Metallophysics and Advanced Technologies
Металофіз. новітні технол.
Metallofiz. Noveishie Tekhnol.
2022, vol. 44, No. 4, pp. 483–491
https://doi.org/10.15407/mfint.44.04.0483
Reprints available directly from the publisher

PACS numbers: 43.35.Ae, 43.35.Bf, 43.35.Cg, 61.72.-y, 62.80.+f, 93.30.Tr

Velocity and Absorption of Longitudinal Ultrasound in an Extruded Mg–5% Sc Alloy

O. S. Bulatov, V. S. Klochko, A. V. Korniyets, V. I. Spitsyna,
I. I. Papirov, A. I. Pikalov, and A. V. Shokurov

National Scientific Center
'Kharkov Institute of Physics and Technology', N.A.S. of Ukraine,
1 Academic Str.,
UA-61108 Kharkiv, Ukraine

The behaviour of the velocity and the change in the absorption of longitudinal ultrasound in the process of structural relaxation is investigated at a frequency of 50 MHz using ultrasonic spectroscopy in the temperature range 77–300 K in the Mg–5% Sc alloy deformed by equal-channel angular extrusion. Peaks of acoustic absorption with localization temperatures of ~232 and 190 K are found. An estimate of the activation energy (~0.5 and ~0.16 eV) indicates that these relaxation processes are due to dislocation relaxation resonance. The influence of the kinetics of the processes of structural relaxation in the extruded alloy on the investigated acoustic characteristics is shown. As found, that the evolution of the temperature spectrum of acoustic absorption in the Mg–5% Sc alloy is caused by the return of the structure after severe plastic deformation.

Key words: longitudinal ultrasound, acoustic absorption, severe plastic deformation, non-equilibrium grain boundary, dislocations, relaxation.

На частоті у 50 МГц методою ультразвукової спектроскопії в області температур 77–300 К у деформованому шляхом рівноканальної кутової екструзії стопі Mg–5% Sc досліджено поведінку швидкости та зміни поглинання поздовжнього ультразвуку в процесі структурної релаксації. Виявлено піки акустичного поглинання з температурою локалізації ~232 та 190 К. Оцінка енергії активації (~0,5 та ~0,16 еВ) вказує на те, що ці процеси релаксації

Corresponding author: Anatoly Vasilievich Korniyets
E-mail: korniets@kipt.kharkov.ua

Citation: O. S. Bulatov, V. S. Klochko, A. V. Korniyets, V. I. Spitsyna, I. I. Papirov, A. I. Pikalov, and A. V. Shokurov, Velocity and Absorption of Longitudinal Ultrasound in an Extruded Mg–5% Sc Alloy, *Metallofiz. Noveishie Tekhnol.*, **44**, No. 4: 483–491 (2022). DOI: 10.15407/mfint.44.04.0483

зумовлені дислокаційним релаксаційним резонансом. Показано вплив кінетики структурної релаксації в екструдованому стопі на досліджувані акустичні характеристики. Встановлено, що еволюція температурного спектру акустичного поглинання у стопі Mg–5% Sc викликана поверненням структури після інтенсивної пластичної деформації.

Ключові слова: поздовжній ультразвук, акустичне поглинання, інтенсивна пластична деформація, нерівноважні границі зерен, дислокації, релаксація.

(Received October 2, 2021; in final version, January 18, 2022)

1. INTRODUCTION

Magnesium and its alloys are of great interest both for engineering applications in many industries and for theoretical issues of fundamental research due to the unique combination of properties they have low specific density (lightness) and good strength [1].

