LNF-92/113

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Mat. Res. Soc. Symp. Proc. Vol. 272 (1992) 303-308

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ABSTRACT

We present an EXAFS study of the local environment of Co dopant atoms in nanocrystalline Cu. Due to the low solubility of Co atoms in bulk Cu, these measurements yield information on the local atomic structure of grain boundaries in nanocrystalline Cu. Previous EXAFS studies on pure nanocrystalline metals have indicated an atomic arrangement in the grain boundary component exhibiting a broad distribution of interatomic spacings which differs from the atomic structure of the crystalline or glassy state. In the present investigation a significantly reduced coordination number around Co is found; also, the first shell bond length varies with dopant concentration from that typical of Co substitutional impurities in Cu to that of bulk Co. These results suggest that Co atoms substitute Cu atoms both in the disordered grain boundaries and in the lattice of the Cu-crystallites and/or form Co-precipitates.

INTRODUCTION

EXAFS studies on nanocrystalline (n-) materials [1,2] show an intensity reduction of the structural signal and of the Fourier transform (FT) comparable to the volume fraction of the grain boundary component [3,4]. This indicates that the atoms situated in the grain boundaries contribute little to the EXAFS oscillations. These results were interpreted in terms of an atomic arrangement exhibiting a broad distribution of interatomic distances which is thought to differ structurally from the crystalline or glassy state.

The aim of the present study was to dope grain boundaries of n-materials with probe atoms. Hence, EXAFS measurements on the absorption edge of these should yield information about their local atomic arrangement in the grain boundaries and on the structure of the grain boundaries themselves. EXAFS is especially suitable for this purpose because of its chemical sensitivity. N-Cu was doped with Co because it is insoluble in Cu, preventing diffusion of the probe atoms into the crystallites. In addition Co does not form intermetallic phases with Cu [5].

Mat. Res. Soc. Symp. Proc. Vol. 272. ©1992 Materials Research Society

EXPERIMENTAL

N-materials were prepared by producing small crystallites and subsequent compaction of the as prepared powder into a solid [1,2]. The small crystallites were prepared by means of an inert gas condensation technique. The material (e.g. Cu) is evaporated from a resistively heated W-crucible into an inert gas atmosphere (about 100 Pa He).

For doping the evaporation process was stopped, high vacuum restored and using a second crucible the probe atoms were evaporated on the surface of the loose powder as a thin film of about 1 monolayer. This procedure was repeated several times; once enough powder was accumulated at the cold finger and after restoring high vacuum the powder was stripped off, funneled into a compaction die and compacted into a solid. The chemical composition was analyzed by EDS. The crystallite size was examined by X-ray diffraction and also by transmission electron microscopy.

The EXAFS measurements were performed at the PULS synchrotron radiation facility in Frascati, Italy, using a channel cut Si(111) monochromator, the transmission geometry and Ar filled ionization chambers; all measurements were carried out at 77 K. EXAFS oscillations were analyzed according to the standard procedure given in ref [6]. Quantitative analysis of the data was performed in k-space. An inverse Fourier transform was performed in the region R= 1.6 Å - 2.6 Å to isolate the first shell contribution. Subsequently a fit of this signal was performed using scattering functions from ref. [7] for Co-Co and Co-Cu pairs in the range 5 to 11 $Å^{-1}$. Errors on the parameters were estimated by doubling the residual at the minimum.

RESULTS AND DISCUSSION

The crystallite diameters and the Co concentrations of the Co doped n-Cu samples are listed in table I.

Table I: Average diameter of the Cu crystallites (D) and Co concentration (C) of the samples investigated.

Sample	1	2	3	4
C (at. %)	0	1.5	2.5	5.0
D (nm)	14	20	17	13

The EXAFS signal at the Cu edge in the doped samples is very similar to that obtained in the undoped sample as can be seen from figure 1 where the first shell coordination number around Cu for all samples is reported in figure 1.This is an indication that the Co dopants do not significantly alter the structure of n-Cu.

In figure 2 the EXAFS oscillations and the FT at the Co-K edge of a Co doped n-Cu sample and of coarse grained Co are shown. It can clearly be seen that the oscillations are distinctly weaker and are slightly phase shifted with respect to those of coarse grained Co. Because of the similar back-scattering properties of Co and Cu it is impossible to decide whether Co is surrounded by Co or Cu based on the back-scattering amplitude and phase shift. However we have found that the structural parameters obtained do

