XAS study of amorphous $Ni_{80}B_{20}$ and the formation of amorphous nickel

M. F. López and A. Gutiérrez
CENIM, Avda. Gregorio del Amo 8, Madrid 28040, Spain

A. Hernando and J. M. Rojo
Departamento de Física de Materiales, Universidad Complutense, Madrid, Spain

Amorphous metallic systems are currently the subject of intensive research. The existence of amorphous phases in some of these systems is frequently the subject of debate. For the case of metals, it seems to be required the presence of a second component, often a metalloid, in order to stabilize amorphous phases [1]. However, some of us have recently proposed that, embedded in a Ni_3B polycrystalline matrix, an amorphous phase of pure nickel can be present at room temperature [2]. Due to the fact that such an amorphous phase has never previously been observed, it seems necessary to report any additional evidence. In this paper we present an x-ray absorption spectroscopy (XAS) study of amorphous $Ni_{80}B_{20}$ which agrees with the presence of an amorphous nickel phase along with the crystal matrix.

The original all-amorphous homogeneous material, prepared by the melt spinning technique from a master alloy of nominal $Ni_{80}B_{20}$ composition, is called state *a*. As most of its related alloys, in the limit of high-temperature annealing (for example, 1h at 750 K) the system devitrifies into a mixture of crystalline Ni_3B and Ni phases, roughly in a 3:1 at.% nickel ratio, which we shall call state *c*. The crucial point is the existence of an intermediate partially devitrified state, that we shall call state *b*, that evolves after an annealing of about 1 h at 600 K, in which the crystallites of Ni_3B have already been formed but the excess nickel appears to be in an amorphous state. After higher temperature annealing does this excedent nickel crystallize.

XAS measurements were carried out at the SX 700/II monochromator of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) operated by the Freie Universität Berlin. The base pressure in the UHV-chamber during measurements was better than 5×10^{-10} mbar. Samples were cleaned by 10 min. Ar^+ bombardment at an ion energy of 3 keV.

Figure 1 shows XAS spectra at the nickel L_{III} absorption threshold from the *a, b,* and *c* states evolved from the original $Ni_{80}B_{20}$, along with a crystalline nickel reference. The main difference between the four XAS spectra can be related to the variation of the width of the main peak. It is largest for the *a* sample, decreases across *b* as the degree of crystallization increases, and decreases still further in state *c* where the degree of crystallization is maximum. The width is minimum for the reference Ni sample. In order to have a quantitative estimation of this behaviour, a least-square fit analysis was performed. To describe the transition from Ni-2*p* core level to discrete 3*d* empty states, an asymmetric Lorentz curve (dashed line) was used. Additionally, others components were taken into account: an arctangent (dash-dotted line) describing transitions into the continuum, a Lorentz line to consider the satellite at ≈857 eV, and a deconvolution with a Gauss function to simulate the experimental resolution.