Among many magnesium alloys, Sc-containing alloys are of particular interest, since they have structural stability and improved high-temperature properties [2–5], which expands their functionality in many industries, including medicine, *e.g.*, for the manufacturing of coronary stents. At the same time, it is relatively difficult to use them to create products due to the limited alloy plasticity caused by the low symmetry of the h.c.p. structure. One of the possible solutions of the problem is to use the equal channel angular extrusion (ECAE) method [6], where the plastic deformation is close to simple shear and the smaller number of slip systems is involved in comparison with other deformation methods. At the same time, in the process of severe plastic deformation (SPD) by means of such extrusion, a homogeneous microcrystalline granular structure is formed in the material that additionally increases its strength and plasticity. In addition, the grains have some structural features. Their grain-boundary atomic structure is substantially non-equilibrium and has a high density of grain-boundary dislocations (GBD). In fact, the GBD system is a non-equilibrium combination of chaotic dislocations, while the grains contain few or almost no dislocations. It should be noted that the volume fraction of the intergranular space is quite high and can reach up to ten percent or more. The non-equilibrium of grain boundaries is clearly manifested in the effect of accelerated diffusion during annealing of SPD materials. For example, the energy of grain-boundary diffusion value can be half of the equilibrium energy and in some cases, it is even close to the value of diffusion activation in the melt [7].

In this regard, it is of particular interest to study relaxation processes in SPD materials in the early period of exposure at room temperature (~300 K) immediately after the completion of plastic deformation. This phenomenon has not been sufficiently studied. In this work, this issue is considered using severe plastic deformed promising magnesium and 5% (weight) scandium (hereinafter Mg–Sc–5) alloy by ultrasonic spectroscopy. Low-temperature (77–300 K) measurements of the V_L velocity and the change in the absorption $\Delta\alpha_L$ of longitudinal ultrasound at 50 MHz frequency makes it possible to trace the relaxation processes development during a holding time at ~300 K temperature.

2. MATERIALS AND RESEARCH METHODS

Binary Mg–Sc–5 alloy is produced by fusion of magnesium with 99.999% purity and scandium—99.95% in a pure argon atmosphere. It is a solid solution with h.c.p. lattice parameters $a = 0.3212 \pm 0.0002$, $c = 0.5205 \pm 0.0007$ nm which has 1.5 mm average grain size.

The SPD of the alloy was carried out in two technological stages. The first stage includes a shrinkage at 633 K temperature to preliminary grind the grain, at the second stage the ECAE is implemented at 573 K temperature for eight cycles along the B_A route (with an alternative rotation of +90 and −90) using a mold which has 90° angle between equal on cross section by cylindrical channels. The extrusion speed remained constant at 1 mm/s.

A sample ∅ 7 × 6.85 mm size and 3.5 μm average grain was investigated. X-ray studies observed axial texture [10.0] along the cylinder axis with a crystallographic grains fraction of this orientation about 18%. The axial texture of deformation [10.0] is retained in the alloy for the entire time of acoustic measurements. The study of the substructural characteristics (D is the size of the coherent scattering regions and ε is the level of microstrains) of the alloy samples was carried out by the Williams–Hall method using the integral half-width of {10.0} diffraction reflections. Silicon powder with ~30 μm particle size was taken as a standard to take into account the instrumental broadening. High-frequency technology using a bridge measuring circuit was used to determine the values of the velocity V_L and absorption α_L of a longitudinal ultrasonic wave at 50 MHz frequency in one experiment at a given temperature. The relative measurement error of V_L and α_L is 10^{-6} and 10^{-3}, respectively. Excitation and detection of sound was carried out by broadband (±2 MHz) piezoelectric transducers made of a lithium niobate single crystal, and the acoustic contact was carried out with silicone oil. Excitation by a high-frequency pulse generator with constant amplitude (~1.5 V) realized the mode of amplitude-independent ultrasonic attenuation. The measurements were carried out with $\Delta T = 1$–2 K temperature interval in the samples warming up mode at a rate of 0.5 K/min. The temperature stabilization of the sample was kept at a level of ±0.05 K.

3. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the longitudinal sound velocity on temperature for the Mg–Sc–5 alloy in the deformed ($V_L^d(T)$) and original ($V_L^0(T)$) states. A regular decrease in the sound speed in the deformed sample is observed, it is due to the structure distortion as a result of SPD. The texture effect is negligible due to the low velocity anisotropy (the axial ratio $c/a \sim 1.621$, which is close to the uniform packing density of the h.c.p. lattice ($c/a \sim 1.633$)). In addition, in the temperature range from 210 to 235 K the $V_L^d(T)$ dependence exhibits a singularity of the stretched step type. In the alloy holding time at 300 K temperature, it smoothes out and after 150 hours it is not detected. At the same time, an essential overall result is the invariability of both the characteristic form of the series of dependences and the absolute values of the sound velocities of the deformed alloy during the holding time. A specific example of the sound speeds stability $V_L^d(T)$ (at 77 K) and $V_L^d(T)$ (at 300 K) for the extruded Mg–Sc–5 alloy after a holding period at 300 K temperature is shown in Table 1. The measurement error is ±25 m/s. This fact indicates that the absolute values difference remains constant, which corresponds to the stability of the dislocation density in the SPD alloy throughout the entire time of the alloy research. In this regard, attention is drawn to researches [8–10], where elastic ultrasonic waves are considered in the approximation of a homogeneous isotropic three-dimensional elastic medium with a dislocation density Λ where, in fact, the Granato–Lukke model is considered with account of the vector nature of multiple scattering. As a result, a relationship is proposed between the change in the vector sound speed,

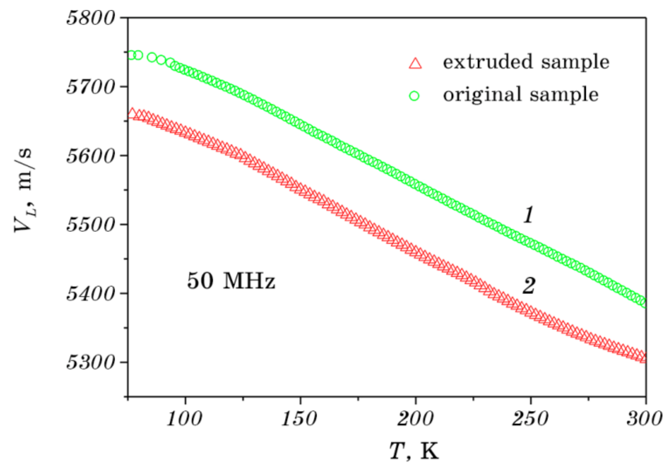

Fig. 1. Temperature dependence of the longitudinal ultrasound velocity at 50 MHz frequency in the Mg–Sc–5 alloy. *1*—the original state, *2*—after ECAE.

TABLE 1. Values of the longitudinal ultrasound velocity at the reference points 77 and 300 K depending on the holding time τ.

τ, h	V_L, м/с	
	77 K	300 K
25	5659.6	5304.7
168	5666.6	5311.9
195	5668.9	5297.3
360	5686.5	5342.2
432	5661.9	5249.8
846	5657.3	5259.5
1440	5657.5	5244.5

scalar dislocation density Λ and the dislocation segment length L. For our case of a longitudinal sound wave the ratio is

$$\frac{\Delta V_L}{V_L^0} = 0.034\frac{1}{(\gamma^2-1)}\frac{\Lambda L^2}{6\ln 10}, \quad (1)$$

where $\gamma = \frac{V_L}{V_t}$, V_t is the speed of the shear sound wave. If $\lambda = 1.7$ is for a pure Mg metal [11], the effective length of the dislocation segment L is about 50 nm and the $\frac{\Delta V_L}{V_L^0} = 4\cdot 10^{-2}$ research data, then the numerical estimate gives the value of the dislocation density in the SPD alloy at the level of 10^{12} cm^{-2}. Since the density of grain-boundary dislocations in SPD materials is much higher than in intragranular ones, their predominant contribution to dislocation absorption of sound is also noted. It is the losses due to internal friction when dislocation segments vibrate in the field of propagating elastic waves. Pinning elements can be impurity atoms, point defects (and their complexes) and the intersection of mobile dislocations formatting a dislocation network.

