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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structural characteristics of cluster-assembled metallic glasses	**Experiment number**: HC-2126
Beamline: BM23	**Date of experiment**: from: 07/10/2015 to: 11/10/2015	**Date of report**: 23/03/2017
Shifts: 12	**Local contact(s)**: Vera Cuartero	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

ANTONOWICZ Jerzy*
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EVANGELAKIS Georgios

Report:

Cluster assembled metallic glasses

Our primary goal for this experiment was to study the local atomic structure of thin-film samples of Zr-Cu cluster-assembled metallic glasses (CAMGs) deposited on borosilicate glassy substrates. The previous results on the samples (exp. rep. HC-620) indicated that the as-prepared samples retain their amorphous structure in the equilibrium conditions even when exposed to air.

The absorption spectra acquired during HC-2126 showed however that all the CAMGs samples have severe oxidation and segregation during the measurement. While the pre-characterization of the samples prior to XAFS experiment did not point to any detectible oxidation of the films, the Zr K-edge XANES spectra of all of the investigates CAMGs closely resembled XANES of zirconium oxide involving a strong white line not present in the metallic state of Zr (Fig. 1). Also, the Cu K-edge XANES spectra of copper did not look like those measured previously for Cu in Zr-Cu glassy ribbon (Fig. 2). Furthermore, we found that Cu K-edge EXAFS spectra of the CAMGs can be reproduced by Cu-crystal local structure model which suggests segregation of Cu.

In the course of the experiment, as well during sample preparation and transportation we took very good care of the oxidation issue by storing the samples in the protective atmosphere and transferring them inside a glove-box from the container to an air-tight sample chamber for the absorption measurement. Despite the above efforts, the samples seemed to severely oxidize and segregate immediately already during the first measurement and the consecutive measurements didn’t show any time evolution of the absorption spectra.

The observed behavior is attributed to beam damage of the samples. The presence of oxygen can be explained by a possible leaks of the sample chamber or by generation of color centers (oxygen vacancies) in the substrate material. The generation of color centers by an X-ray beam was observed optically by darkening of the substrate which disappeared after thermal annealing at 300 deg C for 1 hour in air.

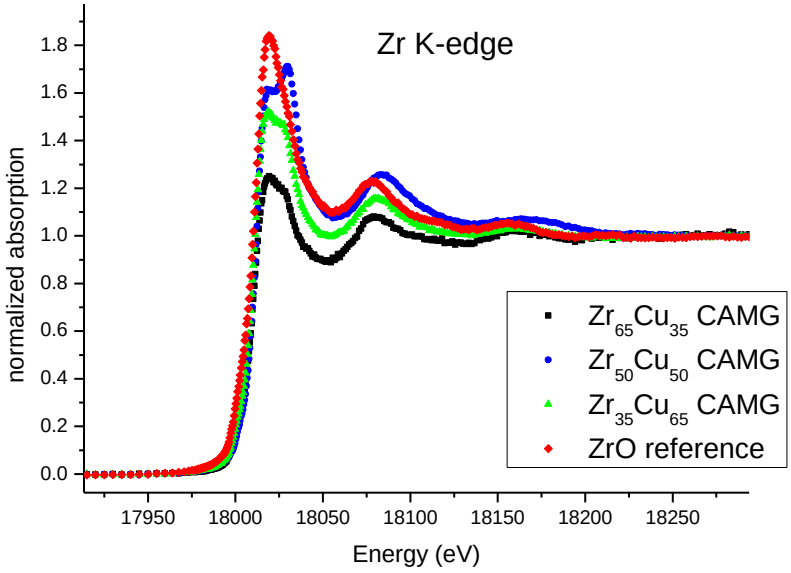

Figure 1. Zr K-edge XANES spectra of the $Zr_{65}Cu_{35}$, $Zr_{50}Cu_{50}$ and $Zr_{35}Cu_{35}$ (composition in at. %) CAMG samples. The spectrum of ZrO reference sample is shown for comparison

