An investigation by EXAFS of local atomic structure in an Mg-Nd alloy after processing by high-pressure torsion and ageing

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Abstract

The local atomic structure of an Mg-1.44Nd (wt.%) alloy was investigated after solution annealing, high-pressure torsion (HPT) processing up to1 and 10 turns and ageing at 250 °C for 5 h using X-ray absorption fine structure (XAFS) measurements at the Nd L_{III} -edge. The results show that HPT processing has no effect on the atomic structure around Nd atoms compared to the unprocessed state, whereas ageing at 250 °C for 5 h induces a significant modification in the coordination number and interatomic distances around the Nd atoms. These variations are analyzed based on the correlations between precipitation, defects and atomic mobility of the chemical species.

Keywords: Ageing; EXAFS; high-pressure torsion; Mg-Nd alloy; Phase transformation; Metals and alloys.

1. Introduction

Magnesium and its alloys are interesting materials for lightweight structural applications [1].Nevertheless, these alloys exhibit in sufficient low temperature formability due to their limited slip systems

and this serves to restrict their use for industrial applications [2]. In practice, small amounts of additions of rareearth (RE) elements can improve the mechanical properties such as the ductility of Mg-based alloys [3]. In addition, the application of severe plastic deformation (SPD) processing, as in high-pressure torsion (HPT), has been used to achieve good mechanical properties through grain refinement and the introduction of high dislocation densities [4]. Thus, alloying elements and deformation processing may influence the sequence and kinetics of phase transformations such as recrystallization and precipitation [5].

The sequence and kinetics of precipitation were investigated in an Mg-1.44Nd (wt.%) alloy before and after HPT processing for up to 10 turns and ageing at 250 °C for 5 h using synchrotron X-ray diffraction and DSC measurements [5]. The results demonstrated that HPT processing modifies the kineticsof β_1 -Mg₃Nd and β -Mg₁₂Nd precipitation and decreases their activation energies relative to the non-deformed state [5].

There areno studies devoted to the local environment of solute species after SPD processing and ageing of Mg-RE alloys using X-ray absorption spectroscopy (XAS) techniques, for example. Thus, the aim of the present investigation was to examine the atomic structure environment around Nd atoms at the L_{III}-edge of the Mg-1.44Nd (wt.%) alloy before and after HPT processing and ageing using EXAFS measurements.

2. Experimental

The Mg-1.44Nd (wt.%) alloy was supplied in an as-cast state. Disk samples were machined with diameters of 10 mm and solution annealed (SA) in sealed glass tubes at 535 °C for 6 h followed by water quenching. These disks were severely deformed by HPT at room temperature up to1and 10 turns with a rotation speed of 1 rpm and an imposed pressure of 6.0 GPa.

The SA and HPT-processed samples were subjected to precipitation ageing at 250 $^{\circ}$ C up to 5 hours and subsequently quenched in water. The samples were investigated by EXAFS measurements at the Nd L_{III}-edge and were labeled SA, SA aged, 1 HPT, 1 HPT aged, 10 HPT and 10 HPT aged.

The EXAFS measurements were carried out on the DIFFABS beamline, Synchrotron SOLEIL, France. The XAFS experiments were performed at room temperature in a fluorescence mode using a 4-element silicon drift detector (Vortex-ME4, Hitachi). The EXAFS data processing was performed using the Athena and the Artemis software [6] following standard procedures. The theoretical backscattering paths, amplitudes and phase shift of the fit were calculated with FEFF6 [7] using α -Mg, β -Mg₁₂Nd and β -Mg₃Nd phases.

3. Results and discussion

Fig. 1 shows the X-ray absorption near edge spectroscopy (XANES) spectra collected at the Nd L_{III}edge of the present alloy after different thermo-mechanical processing schemes. All spectra exhibit an intense peak (indicated by an arrow) which records the absorption at the L_{III} -edge of the Nd atom, followed by small peaks or oscillations due to constructive and destructive interferences which arise from the sum of the outgoing photoelectron wave from the Nd absorbing atoms and those backscattered by neighboring atoms. The shift and the amplitude of these oscillations depend on the thermo-mechanical history of each sample.