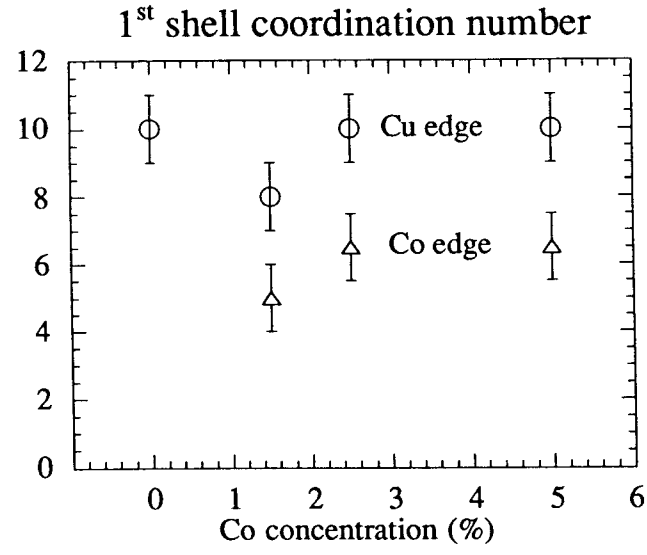

Fig. 1: First shell coordination numbers at the Cu and Co edges.

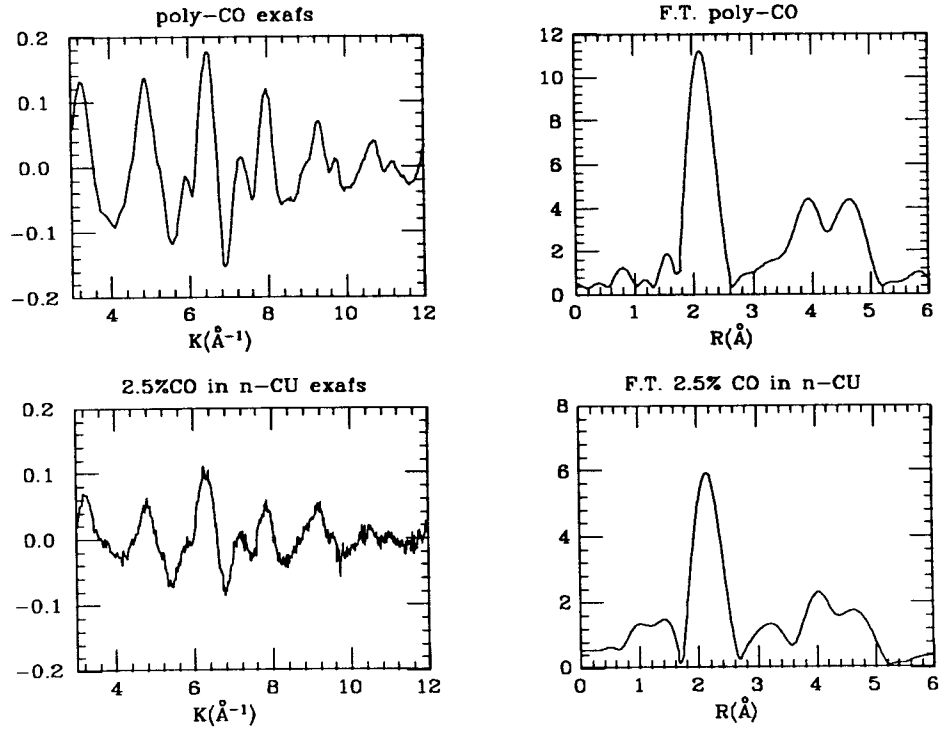

Fig. 2: EXAFS oscillations and the Fourier transform of coarse grained Co and Co doped n-Cu at the Co-K edge.

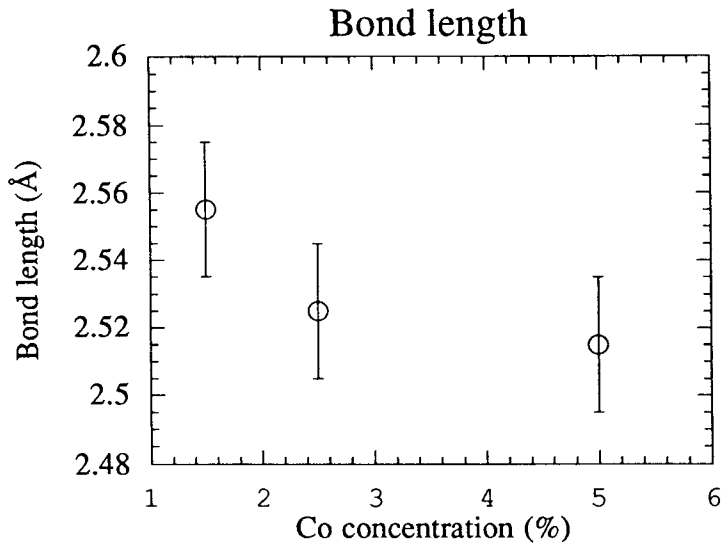

Fig 3: First shell bond length around Co atoms.

not depend significantly on whether we use Co or Cu backscatterers (differences are within the error bar).

In figures 1 and 3 we report values obtained for the first shell coordination number and bond length. The coordination number around Co is found to be significantly smaller than that measured around Cu, in agreement with visual inspection of figure 2.