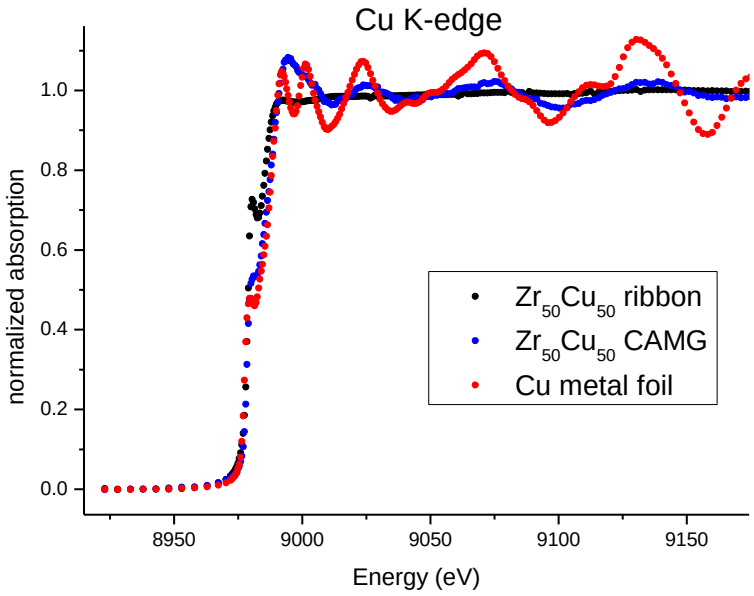

Figure 2. Cu-Kedge XANES spectra of $Zr_{50}Cu_{50}$ metallic glass in a form of a ribbon, $Zr_{50}Cu_{50}$ CAMG and crystalline Cu reference foil.

Ti-Cu thin film metallic glasses

Since we have experienced some unexpected problems with the CAMG samples, we have decided to use the remaining beam time to study thin film Ti-Cu metallic glass prepared by magnetron sputtering on silicon substrates. During the last day of our experiment we have successfully measured high quality Cu K-edge EXAFS spectra of a series of over 20 Ti-Cu thin films both in the as-deposited state and after oxidation treatment. Figure 3 shows Fourier transformed EXAFS spectra of selected as-deposited Ti-Cu amorphous films.

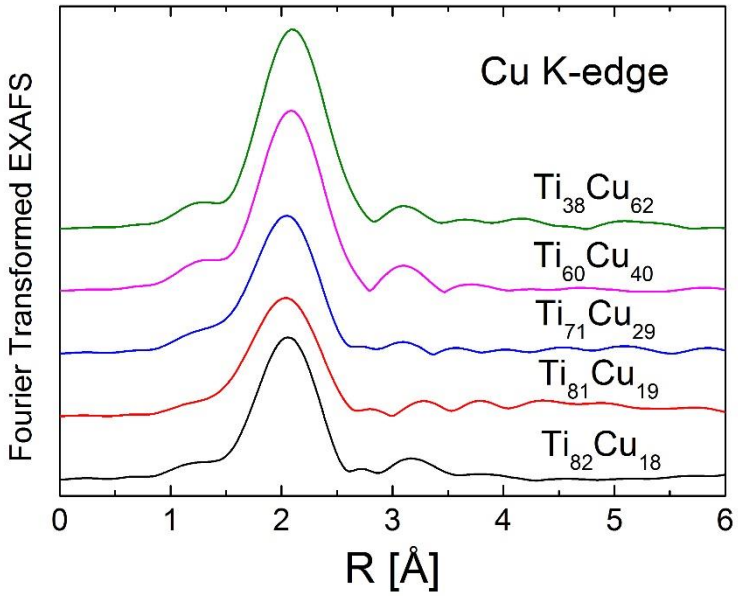

Figure 3. Fourier transformed EXAFS of selected as-deposited Ti-Cu glassy films.

The EXAFS spectra were fitted to obtain the parameters of local atomic environment of Cu atoms in the investigated systems. Figure 4 shows the results of EXAFS fitting. As demonstrated in Fig. 4a, the interatomic distances Cu-Cu and Cu-Ti are approximately constant over the studied composition range and are nearly perfectly equal to the sum of the metallic radii (2.56 and 2.74 Å respectively). According to EXAFS results the disorder in atomic distances (Debye-Waller factor) is significantly higher for Cu-Ti pairs as compared to Cu-Cu. The disorder parameter of Cu-Ti pairs decreases continuously with increasing Cu content (Fig. 4b). The values of the Debye-Waller factor are typical for those observed in other amorphous metallic systems. We observed that the fraction of Cu-Cu pairs increases continuously with the increasing Cu content and saturates at about 60% of Cu reaching the value corresponding to that derived for random atomic mixing (Fig. 4c). Finally, it we found that small addition of Al atoms (up to 3%) does not affect the short range order of the amorphous films.

Figure 5 demonstrates a comparison of Cu K-edge XANES spectra for oxidized Ti-Cu samples with different composition. A pronounced variation of the shape of XANES indicates a strong compositional dependence of the electronic state of copper atoms. A detailed analysis of XANES data is in progress and will allow as to interpret the current data together with the results from other experimental methods (Raman spectroscopy and X-ray diffraction).