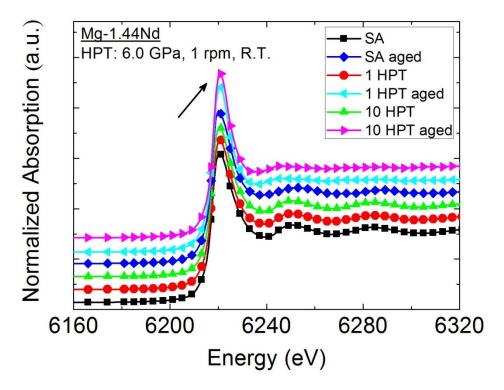


Fig.1. XANES spectra collected at the Nd atom at the L_{III}-edge.

Fig. 2 shows the experimental and best fit k^3 -weighted EXAFS spectra at the Nd L_{III}-edge for all samples and their corresponding Fourier Transform magnitudes, respectively. The structural parameters including the atomic bond, number of atoms, bond length and the Debye–Waller factor obtained from these fits are summarized in Table 1.

The Fourier Transform magnitudes of the EXAFS signal of the un-aged and aged samples show four peaks. The first, third and fourth peaks are associated with the Nd-Mg (α -Matrix) bonds while the second peak that locates to the right of the first peak is linked to the band of Nd-Mg of the second phase β -Mg₁₂Nd. Weak intense peaks are visible between 6 and 7 Å for all samples which may be associated with the Nd-Mg (α -Matrix).

The fitted results of un-aged samples show that the Nd atoms are surrounded by ~8 Mg atoms at ~3.27 Å (first shell), 1.2 Mg atoms at ~3.71 Å (second shell), 4 Mg atoms at ~4.5 Å (third shell) and 15 Mg atoms at ~5.55 Å (fourth shell).

The fitting parameters of the SA and HPT-processed samples demonstrate that HPT processing up to 1 and 10 turns has no major effect on the atomic structural environment around the Nd atoms as well as the amount of the β -Mg₁₂Nd second phase. Such behavior may be ascribed to the occurrence of dynamic recrystallization (DRX) which leads to a decrease in the number of defects in the microstructure. Recently published data for the same alloy showed a saturation of microhardness between 1 and 10 turns [4] where this saturation was a consequence of an equilibrium between the generation of dislocations and their annihilation by a DRX mechanism during straining.

However, it is apparent also that the ageing treatment strongly affects the structural parameters around the Nd absorbing atoms. The EXAFS fitting results of the aged samples show that an average number of the first nearest shell are 6.9 Mg (α -Matrix) atoms at ~3.13 Å for the SA aged sample where the coordination number of this shell decreases with increasing number of HPT turns to 2.9 Mg atoms at ~3.06 Å. The second neighbors are associated with the Nd-Mg (β -Mg₁₂Nd) bond in the SA aged sample with 4 Mg atoms at ~3.72 Å. Increasing the number of HPT turns to 10 appears to promote precipitation of the β -Mg₁₂Nd phase by increasing the magnitude to 5.6 atoms for the Nd-Mg bond at ~3.76 Å. The coordination number of the third shell ranges from 0.7 to 4.30 Mg (α -Matrix) atoms at ~4.60 Å for the SA aged and 1 HPT aged, respectively.

It is readily apparent that the effect of the SPD processing on the structural parameters of the aged samples is more obvious as shown in Table 1. As reported previously, *in situ* ageing at 250 °C up to 5 h for the same alloy led to a precipitation of the β -Mg₁₂Nd phase with increasing numbers of HPT turns [5]. This effect arises from the enhanced decomposition of the solid solution and the non-negligible amounts of defects which accelerate the precipitation kinetics during aging of deformed samples.

Moreover, it has been demonstrated that the competition between the precipitation and the dissolution of precipitates could take place during HPT processing [8, 9] which lead to a steady-state with a certain concentration in the solid solution corresponding to the solubility at a temperature called the effective temperature (T_{eff}) [9]. In the present study, the portion of Nd-Mg bonds in the matrix and in the β -Mg₁₂Nd phase after HPT processing remain equal to the portion in the SA sample after solution annealing at 535 °C. Meanwhile, it changes during the annealing at 250 °C. This means that the T_{eff} for the Mg-1.44Nd alloy after HPT processing is close to 535 °C and is far removed from 250 °C.

