



# THE MEDIUM RANGE STRUCTURE OF HYDROGENATED Cu-Ti AMORPHOUS ALLOYS STUDIED BY ANOMALOUS SMALL-ANGLE SCATTERING OF X-RAYS AND NEUTRON DIFFRACTION

P. Goudeau, A. Naudon, B. Rodmacq, P. Mangin, A. Chamberod

## ► To cite this version:

P. Goudeau, A. Naudon, B. Rodmacq, P. Mangin, A. Chamberod. THE MEDIUM RANGE STRUCTURE OF HYDROGENATED Cu-Ti AMORPHOUS ALLOYS STUDIED BY ANOMALOUS SMALL-ANGLE SCATTERING OF X-RAYS AND NEUTRON DIFFRACTION. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-479-C8-483. 10.1051/jphyscol:1985874 . jpa-00225224

**HAL Id: jpa-00225224**

**<https://hal.science/jpa-00225224>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# THE MEDIUM RANGE STRUCTURE OF HYDROGENATED Cu-Ti AMORPHOUS ALLOYS STUDIED BY ANOMALOUS SMALL-ANGLE SCATTERING OF X-RAYS AND NEUTRON DIFFRACTION

P. Goudeau, A. Naudon, B. Rodmacq\*, P. Mangin\*\* and A. Chamberod\*

*Laboratoire LURE, Bâtiment 209 C, 91405 Orsay, France*

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

*\*CEN Grenoble, DRF/SPh/MP, Avenue des Martyrs, 85 X, 38041 Grenoble, France*

*\*\*Institut Laue-Langevin, 156 X, 38042 Grenoble, France*

**Résumé** - Les alliages amorphes Cu-Ti donnent une forte diffusion centrale après hydrogénation. Celle-ci est analysée par diffusion anormale des rayons X sur les seuils K du cuivre et du titane. On peut alors conclure à la présence de très petits agrégats d'hydrure de titane de composition  $TiH_2$ . Ces résultats sont en accord avec ceux obtenus par diffraction des neutrons en utilisant soit l'hydrogène ( $b < 0$ ), soit le deutérium ( $b > 0$ ) pour l'hydrogénation des échantillons.

**Abstract** - Amorphous Cu-Ti alloys, when hydrogenated, reveal a strong small-angle scattered intensity. The anomalous X-ray scattering effect is used to analyse this SAS intensity on both copper and titanium edges. It allows to assert the presence of very small clusters of titanium hydride having the  $TiH_2$  composition.

These results are in good agreement with those obtained by neutron scattering experiments when using either hydrogen ( $b < 0$ ) or deuterium ( $b > 0$ ) for the hydrogenation of the samples.

## I - INTRODUCTION.

At the time where the local atomic structure of metallic glasses is better and better known with techniques such as X-ray and neutron diffraction, EXAFS, NMR and Mössbauer spectrometry, it is not the same for their medium range structure despite an increasing number of X-ray and neutron small-angle scattering experiments (SAXS and SANS). Such a thing can be explained by at least three facts : first of all the presence or not of a SAS is linked to the method of preparation of the samples. Whereas it does not happen in splat cooled or melt spun samples before annealing treatments excepted in the very low  $q$  region, it generally occurs in as prepared sputtered or co-evaporated samples. Secondly it is not obvious to determine the genuine nature of the heterogeneities associated with the SAS signal because assumptions are needed to analyse it. The third fact is that the SAS behaves differently very close to the primary beam and in a wider angular domain where a maximum is generally observed before the pre-peak region.

So, different explanations have been proposed :

The  $q^{-3}$  law observed by SAS of neutrons in the very low  $q$  region in melt spun alloys has been interpreted in terms of quasi-dislocations (1). An anisotropy attributed to columnar structures in sputtered metallic glasses has been proposed (2). The observation of the crystalline phase which appears when heating a sample is an indication that the SAS is due to clusters of that crystalline product (3). An assumption is to say that space correlated fluctuations between the initial composition of the alloy and that of the final product exist and develop during the heating (4). Another possibility for the explanation of the SAS is the presence of argon bubbles in sputtered samples, or also hydrogen bubbles in alloys where it is a strong getter (5). Artefacts revealed by SANS such as surface imperfections (6) or magnetic heterogeneities (7) have also to be avoided before conclusions could be drawn from the SAS data.

As a real problem does exist for determining the genuine nature of the heterogeneities responsible for the observed small-angle intensity, we have chosen a new way of studying the medium range structure in metallic glasses by using the anomalous effect of the X-ray scattering factor. Such a technique called ASAXS (Anomalous Small-Angle X-ray Scattering) is able to determine which resonant atom is inside the heterogeneities giving rise to the SAS pattern.