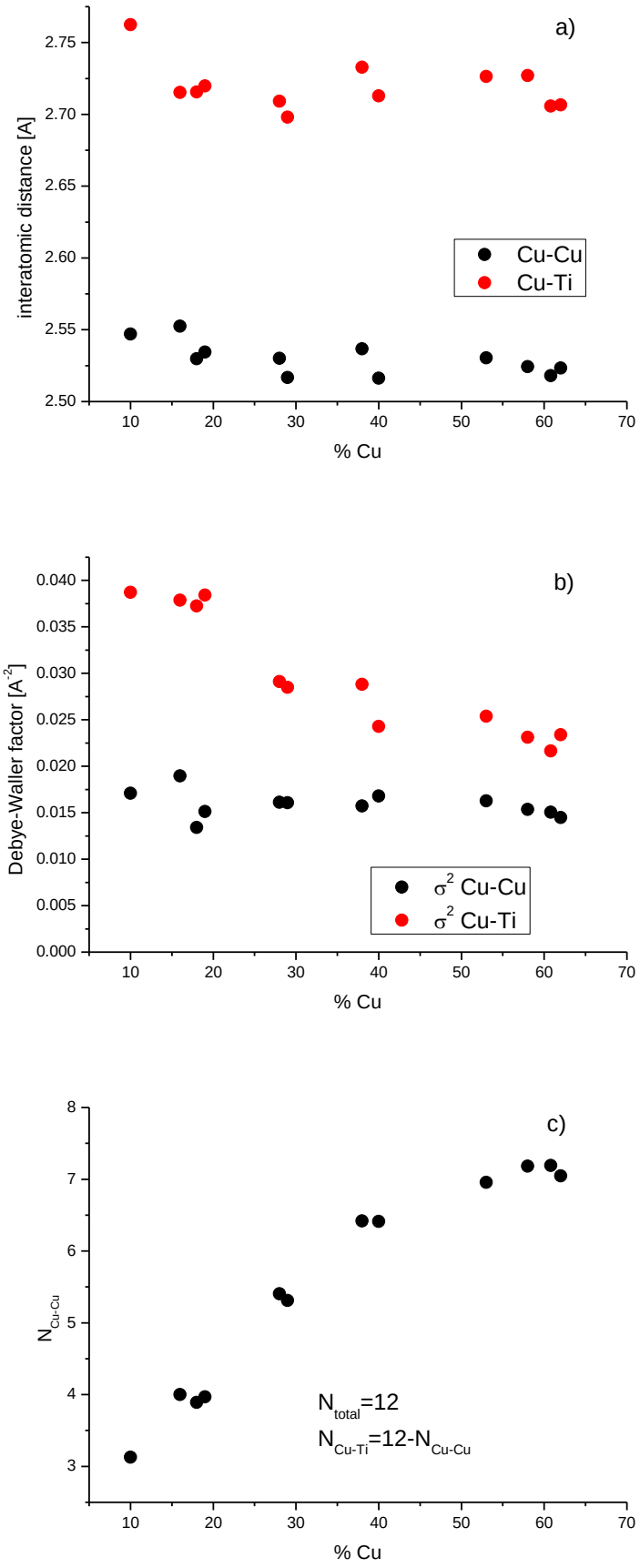

Figure 4. Results of EXAFS fitting: a) interatomic distances, b) Debye-Waller factors, c) N Cu-Cu coordiantion number

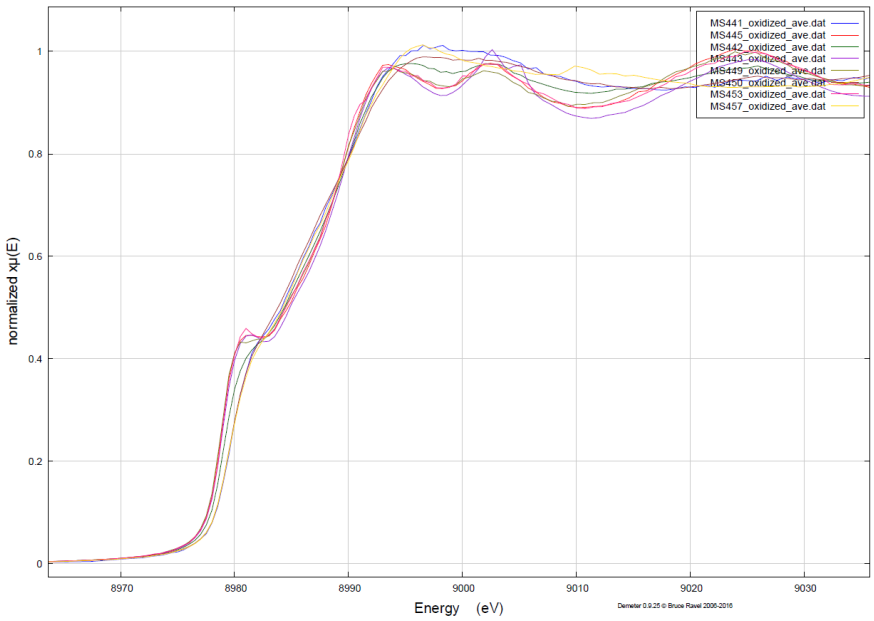

Figure 5. XANES Cu K-edge specta of Cu-Ti thin films after oxidation treatment.