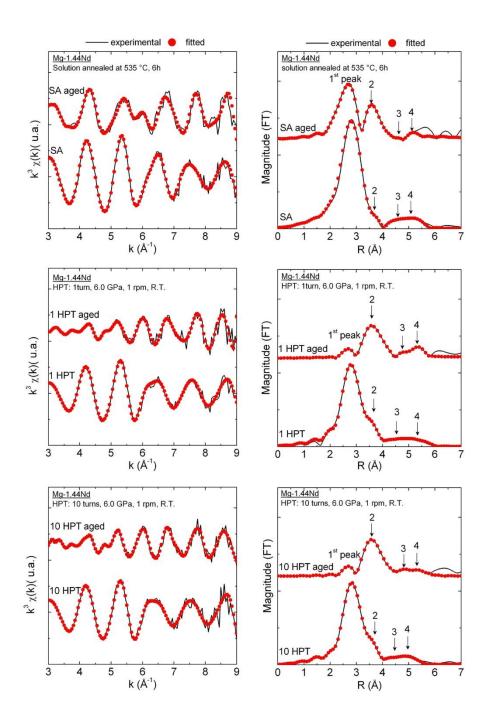


Fig.2. k³-weighted EXAFS spectra and their corresponding Fourier Transform magnitudes.

From Table 1, the σ^2 Debye–Waller factor which reflects the disorder in the neighbor distances is almost the same for all samples except for the 1 and 10 HPT aged samples. It can be speculated that the decrease for these latter sample may be attributed to the decrease in dislocation density and vacancy concentration caused by the ageing and consequently to the lower level of the distortion of lattice points.

Sample	Atomic bond	Number of atoms	Bond length (Å)	$\sigma^2 (10^{-2} \text{\AA}^2)$
SA	Nd-Mg (α-Matrix)	8.12	3.276	
	Nd-Mg (Mg ₁₂ Nd)	1.20	3.710	1.78
	Nd-Mg (α-Matrix)	4.20	4.524	
	Nd-Mg (α-Matrix)	15.00	5.571	
SA aged	Nd-Mg (α-Matrix)	6.90	3.133	
	Nd-Mg (Mg ₁₂ Nd)	4.00	3.721	0.93
	Nd-Mg (α-Matrix)	0.75	4.546	
1 HPT	Nd-Mg (α-Matrix)	8.19	3.295	
	Nd-Mg(Mg ₁₂ Nd)	1.20	3.705	1.51
	Nd-Mg (α-Matrix)	3.70	4.504	
	Nd-Mg (α-Matrix)	14.40	5.634	
1 HPT aged	Nd-Mg (α-Matrix)	4.00	3.198	
	Nd-Mg (Mg ₁₂ Nd)	4.70	3.662	0.66
	Nd-Mg (α-Matrix)	4.90	4.451	
	Nd-Mg (α-Matrix)	14.70	5.696	
10 HPT	Nd-Mg (α-Matrix)	8.05	3.291	
	Nd-Mg (Mg ₁₂ Nd)	1.15	3.695	1.68
	Nd-Mg (α-Matrix)	4.00	4.495	
	Nd-Mg (α-Matrix)	14.85	5.529	
10 HPT aged	Nd-Mg (α-Matrix)	2.98	3.059	
	Nd-Mg (Mg ₁₂ Nd)	5.60	3.765	0.78
	Nd-Mg (α-Matrix)	4.30	4.772	
	Nd-Mg (α -Matrix)	13.70	5.471	

Table 1 Structural parameters from the fit of the EXAFS signals.

Finally, it is necessary to note that the β_1 -Mg₃Nd phase was found to introduce strong discrepancies in the fitting of the experimental k^3 -weighted EXAFS spectra and therefore this phase was not included in the fitting procedure.

4. Summary and conclusions

 The local atomic structure around Nd atoms in the Mg-1.44Nd alloy was investigated using XAFS measurements after solution annealing, HPT processing and ageing at 250 °C up to 5h.

- 2. Excluding the β_1 -Mg₃Nd phase, the EXAFS fitting for all samples showed that the first, third and fourth bonds were ascribed to the Nd-Mg (α -Matrix) bond while the second was associated with the Nd-Mg bond from the β -Mg₁₂Nd second phase.
- The interatomic distance and the coordination number are strongly influenced by HPT processing and ageing.

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