Results given by ASAXS on hydrogenated Cu-Ti metallic glasses are presented in this paper together with neutron scattering experiments performed on the same alloys.

## II - THE SAMPLES.

Amorphous  $\text{Cu}_{67}\text{Ti}_{33}$  alloys were prepared by the melt spinning technique in the form of ribbons 8 mm wide and about 40  $\mu\text{m}$  thick.

The hydrogenation of the samples was carried out at room temperature by electrolysis. The percentage of hydrogen was determined by weighting the samples before and after the loading.

X-ray scattering curves on figure 1 show the influence of hydrogen in the small-angle region and on the first diffraction halo. The more the hydrogen content and the stronger the SAS intensity, which is correlated with a shift and a broadening of the first diffraction halo relevant to a modification of the local atomic structure (8).

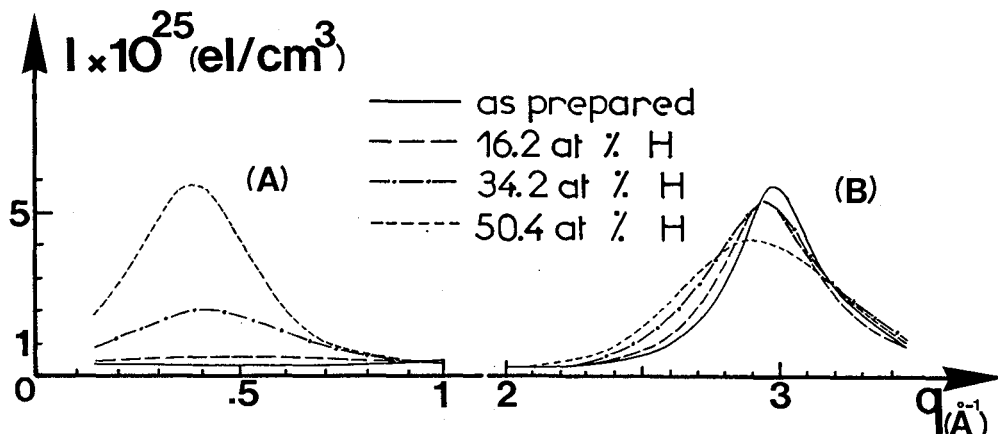


Fig.1 : Influence of the hydrogen content on the  $\text{Cu}_{67}\text{Ti}_{33}$  amorphous alloy.

(A) : Small-angle scattering region

(B) : First diffraction halo region.

Figure 1(A) shows an intensity maximum which appears at  $q \approx 0.4 \text{ \AA}^{-1}$  indicating that the scattering entities are spatially correlated with a wavelength of about 1.5 nm.

The question which is raised now is to determine the nature of these scattering entities. They might be clusters, fluctuations in composition, gas bubbles or something else. For this reason, ASAXS has been used on both K edges of Cu and Ti which are available at LURE.

## III - ANOMALOUS SAXS STUDY.

The principle of this method and its feasibility has recently been shown on Guinier-Preston zones in Al-Zn alloys (9). Its application to metallic glasses is on the way (10).

It can be briefly said that this method relies on the fact that a photon becomes resonant when its energy  $E$  is close to one absorption edge. The expression of the

scattering factor is given by :

$$f(q,E) = f_0(q) + f'(q,E) + if''(q,E)$$

where  $q = 4\pi(\sin \theta/\lambda)$ ,  $f$  is the energy independent part of the X-ray atomic scattering factor.  $f'$  and  $f''$  are the dispersions terms (11).

Consequently the variation of the structure factor of the resonant atom produces a variation of the contrast of the heterogeneities responsible of the observed SAS. The change in total scattered intensity is a known function of the anomalous dispersions factors and of the concentration of the probed element in the scattering volume.

Application of this method has been used on the melt spun  $\text{Cu}_{67}\text{Ti}_{33}$  amorphous alloy loaded with 40% at. hydrogen. The SAS curves near the edges of both Cu and Ti are shown in figure 2. These data have been obtained with the following procedure :

- First of all, the double crystal monochromator is calibrated by measuring the edges of either Cu or Ti in absorption experiments.
- 4 energies below the edge ranging from a few eV to 150 eV or more have been selected.
- At each energy one measures the scattering from the sample in the SAS  $q$  range and in the first diffraction halo region.
- The data have been corrected from beam decay, detector response, sample absorption, parasitic scattering and monotonic Laue scattering.