Figure 2 shows the dependence of the change in the absorption of longitudinal sound at 50 MHz frequency on temperature for the SPD Mg–Sc–5 alloy after a period of exposure τ at room temperature. Fig. 2, *a*, *b* presents the dependence of original $\Delta\alpha_L^0(T)$ and deformed $\Delta\alpha_L^d(T)$ alloy after holding for 25 hours, respectively. The absorption spectrum of the deformed alloy is characterized by the presence of peaks P_1 and P_2, respectively, at 232 K and 190 K. The P_1 absorption peak at 232 K temperature and a characteristic 'step' in the dependence (Fig. 3) in the vicinity of this extreme determine the Hasiguti type relaxation resonance. An estimate of the activation energy from the width of the peak at half its height, determined according to the equation [12]:

$$E_a = 2.63R\frac{T_1T_2}{T_2 - T_1}, \quad (2)$$

where R is the molar gas constant, T_1 and T_2 are the temperatures of the peak at half height, is ~0.5 eV. The activation energy of the P_2 peak is ~0.16 eV, which is characteristic of a relaxation resonance of the Bordoni type, which is also observed in the original sample (Fig. 2, *a*). The complex shape of the absorption spectrum indicates that the revealed relaxation processes are characterized by more than one relaxation time. SPD materials are known to have an extended, deformation-modified non-equilibrium (metastable) grain-boundary region contain-

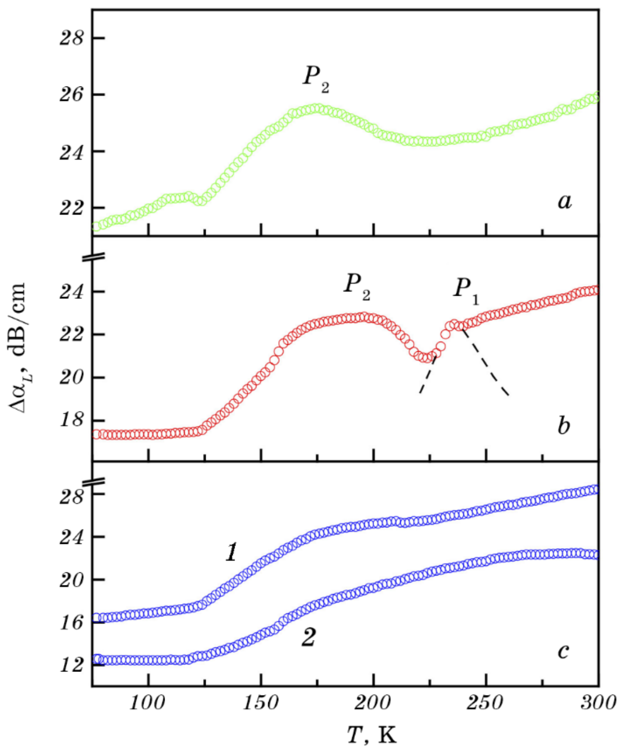

Fig. 2. Temperature dependence of the change in the absorption of longitudinal ultrasound at 50 MHz frequency in the Mg–Sc–5 alloy. *a*—the original state, *b*—in the deformed state, after holding at 300 K for 25 hours; *c*—in deformed state, after holding at 300 K 1440 hours (*c*, curve *1*) and 0.5 years (*c*, curve *2*).

ing an excess density of oriented misfit dislocations and products of their delocalization [13–15]. Such defects have a significant effect on the boundaries properties, changing their free volume, energy, and diffusion permeability. In addition, being distributed along the grain boundaries, they create short-range and long-range fields of internal stresses, which affect the kinetics of the evolution of the structure when the temperature is maintained. The measure of the boundaries disequilibrium is the free volume value. After further exposure at room (~$0.3T_m$, T_m—melting temperature) temperature, the $\Delta\alpha_L^d(T)$ dependence undergoes a disordered transformation and, after 2 months, gains characteristic, Fig. 2, *c*, curve *1*, view.

