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Observation of a Strong Short Range Order in Co Rich Amorphous Alloys Prepared by Different Methods

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Abstract. X-ray absorption spectroscopy has been used to compare the short range order of some Fe-Co based amorphous alloys with low Fe concentration prepared by different methods: melt spinning (samples of FeCoSiB) and electrodeposition (FeCoP). Both the EXAFS and XANES analysis indicates that the chemical affinity of the metalloids Si or P for the Co atoms underlies the strong increase of the topological short range order around the Fe atoms. This ordering enhancement involves several coordination shells above the first one and results to be independent of the sample preparation procedure as well as the nature of the metalloids (Si or P). The large differences observed between the local structure around the Fe and Co atoms strongly suggest the existence of an inhomogeneous distribution of Fe, or Fe-B, in the bulk amorphous structure of the Co rich alloys, which takes places when the Si or P concentration is higher than the Fe one.

1. INTRODUCTION

The Co-rich amorphous alloys have been the subject of an active field of research. In particular, recent crystallization studies on Co-based amorphous alloys suggest that the addition of Fe to CoSiB(Nb,Cr) alloys give rises to the formation of Fe rich crystal-like clusters acting as the nucleation sites for the growth of a BCC phase. These results would imply the existence of a medium range order [1].

In a recent work devoted to the EXAFS and XANES study of the $(\text{Fe}_{0.2}\text{Co}_{0.8})_{75}\text{Si}_y\text{B}_{25-y}$ ($y=0-15$) metallic glass series [2], we have proved the existence of an important chemical short range order (CSRO) with a preferential coordination of the Si atoms with the Co ones and of B with Fe. This chemical affinity yields the topological short range order (TSRO) to enhance around Fe when Si concentration increases. In the sample with $y=15$ ($\text{Fe}_{0.2}\text{Co}_{0.8})_{75}\text{Si}_{15}\text{B}_{10}$, the Fe neighbourhood exhibits a BCC-like radial arrangement and the atomic order extend to several atomic shells (up to $\approx 5 \text{ \AA}$).

In the present work we show that the occurrence of this strong SRO is not related to the sample preparation method. For this purpose we have compared the EXAFS results obtained in the sample $(\text{Fe}_{0.06}\text{Co}_{0.94})_{75}\text{Si}_{15}\text{B}_{10}$, prepared by melt-spinning (named in the following as Fe6/MS), and the electrodeposited $(\text{Fe}_{0.08}\text{Co}_{0.92})_{83}\text{P}_{17}$ (Fe8/ED) with those obtained in the sample $(\text{Fe}_{0.2}\text{Co}_{0.8})_{75}\text{Si}_{15}\text{B}_{10}$ (FE20/MS), ref.2.

2. EXPERIMENTAL AND DATA ANALYSIS

The sample Fe6/MS, prepared by melt spinning in the form of long ribbon, has a cross section of 0.5 mm wide and 20 μm thick, while the electrodeposited one [3], Fe8/ED, is about 25 μm thick and was cut in a 15x15 mm^2 piece for the absorption experiments. In both samples, the amorphicity was checked by X-ray diffraction.

X-ray absorption spectra on Fe and Co K-edges were recorded at room temperature in 7.1 station at Daresbury Synchrotron Radiation Source, using Si(111) monochromator in the usual transmission geometry. The storage ring was running typically with an electron energy of 2 GeV and a current between 120 and 250 mA.

The normalized EXAFS functions, $\chi(k)$, were extracted from the raw data using a standard procedure [4]. The Fourier Transform (FT) of $\chi(k)$ was performed with a k^3 weight and a Hanning window function. The Inverse Fourier Transform (IFT), $k\chi^F(k)$, has been fitted to an expression which takes into account the characteristic asymmetry of the radial distribution function of amorphous samples. In the framework of dense random packing of hard spheres model, De Crescenzi et al [5], have proposed a function, which has proved to give very good results in other amorphous samples [2,6, 7] given by:

$$k\chi^F(k) = \sum_j N_j f_j(k, \pi) \frac{e^{-2\sigma_j^2 k^2} e^{-2i\Gamma_j/k}}{R_j^2} \frac{1}{\sqrt{1 + 4k^2 \sigma_{D_j}^2}} \sin \left[2kR_j + \tan^{-1}(2k\sigma_{D_j}) + \phi_j \right]$$

