spinodal mechanism (7). Finally at 240°C appears a f.c.c. transitional phase with parameter $a = 5,15 \text{ \AA}$. The crystallographic systems of copper oxide or Y_2O_3 does not appear.

A more interesting amorphous system is Ni-Y because we have 6 different compositions ranging from 5 to 33 at. % Y. They all crystallize in the Ni_5Y phase which is a Hauke phase (8), but their S.A.S. curves evolve differently. Figure 6 shows what happens with the composition Y_2Ni_7 :

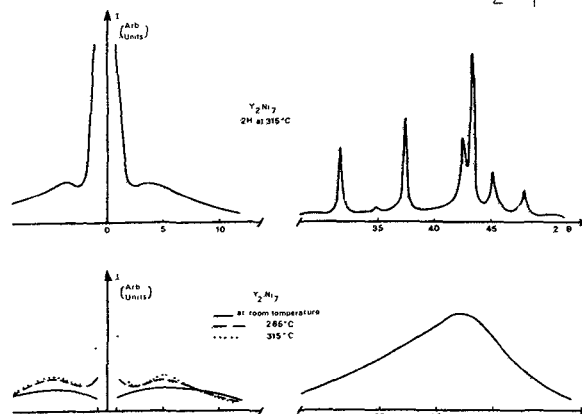


Fig. 6 : Scattered intensities of Y_2Ni_7

There is a weak evolution of the ring up to 315°C and a two hours aging at this temperature leads to crystallization, while it occurs at 370°C after a rapid heating. It does not appear nor hydrides nor oxides in the diffraction region.

A small-angle integrated intensity Q_0 can be measured :

$$Q_0 = 4\pi \int_0^\infty s^2 i(s) ds$$

with $s = \frac{2 \sin \theta}{\lambda}$ and a cut-off at $s = 0.1 \text{ \AA}^{-1}$.

In a two-phase system, this integrated intensity Q_0 can also be written :

$$Q_0 = c(1-c) \Delta\rho^2 V_a$$

where c is the volume fraction of the diffracting particles, $\Delta\rho$ the difference between their electronic density and the medium where they are; V_a is the mean atomic volume. We can determine c by their number and their size, that is to say by the S.A.S. peak and the radius of giration given by the Guinier plot. Consequently, a value of $\Delta\rho$ is deduced. But in amorphous materials, where fluctuations in composition could certainly be linked with density fluctuations, such a value is not so meaningful than with Guinier-Preston zones in aluminum alloys or small oxide particles in internally oxidized alloys (9). Nevertheless a value of about 15 % can be estimated. Furthermore the integrated intensity is very weak for YNi_4 , more important for Y_2Ni_7 and much more for YNi_3 and this is an argument for the existence of a metastable miscibility gap. But its boundaries are difficult to determine because the initial states of the amorphous alloys are not identical and principally do not display a flat S.A.S. curve proving that they are in a really homogeneous state.

CONCLUSION

Here are preliminary studies upon some metallic glasses which display a ring in the small-angle scattering pattern. The size and thickness of the samples imply a punctual X-ray collimation and consequently the intensities are weak, so is the accuracy. This is the reason why experiments are planned with the synchrotron radiation.

Emphasis has been made in this study on the initial state of the alloys because their evolution during a heating depends on it. Rare are the sputtered amorphous alloys having a flat S.A.S. curve. When a ring appears, it is linked in our opinion with correlated fluctuations in electron density. They are associated with fluctuations in composition, then they create particles which are a transitional state towards the equilibrium precipitates as for the Ni-Y system where the crystallisation state is always YNi_5 .

It is not doubtfull that some physical properties of such alloys should be different according to their middle range structure which appears on the small-angle scattering pattern, while their diffraction halo remains smooth.

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BIBLIOGRAPHY

- (1) P. DUWEZ. Rapidly quenched metals III, vol.2, Metals Society (1978) p. 465.
- (2) A.B. BATHIA and D.E. THORNTON. Phys. Rev. B2 (1978) 3004.
- (3) A.M. FLANK, M. HARMELIN, M. JAULIN and A. NAUDON. To appear in Rev. Phys. Appl.
- (4) C.B. WALKER and A. GUINIER. Acta Met., 1, 568 (1953).
- (5) K.B. RUNDMAN and J.E. HILLIARD. Acta Met., 15, 1025 (1967).
- (6) J. MIMAUT, J. DELAFOND, A. JUNQUA, A. NAUDON and J. GRILHE. Phil. Mag. B, 38, 255 (1978).
- (7) J.S. LANGER. Phys. Rev. A, 11, 1417 (1975).
- (8) J.F. SADOC and A. LIENARD. Rapidly quenched metals III, vol. 2, The Metals Society (1978) p. 405.
- (9) J. ALLAIN, A. NAUDON, J. CAISSO. Acta Met., 27, 545 (1979).