While the backscattering amplitude cannot be used to advantage in this case we will use the observed interatomic distance to distinguish between different bonding situations. In fact, the interatomic distance in polycrystalline Co is 2.50 Å and a value of 2.55 Å has been measured for the bond length of Co substitutional impurities in Cu [8]. Hence we will take a distance of 2.50 Å as indicating Co-Co bonding while 2.55 Å a Co atom in a Cu environment.

Based on these results we propose that Co atoms substitute Cu both in the grain boundaries and in the lattice of the Cu-crystallites in the vicinity of the grain boundaries and/or form small Co precipitates. In the three samples studied there are differences in the Co incorporation which are related to the Co concentration. For the 1.5 at% Co doped n-Cu sample the observed nearest neighbour distance (coincident with that of Co impurities in Cu) indicates that most Co atoms substitute Cu atoms. From the greatly reduced coordination number we conclude that a large fraction of Co atoms are situated in grain boundary configurations which contribute little to the structural signal. This finding is compatible with the immiscibility of Co in Cu and with previous findings on the structure of grain boundaries in n-materials.

We note however that the damping of the EXAFS signal is not total and that the observed nearest neighbour distance indicates that a considerable number of Co atoms are situated in atomic arrangements which are similar to the Cu lattice although the solubility of Co in coarse grained Cu is very low (<.1 at% at T

< 500°C) [5]. Such atomic arrangements can be located in slightly distorted regions of the crystallites in the vicinity of the grain boundaries indicating local stresses. Such distorted regions have been observed by high resolution microscopy studies on n-Pd[9]. Additionally, lattice strains of about 0.6% were deduced from XRD analysis on n-Pd [10]. In figure 4 a simple model for the proposed atomic structure of 1.5 at% Co doped n-Cu

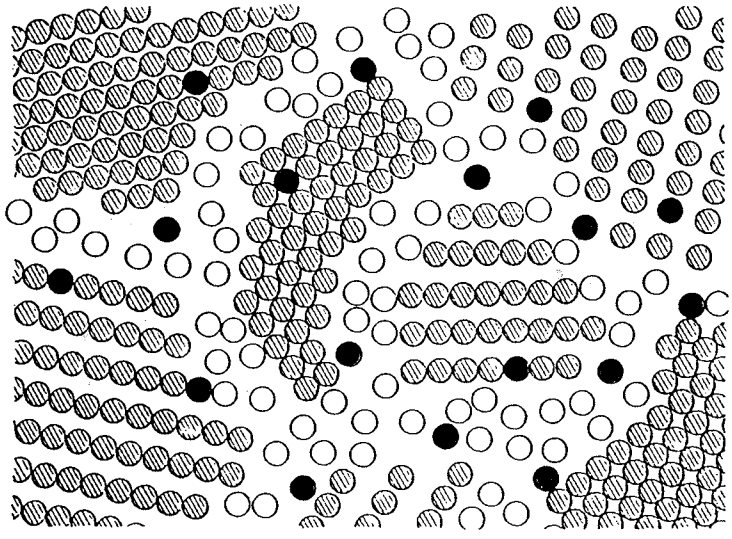

Fig. 4: A simple model for the proposed atomic structure of 1.5 at% Co doped n-Cu. The hatched circles indicate the Cu atoms on lattice sites, the open circles Cu atoms in the grain boundaries and the filled circles Co atoms in the grain boundaries as well as on lattice sites in the Cu crystallites.

is shown.

A similar 'alloying effect' was recently observed in a binary mixture of nanometer sized Fe and Ag crystallites [11]. In spite of the insolubility of the Fe/Ag system even in the liquid state, the formation of alloy phases, that is Fe atoms incorporated in Ag-rich regions and vice versa, is reported for the binary mixture of nanometer sized Fe and Ag crystallites. The formation of these alloys was proposed to take place in the interphase boundary region by rearrangement of atoms over short distances. The driving force for such a rearrangement seems to be the reduction of the free energy of the entire system of crystallites and boundary regions due to an enhancement of the configurational entropy [11].

Increasing Co content leads to a reduction of the mean nearest neighbour distance. This indicates that with increasing Co content the tendency to form Co precipitates increases because the solubility of Co in n-Cu is exceeded.

The behaviour of the present system can be contrasted to what is found for Bi doped n-Cu [12]. In that case the dopant was found only in low coordination grain boundary configurations and significant changes of the EXAFS signal of the host n-Cu were found, unlike the present case. These changes are linked with all probability to a reduction of the free volume of the grain boundaries due to the large atomic radius of Bi compared to Cu.

In conclusion EXAFS measurements on Co doped n-Cu has provided new evidence for the proposed atomic structure of grain boundaries in nanocrystalline materials. Further, these results indicate that alloying of normally immiscible elements is possible to some degree in grain boundaries and in the lattice in the vicinity of the grain boundaries in nanocrystalline materials. A more extensive discussion of the present results appears in [13].

ACKNOWLEDGEMENTS

This work was supported by the BMFT and the DFG (G.W. Leibniz Program).

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