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EXPERIMENTAL EVIDENCES OF LATTICE DISTORTION IN NANOCRYSTALLINE MATERIALS

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Abstract *– Lattice parameters for nanocrystalline (nc) materials were found to be alerted with respect to the corresponding coarse-grained polycrystalline counterparts in several systems. In this work, experimental evidences of the lattice structure distortion in various nc materials processed by means of different approaches will be summarized and discussed. Strong evidences showed the lattice structure distortion in nc samples which is manifested by an evident change in the lattice parameters, Debye-Waller parameter, and the thermal properties of the nanocrystalline lattice. These results imply that the property changes of nc materials should be attributed not only to the numerous non-equilibrium grain boundaries, but to the distorted nanocrystallites as well.* ©*1999 Acta Metallurgica Inc.*

INTRODUCTION

Owing to the ultrafine-grained structure, nanocrystalline (nc) materials exhibit many properties that are found to be fundamentally different from, and often superior to, those of the conventional polycrystalline counterparts [1,2]. The property enhancements in nc materials are frequently attributed to either the numerous amount of grain boundaries and/or the specific grain boundary structure that was claimed to differ fundamentally from that of the conventional grain boundary [1]. While many structure investigations on the nc grain boundary structure yield rather controversy results [3,4], the structure characteristics of the nm-sized crystallites, which still constitute a major part of nc materials, has received seldom attention.

In recent years, a series of experimental investigations have been carried out on the microstructure and properties of the nm-sized crystallites in nc materials. It shows that the lattice structure parameters in nc materials differ evidently from those in their conventional coarse-grained counterparts [2,5,6]. In this paper, we will summarize the experimental evidences on the lattice structure parameter measurements in different nc materials processed by means of different synthesis techniques.

EXPERIMENTAL RESULTS AND DISCUSSION

Lattice parameters

Lattice parameters in a number of nc samples have been measured by means of the quantitative x-ray diffraction (XRD) technique. Table 1 summarizes the experimental data on lattice parameter of nc materials reported in the literature. For bcc metals (Cr and Fe) and fcc metal (Cu) synthesized by means of different approaches (e.g., consolidation of ultrafine powders, ball-milling, electrodeposition, and severe plastic deformation etc.), lattice parameters of nanocrystallites were found to be slightly increased (0~0.09%) with respect to the equilibrium lattice constant for bulk materials. An evident grain size dependence of lattice parameter was observed in fully-dense nc Cu samples [10] (made by means of electrodepsition, ball-milling, and severe plastic deformation, respectively) and ball-milled nc Fe samples [8] that a value increases with a reduction of grain size following an approximate $1/d$ rule. The only negative Δa value found in the nc Pd sample, as listed in Table 1, might be attributed to the porosity effect in the sample of which the density is only 80% of the bulk value [4]. It is reported that the lattice parameters for ultrafine metal particles are decreased (lattice contraction) owing to the large surface tension [15].

For nc semiconductors (Si, Ge and Se), significant lattice parameter changes were observed. Evident lattice distortion (up to about 0.2% in the lattice parameter) was seen in ball-milled nc Si and Ge prior to their solid state amorphization process [11,12]. In a nc Se sample with a mean grain size of about 13 nm, a value is about 0.30% higher than the tabulated bulk value, while c is about 0.12% smaller. The overall unit cell volume is increased by as high as 0.7% relative to that of the conventional polycrystalline Se. The grain size dependence of the lattice parameters in the crystallized nc Se samples (from amorphous Se) agrees well with that in the ball-milled nc Se. For nc bct intermetallic compounds (Ni_3P and Fe_2B), a similar variation tendency of lattice parameters with grain size was detected, *i.e.*, when grain size reduces, a increases but c decreases, resulting in an evident increase in the unit cell volume (as much as 0.3%) [6,14].

Debye-Waller Parameters

The Debye-Waller parameter (DWP) is a measure of the displacement of atoms from their ideal positions. In the nc element samples, DWPs determined from quantitative XRD measurements by using the Warren method or other methods, show an evident enhancement relative to the tabulated values for bulk polycrystals. The static DWP in various nc samples, which reflects the static atomic displacement, increases by 100~900% compared to the equilibrium values, as listed in Table 1. This behavior verifies the existence of the lattice distortion in the nanocrystallite lattice. Measurement results in the nc Se crystallized from amorphous Se [16] and in the nc Cr sample [7] indicated that the static DWP increases with a reduction of grain size following an approximate $1/d$ rule.

