Diffraction Anomalous Fine Structure (DAFS)

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DAFS experiments for phase-sensitive determination of local structure around Zr in Co/Zr multilayers

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Diffraction Anomalous Fine Structure (DAFS) experiments were applied to support EXAFS analysis for studying amorphisation behaviour of Co/Zr multilayers stimulated by annealing below the crystallisation temperature. The layers, prepared by electron beam vaporisation, initially polycrystalline, exhibited hcp structure. The solid state reaction (SSR) during annealing was indicated by decreasing X-ray reflection intensities. This information and the knowledge of short-range order in Zr crystallites determined by DAFS enabled contributions of amorphous and crystalline phases to the average EXAFS signals to be separated. DAFS experiments were carried out at the Zr-K absorption edge using Zr 0002 reflection in symmetric geometry. A strong [0002] fibre texture was observed which did not change during annealing. After more than 1 hour annealing at 250°C Co atoms have been detected in the Zr crystallites at a Zr-Co distance of 3.03Å.

1. Introduction

The system Co/Zr belongs to a series of elemental combinations showing a crystal to glass transition during annealing below the crystallisation temperature as first discovered by Schwarz and Johnson (Schwarz et al. (1983)). In a previous paper (Kupsch et al. (1998)) we have investigated amorphisation in Co/Zr multilayers by comparison of Extended X-ray Absorption Fine Structure (EXAFS) measurements and Wide Angle X-ray Scattering (WAXS). This enabled crystalline and amorphous phases to be separated. Results rely on the assumption that there are no changes in short-range order of the remaining crystalline phase. It is the aim of the present communication to reveal short-range order of the crystalline parts of the specimen independently by DAFS experiments in the vicinity of the Zr-K absorption edge using Zr 0002 reflection intensities in symmetric geometry. For details of the method cf., e.g., Sorensen et al. (1994). Because of strong fibre texture of the single layers which did not change during SSR qualitatively, this information refers to crystallites separated with regard to their orientation.

2. Experimental

The Co/Zr layers under investigation were prepared by U. Herr, M. Moske and K. Samwer (University of Augsburg, Germany) using electron beam vaporisation. The layers initially appeared in a polycrystalline hcp structure.
DAFS experiments were carried out at storage ring DORIS (beamline CEMO at HASYLAB) using a Si double crystal monochromator (220 reflection). As detectors thermoelectrically cooled Si-PIN-photodiodes (Meyer et al. (1995a)) had been used. Figure 1 shows the reflection behaviour within an energy range in the vicinity of the Zr-K absorption edge at about 17998 eV.

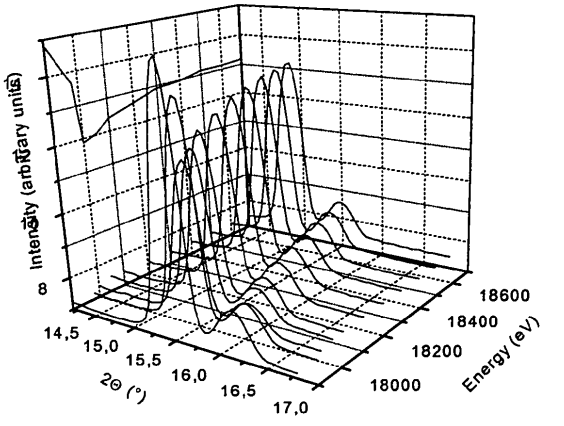

Figure 1
Reflection behaviour of Zr 0002 and Zr 10-11 reflections within an energy range in the vicinity of the Zr-K absorption edge. The projection indicates the development of the Zr 0002 DAFS curve.

In figure 2 the Zr 0002 DAFS intensities of a set of specimens representing the different stages of the SSR are shown. Zr 0002 intensities decrease as a function of annealing time at 250°C. Simultaneously measured Zr-K fluorescence EXAFS intensities are also shown in figure 3.
Then Fourier transforms of the imaginary part of the complex fine structure function have been derived from both DAFS (corrected with respect to absorption and deconvoluted by a Kramers-Kronig formalism (Sorensen et al. (1994))) and XAFS signals (taking matrix effects and self absorption into account as described in Meyer et al. (1995b)).
The subsequent steps of quantitative analysis were: back transformation (filtering) of parts of Fourier spectra and fit of model functions to obtain the parameters of local structure. Comparing the theoretical backscattering amplitudes (McKale et al. (1988)) and the theoretical total phase shifts of the photoelectron waves of Co and Zr one notes that Co contributes as backscatterer mainly at lower values of the wave vector k whereas the same holds for Zr at higher values of k. For Zr-K DAFS/EXAFS the total phase shift for Co as backscatterer in the k-range of interest differs clearly from that of Zr as backscatterer, the relative shift for both cases is about π. That means that Co or Zr as backscatterers positioned at comparable distances result in signals, which are 180° phase shifted to each other which complicates the quantitative analysis by mutual damping. This let us run the fit procedure under the constraint of constant sum of effective Zr/Co coordination numbers given by conservation of mass density determined by X-ray reflectometry. The range of the wave vector between 4 and 6 $Å^{-1}$ is very sensitive for an insertion of Co in the existing Zr neighbourhood to be detected. Thus replacement of Zr by Co should be noticeable in this range.