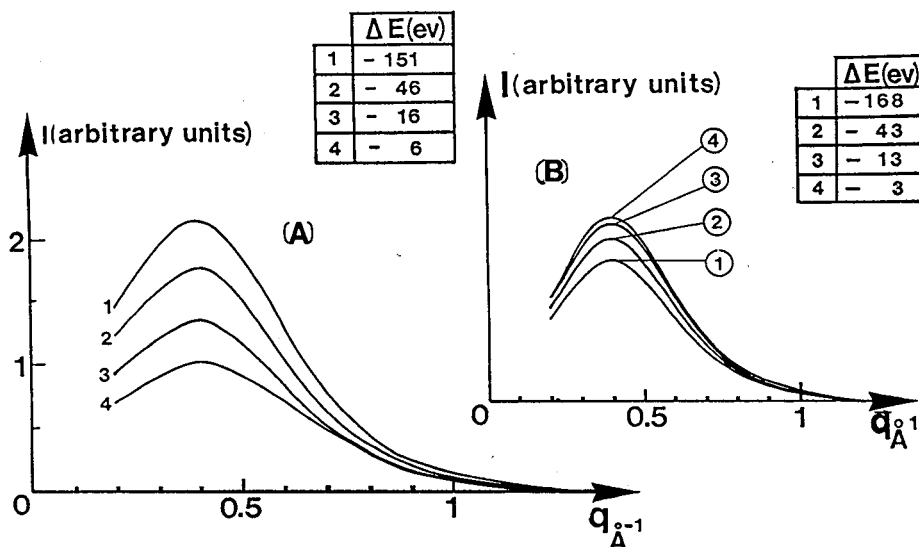


Fig.2 :  $\text{Cu}_{67}\text{Ti}_{33}$  amorphous alloy loaded with 40%at. hydrogen.  
ASAXS curves near the copper edge (A) and near the titanium edge (B).

The anomalous effect is clearly seen in figure 2 indicating a decrease of the SAS for the copper edge (fig.2A) and an increase for the titanium edge (fig.2B). For the Cu edge, the decrease of the SAS between curves (1) and (4) is equal to 53% and is larger than the one for the diffraction halo (30%). This indicates that the atomic copper has not the same influence in the scattering entities than in the whole sample.

For the first diffraction halo, the intensity is linked to the square of the average structure factor of the alloy  $\langle f \rangle$ . For the SAS due to heterogeneities

considered as particles having an electron density  $\rho_2$ , inside a matrix of electron density  $\rho_1$ , the SAS intensity is simply proportional to the square of the contrast  $(\rho_2 - \rho_1)$ . So, it is quite obvious that fluctuations of the atomic composition of the alloy cannot explain different changes of the intensities for the SAS and the first diffraction halo.

Simple calculations (12) of contrast variation for the different energies with  $f'$  values drawn out from Hoyt (13) and Int. tables of crystallography (14) allow us to reject the possibility of hydrogen bubbles being responsible of the observed SAS.

The only possibility which fits the data is the presence of clusters of titanium hydride having the  $TiH_2$  composition. In this case the calculated decrease of the SAS intensity near the Cu edge is 50 %, in good agreement with the experimental value 53 %. Furthermore, near the titanium edge, the calculated value is an increase (34 %) and the experimental one is also an increase (28 %).

#### IV - NEUTRON DIFFRACTION STUDY.

Neutron scattering experiments have also been performed on these hydrogenated  $Cu_xTi_{1-x}$  amorphous alloys (8).

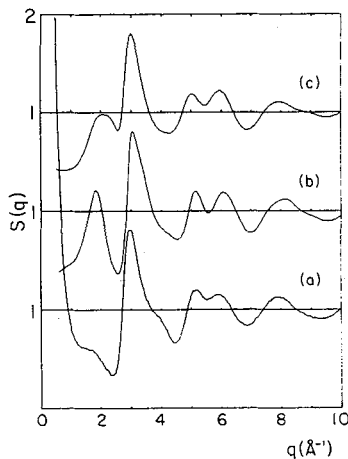


Fig.3 : Neutron interference functions

$S(q) = I_{coh} / \langle f^2 \rangle$  of amorphous  $Cu_{67}Ti_{33}$  ( $H, D$ )<sub>x</sub> alloys.

(a)  $x_H = 0.40$ , (b)  $x = 0$ , (c)  $x_D = 0.30$ .