The Debye characteristic temperature for nc materials decreases significantly with a reduction of grain size. The Debye temperature in a nc Se (with an average grain size of 13 nm) is only 119 K compared to the tabulated value of 136 K for bulk Se [16]. The depressed Debye temperature in nc samples implies a decrease in the cohesion of atoms in the nanocrystallites, which agrees well with the measured grain size dependence of static DWP and lattice parameters (unit cell volume expansion).

Lattice thermal expansion behavior

Thermal expansion behavior of nanocrystallites, that is closely related to the lattice structure, has been measured in several nc materials by using XRD at different temperatures. With decreasing grain size, thermal expansion coefficient in nc Se samples increases, but that exhibits evident anisotropy, i.e., upon heating, a value increases but c decreases. The overall unit cell volume expands at elevated temperatures [16]. For the ball-milled nc Fe, enhanced thermal expansion coefficient by about 100% was detected when grain size is down to 8 nm [8]. The Debye temperature deduced from the grain size dependence of the thermal expansion coefficient in nc Se coincides with that of the direct measurements. It means the lattice distortion is obviously reflected from the thermal property of the nanocrystallites.

From the results presented above, one may see that the lattice distortion exists in various nc materials synthesized by means of different techniques. Similar grain size dependence of lattice parameter change was observed for nc samples (Cu and Se) with different synthesis methods. It is also noticed that lattice distortion is sensitive to various influencing factors such as sample porosity, contamination, segregation, etc. Therefore, more systematic experimental investigation with ideal (clean and dense) nc samples is highly needed prior to a clear understanding of the intrinsic nature of the lattice distortion in nc materials.

The observed lattice distortion in nc materials, which is characterized by lattice expansion and increased atomic displacement (or depressed cohesion of atoms), will definitely result in property variation with respect to that of the perfect lattice. For instance, elastic modulus is expected to be depressed when the crystal lattice is dilated, that may lead to more or less softening of the material. The observed abnormal hardening/softening behaviors in nc materials may be intrinsically related with the lattice structure distortion. It is noticed that grain refinement in the nanometer regime yields hardening for most bcc and fcc metals but softening for alloys and intermetallic compounds [17]. This result may be correlated to our observation that lattice distortion is rather small for bcc and fcc metals, while a relative large lattice distortion is seen for nc intermetallics (Ni_3P and Fe_2B). The nc lattice distortion is also found to be correlated with the apparent thermal expansion behavior of nc samples [18]. Further intensive studies are necessary to reveal the lattice distortion effect on the property variation in nc materials.

CONCLUDING REMARKS

Solid experimental evidences of lattice distortion have been obtained in various nc materials made by means of different synthesis methods. The nanocrystallite is found to exhibit dilated lattice with an increased unit cell volume and atomic displacement (or depressed cohesion of atoms) with respect to the corresponding perfect crystal lattice. The lattice distortion is weak for most nc fcc and bcc metals, while much significant for nc intermetallic compounds and semiconductors. Such a lattice structure distortion may intrinsically related to the observed property variation in nc materials, that deserves further intensive investigations in the future.

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TABLE 1

A list of the lattice parameter changes ($\Delta a=(a-a_0)/a_0$ and $\Delta c=(c-c_0)/c_0$) and the static DWP change ($\Delta B_s=(B_s-B_{s0})/B_{s0}$, where a_0, c_0 and B_{s0} are the equilibrium tabulated values) in various nc samples processed by means of different techniques (UFP = ultrafine powder consolidation, BM = ball-milling, SPD = severe plastic deformation, ED = electrodeposition, XL = crystallization from amorphous solids).

Sample	d (nm)	Synthesis	Lattice Distortion		Reference
			Δa, Δc	ΔB	
Cr (bcc)	11	UFP	Δa =+0.04%	ΔB_s=+230%	7
Fe (bcc)	8	BM	Δa =+0.09%	ΔB_s=+110%	8
Cu (fcc)	85	SPD	$\Delta a \approx 0$	ΔB_s=+100%	9
Cu (fcc)	11	BM	Δa =+0.06%	---	8
Cu (fcc)	27	ED	Δa =+0.06%	---	10
Pd (fcc)	8	UFP	Δa =-0.04%	ΔB_s=+220%	4
Si (diamond)	8	BM	Δa =+0.20%	---	11
Ge(diamond)	4	BM	Δa =+0.20%	---	12
Se (trigonal)	13	XL	Δa =+0.30% Δc =-0.12%	ΔB_s=+900%	13
Se (trigonal)	14	BM	Δa =+0.15% Δc =-0.01%	---	8
Ni_3P (bct)	7	XL	Δa =+0.21% Δc =-0.13%	---	6
Fe_2B (bct)	23	XL	Δa =+0.20% Δc =-0.23%	---	14