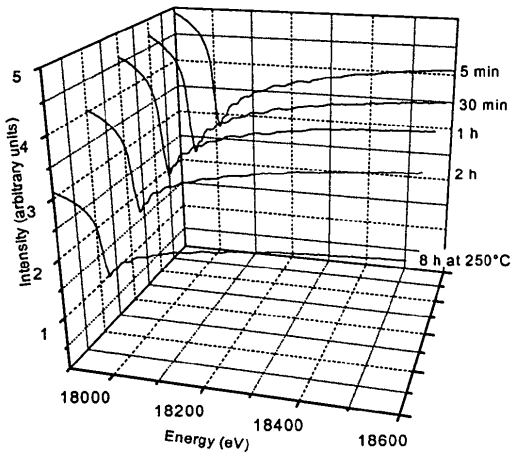

Figure 2
Zr 0002 DAFS intensities of a set of specimens representing different annealing stages.

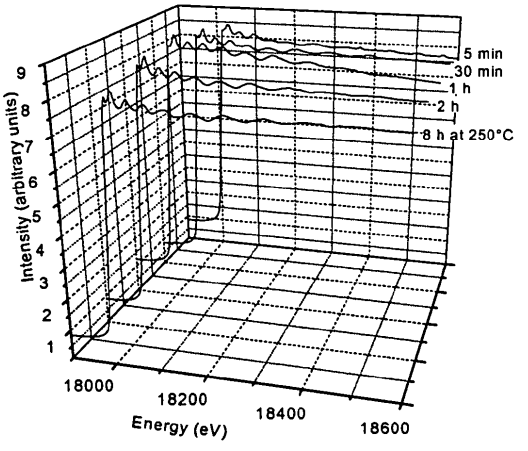

Figure 3
Zr-K fluorescence intensities of a set of specimens representing different annealing stages measured simultaneously to Zr 0002 DAFS (cf. fig. 2)

Quantitative fit of local structure models to imaginary parts of the complex fine structure function of DAFS did not indicate any change of local structure of remaining crystallites for the samples annealed at 250°C up to 1 hour. Assuming an insertion of approximately one Co atom into the neighbourhood of Zr within the crystallites, good correspondence between backtransform and model function was achieved for the stages of 2 and 8 hours annealing. The Zr-Co distance has been refined simultaneously. Coordination numbers in Tab.1 have a relative error of 10% while interatomic distances are matched with a reliability of 0.02Å. The coordination numbers were calculated on the base of effective coordination numbers taking different orientations of the electric field vector into account. To improve accuracy of quantitative analysis in case of Zr we have used experimentally determined backscattering amplitudes obtained via measurement with a Zr standard foil. In this case considerable discrepancies occurred between theoretical and experimental values. Making use of the local structure as determined by DAFS the averaged EXAFS signal of all excited atoms in the sample could be divided into distinct parts due to both the crystalline and amorphous phases. The amorphous contribution to the average EXAFS was analysed using standard procedures. Results are given in Tab. 1.

Table 1
Radial distribution parameters as obtained by fitting Zr 0002 DAFS and EXAFS spectra of a 10*(344Å Co +576Å Zr) multilayer: *t* annealing time (annealing temperature *T*=250°C); *V* relative volumes of crystalline and amorphous phases (in Vol. %, c. crystalline, a. amorphous); *X* species of neighbouring atoms; *N* coordination number of *X* atoms around the central atom; *r* interatomic distance between central and neighbouring atom.

		Zr-K EXAFS			*Zr 0002 DAFS*		
t	*V*	*X*	*N*	*r* / Å	*X*	*N*	*r* / Å
0	100 % c.	Zr	6.4	3.16	Zr	7.0	3.16
		Zr	5.7	3.21	Zr	5.7	3.22
5 min	93 % c.				Zr	6.8	3.16
					Zr	5.9	3.21
	7 % a.	Zr	6.6	3.30			
		Zr	6.0	3.07			
0.5 h	78 % c.				Zr	6.8	3.18
					Zr	5.9	3.23
	22 % a.	Zr	6.9	3.30			
		Zr	5.3	3.07			
1 h	73 % c.				Zr	6.8	3.18
					Zr	5.8	3.22
	27 % a.	Zr	7.0	3.30			
		Zr	5.2	3.07			
8 h	31 % c.				Zr	5.8	3.18
					Zr	5.8	3.22
					Co	0.7	3.03
	69 % a.	Zr	7.4	3.30			
		Zr	4.7	3.06			
		Co	0.5	2.66			
		Co	1.2	2.81			

3. Conclusion

By using DAFS/EXAFS methods we could determine the local structure for different phases (crystalline and amorphous) of annealed Co/Zr multilayers separately. The results show that the determination of local structure in different amorphous phases based on the assumption of invariable structure of the remaining crystalline phase (Kupsch et al. (1998)) is correct up to the latest stages of SSR. When annealing the sample for 2 hours at 250°C insertion/accumulation of Co into the Zr crystallites at a Zr-Co distance of 3.03Å became detectable.

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