In this equation, the N_j is the number of j type atoms around the absorbing one, R_j is the distance between the centres of the two touching spheres, and σ_{D_j} is the root mean square deviation of the distribution of distances. Then, the average distance of the j -species is given by $\bar{R}_j = R_j + \sigma_D$. Amplitude and phase of backscattering, $f_j(k, \pi)$ and ϕ_j , as well as the mean-free-path

Figure 1 Fourier transform of (a) the Fe K-edge of Fe6/MS and Fe20/MS, (b) the Fe K-edge of Fe6/MS and Fe8/ED and (c) the Co-K edge of the three samples.

term, Γ_j , have been taken from FEFF3 codes [8]. The optimization of the scattering factors has been done using FCC-Co, CoSi₂, BCC-Fe, Fe₂B and Fe₃Si as reference compounds. Fe and Co are considered as identical backscatterers, "M", because of the very similar atomic number. The details of data analysis are discussed elsewhere [2].

3. RESULTS AND DISCUSSION

In Fig. 1 we present the Fourier Transform (FT) of Fe and Co K-edge of the two studied samples compared with those of Fe20/MS. It is observed, first, that the main peak of the FT of the Fe K-edge EXAFS spectra for Fe20/MS (Fig.1(a)) presents a shoulder which has been related [2] with the splitting of the Fe environment in two "subshells", in a BCC-like structure. The splitting of the main peak becomes evident in the two samples with less Fe content (Fig.1(b)). The quantitative results presented in Table I indicate that the Fe environment for the samples Fe6/MS and Fe8/ED is indeed very similar to that already found for the sample Fe20/MS (ref.2). It consists of two shell of Metals, whose distance ratio is 1:1.22 for the nearest distance (R_{Fe-M}), and around 1:1.16 for the average distance ($\bar{R}_{Fe-M}$). This relation is very close to 1:1.15, the distance ratio of the Fe BCC structure. Second, the FT of the Fe K-edge EXAFS spectra of the three samples presents similar structures up to 5 Å, an indication of identical radial structure around Fe and the extension of the short range order up to a medium range order. The ratio of the peaks position is 1:1.3:1.55:1.8, as it is marked in fig. 1(a). The unfiltered EXAFS signals are quite well reproduced using the parameters of table I for the first and second shells with two additional shells of Metals at 3.5 Å and 4.1 Å. Finally, the FT of the Co K-edge EXAFS spectra (Fig.1(c)) presents a single peak, which means that only the first shell contribution is present, without any significant structure at high R values. The lack of variation in the Co environment along the composition range in which the Fe atoms participate in a highly ordered structure suggests that the last conform well defined structural units that are distributed in a uniform Co and Si (or P) amorphous matrix.

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Table I: Values of the structural parameters obtained in the fittings of the Fe-K edge of Fe6/MS and Fe8/ED.

	N_M	$R_{Fe-M}(\text{\AA})$	$\sigma_{DFe-M}(\text{\AA})$	$\bar{R}_{Fe-M}(\text{\AA})$	N_R	$R_{Fe-R}(\text{\AA})$	$\sigma_{DFe-R}(\text{\AA})$	$\bar{R}_{Fe-R}(\text{\AA})$
Fe8/ED	8.8 (7)	2.382 (5)	0.15 (1)	2.54 (2)	-	-	-	-
	1.2 (7)	2.91 (3)	0.05 (2)	2.96 (5)				
Fe6/MS	7.2 (7)	2.345 (3)	0.18 (3)	2.53 (3)	2.1 (7)	2.14 (2)	0.01 (3)	2.15 (5)
	1.9 (7)	2.86 (4)	0.17 (4)	3.03 (6)				

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