Figure 3 shows the interference functions  $S(q) = I_{coh} / \langle f^2 \rangle$  corresponding to  $Cu_{67}Ti_{33}H_{40}$  (fig.3a),  $Cu_{67}Ti_{33}$  (fig.3b) and  $Cu_{67}Ti_{33}D_{30}$  (fig.3c) alloys. The pre-peak at about  $1.8 \text{ \AA}^{-1}$  is much more intense in the case of neutron scattering as compared to the X-ray case, as a consequence of the negative (titanium) and positive (copper) scattering lengths of the elements.

At still lower angle one observes a very intense signal in the case of the hydrogenated sample. It corresponds to the small-angle maximum at  $q = 0.4 \text{ \AA}^{-1}$  observed in figure 1 for X-ray experiments. This small-angle signal completely disappears in the case of the deuterated sample (fig.3c). Owing to the relative scattering lengths of hydrogen ( $b < 0$ ) and deuterium ( $b > 0$ ), this signal thus corresponds to hydrogen (deuterium) - rich regions.

If one supposes (as above for the X-ray case) that this signal corresponds to small  $TiH_2$  clusters, the contrast will be between  $TiH_2$  and  $Cu_{83}Ti_{17}$  in the first case and between  $TiD_2$  and  $Cu_{79}Ti_{21}$  in the second case. The corresponding scattering lengths per unit volume are:

$$b(TiH_2) = -0.084 \times 10^{10} \cdot \text{cm}^{-2}; \quad b(TiD_2) = +0.076 \times 10^{10} \cdot \text{cm}^{-2}$$

$$b(Cu_{83}Ti_{17}) = +0.075 \times 10^{10} \cdot \text{cm}^{-2}; \quad b(Cu_{79}Ti_{21}) = +0.069 \times 10^{10} \cdot \text{cm}^{-2}.$$

The contrast will be proportional to the square of the scattering length difference. According to the numerical values given above, one can see that this contrast will be large for the hydrogenated sample, and extremely small for the deuterated sample. This is totally in agreement with the experimental results of both neutron and X-rays experiments.

#### V - CONCLUSION

Amorphous Cu-Ti alloys when hydrogenated reveal a strong SAS intensity whose genuine nature is not easy to determine with a classical SAS device, because assumptions are needed before conclusions could be drawn from the experiments. With a synchrotron source, it is now possible to use the anomalous effect of the X-ray atomic structure factor for a clear-cut interpretation of the SAS data. For the  $\text{Cu}_{67}\text{-Ti}_{33}$  amorphous alloy loaded with 40 % at. hydrogen, both copper and titanium edges have been analysed. The decrease of the SAS for the former and its increase for the latter clearly indicate that neither concentrations fluctuations nor hydrogen bubbles are responsible of the observed SAS curves. The origin of the SAS is only due to very small clusters of titanium hydride having the  $\text{TiH}_2$  composition. These clusters are space-correlated with a wavelength of about 1.5 nm at room temperature.

Neutron diffraction experiments, when using either hydrogen ( $b < 0$ ) or deuterium ( $b > 0$ ) for the hydrogenation of the samples, are totally in agreement with the X-ray conclusions.

#### REFERENCES

- /1/ Nold, E., Steeb, S., Lamparter, P. and Reiner-Harbach G. (1980) J. Physique (Paris) C8-186.
- /2/ Cargill, G.S., Proc.3rd. Conf. on rapidly quenched metals. Brighton (1978) 364.
- /3/ Osamura, K., Susuki, R and Murakami, Y. Proc. 4th Int. Conf. on rapidly quenched metals, Sendai (1981) 431.
- /4/ Naudon, A. and Flank, A.M., ib. Sendai (1981) 425.
- /5/ Boucher, B., Chieux, P., Convert, P. and Tournarie, M.. (1983) J. Phys.F.: Met. Phys. 17, 1339.
- /6/ Rodmacq, B., Mangin, P. and Chambérod, A., Phys. Rev. B .30 (1984) 6188.
- /7/ Janot, C. and George, B. J. Phys. Lett. (1985) 46 L 85.
- /8/ Rodmacq, B, Mangin, P. and Chambérod, A., J. Phys. F : Met. Phys. (in press).
- /9/ Goudeau, P., Naudon, A., Fontaine, A. and Williams, C.E., J. Phys. Lett. 46 (1985) L 255.
- /10/ Goudeau P., Naudon, A., Chambérod, A. and Rodmacq, B. (to be published).
- /11/ James, R.W.. The optical principles of the diffraction of X-rays (Bell and sons Ltd, London) (1965).
- /12/ Hoyt, J., J. Appl. Cryst. 17 (1984) 344.
- /13/ International tables of crystallography (1984) vol. IV, Birmingham Kynoch press.