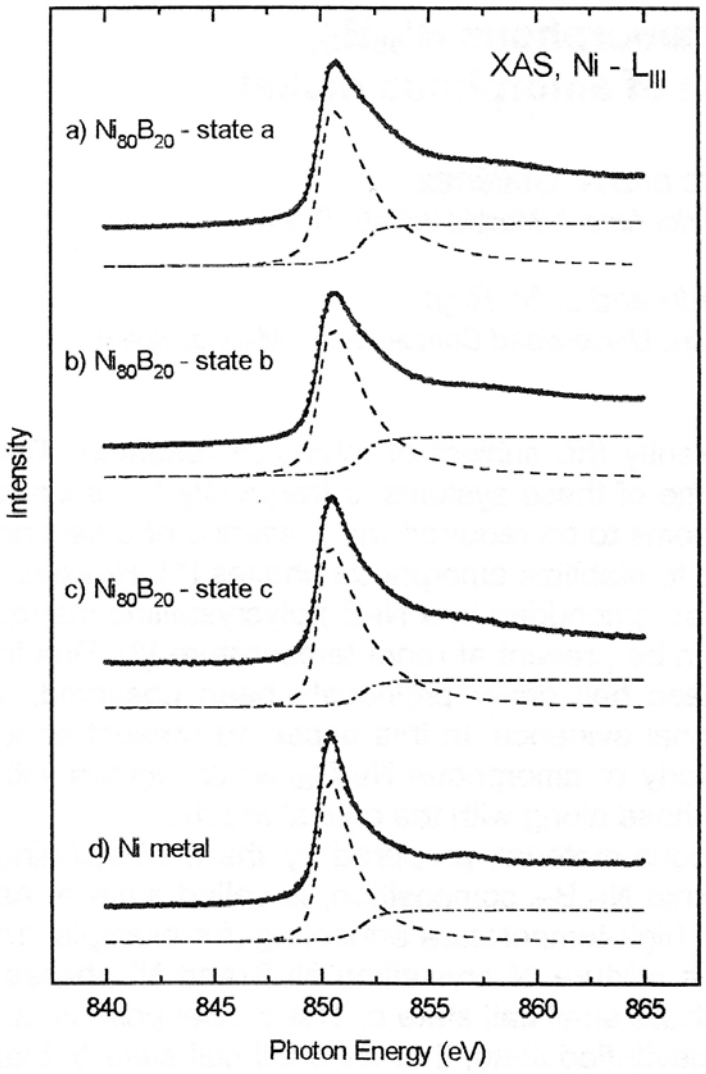

Figure 1: X-ray absorption spectra at the nickel L_{III} edge of a $Ni_{80}B_{20}$ alloy in amorphous state (a), partially devitrified state (b), and totally recrystallized state (c), and crystalline nickel as reference (d).

After performing the spectral least-square analysis the FWHM values of the XAS spectra main peak for the different samples were obtained. For the *a* state sample, that corresponds to amorphous $Ni_{80}B_{20}$, the FWHM value was 2.51 eV. For the *b* state sample which corresponds to a mixture of crystalline Ni_3B and an excess of Ni in amorphous state the FWHM value was 2.3 eV. For the case of the *c* state sample that is a mixture of crystalline Ni_3B and Ni phases the FWHM value was 2.12 eV. And finally, for the Ni reference sample the FWHM value was 1.6 eV. By comparing the FWHM values corresponding to samples *c* and crystalline nickel, it is clear that $\sigma_{Ni3B} > \sigma_{Ni(cr)}$, the latter being the FWHM of crystalline nickel. Also, from a comparison of *b* and *c* one concludes that the value of σ for the excess component of nickel $\sigma_{Ni(ex)}$ in *b* is definitely larger than the corresponding value in crystalline nickel. This shows that the excess nickel in state *b* is not the normal crystal phase and is most likely disordered. Assuming true Lorentzian peaks, one can make use of additiveness of Lorentzian widths and assign absolute values to the FWHM of the individual components in the mixtures corresponding to the samples *b* and *c*. Assuming a 3:1 ratio for the Ni concentrations in Ni_3B and Ni (either crystalline in *c* or amorphous in *b*) we immediately obtain intrinsic FWHM's for the two phases: σ_{Ni3B}=2.29 eV, $\sigma_{Ni(ex)}$=2.33 eV. The latter value is higher than the crystalline nickel

value (1.6 eV). Therefore, this result is in perfect agreement with our previous finding stating that nickel in state *b* is actually amorphous.

In the case of transition metals the x-ray absorption spectra corresponding to the L threshold can be quite complicated because the interaction of the excited *3d* electron and the *2p* hole leads to multiplets states [3]. Due to the local crystal field that produces important perturbations in the intraatomic interactions, these spectra are rather sensitive to the atomic environment. In the amorphous phase, a broadening of the XAS spectrum is expected as a result of the enlarged distribution of neighboring atoms, which results in a high dispersion of crystal field values at the absorbing site. Therefore, the FWHM values obtained from the XAS spectra support also the expecting results.

In summary, X-ray absorption spectroscopy was used to characterize the different states resulting from the controlled devitrification of an initially homogeneous amorphous alloy $Ni_{80}B_{20}$. An intermediate, partially devitrified state is observed, in which the nickel component has a FWHM about 50% larger than that corresponding to crystalline nickel. These XAS measurements support previous x-ray diffraction results performed on this amorphous nickel phase at room temperature.

This work was supported by the BESSY-EU Project No. CHGE-CT93-0027 of the Human Capital and Mobility program of the European Union. We acknowledge the BESSY staff for their help.

[1] T. Egami and Y. Waseda, J. Non-Cryst. Solids, 64, 113 (1984).
[2] J. M. Rojo, A. Hernando, M. El-Ghannami, A. García-Escorial, M. A. González, R. García-Martínez and L. Ricciarelli, Phys. Rev. Lett., 76, 4833 (1996).
[3] F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom., 67, 529 (1994).