This behaviour is caused by a noticeable decrease in the relaxants density, which may be associated with the manifestation of the onset of boundaries migration with grain growth and a decrease in the internal stresses level. Non-equilibrium dislocation systems of boundaries are known to be characterized by the presence of long-range fields of elastic stresses and excess elastic energy, that is, the interaction forces between dislocations are not balanced. Stressed ensembles of boundary dislocations are metastable and upon exposure to temperature relax through annihilation (which happened in the first hours after ECAE) and the formation of equilibrium structures. This process goes in the direction of decreasing energy, lowering the level of stress. In addition, the contribution of a decrease in the intragranular relaxants density due to the completion of polygonization and migration of unstable point defects (their complexes) interacting with dislocations to sinks is

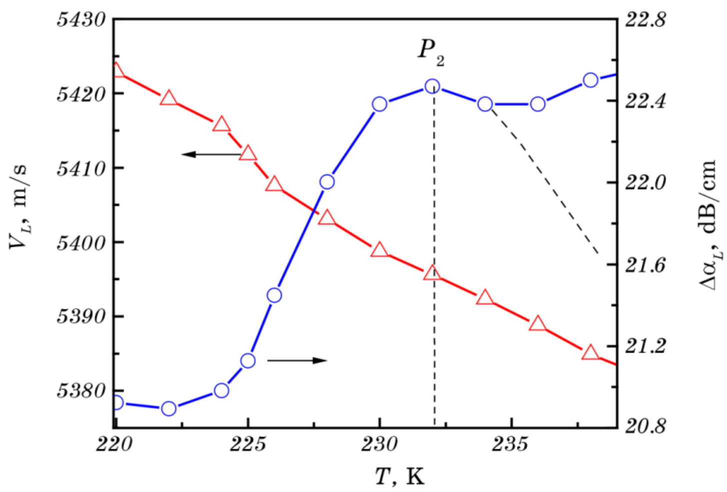

Fig. 3. Temperature dependence of the velocity V_L and the change in absorption $\Delta\alpha_L$ of longitudinal ultrasound at 50 MHz frequency in the vicinity of the relaxation peak of acoustic absorption.

not excluded. The study of the substructural characteristics of the alloy showed that a structure with a coherent scattering region $D \sim 213$ nm and a level of microstrains $\varepsilon \sim 3.4 \cdot 10^{-3}$ was formed in a freshly deformed sample. After a 2 month exposure at room temperature, an increase in D to 415 nm and a decrease in ε to $\leq 7 \cdot 10^{-4}$ are found. At the same time, there was a return and a corresponding decrease in the free volume value, and hence the level of non-equilibrium of the boundaries. The high rate of return processes—the removal of non-equilibrium, is mainly due to the small length of the accommodative diffuse mass transfer. After 6 months of exposure the initial level of non-equilibrium is completely lost and takes on a stable (see Fig. 2, *c*, curve *2*) S-shaped dependence, characteristic of anharmonic phonon–phonon interaction.

4. CONCLUSIONS

As a result of low-temperature (77–300 K) studies of the behaviour of the velocity and changes in the absorption of longitudinal ultrasound at 50 MHz frequency in the Mg—5% Sc alloy deformed by equal-channel angular extrusion, the following was established.

1. The decrease in the value of the longitudinal sound velocity in the extruded sample is due to the distortion of the structure. The effect of texture is insignificant due to the low degree of anisotropy of the sound speed in the alloy (the axial ratio of the h.c.p. lattice $c/a \sim \sim 1.621$).
2. The peaks of acoustic absorption at 232 and 190 K temperatures in the extruded alloy are caused by the development of relaxation processes of the Hasiguti ($E_a \sim 0.5$ eV) and Bordoni ($E_a \sim 0.16$ eV) type.
3. Exposure of the extruded alloy at room temperature ($\sim 0.3T_m$) leads to disordered transformation of the peaks and, after 0.5 years, to disappearance due to a decrease in the density of relaxants in the process of return after SPD.

REFERENCES

1. Z. Yang, J. P. Li, J. X. Zhang, G. W. Lorimer, and J. Robson, *Acta Metall. Sinica (English Letters)*, **21**, Iss. 5: 313 (2008).
2. A. X. Amal Rebin, S. Kumaran, and T. Srinivasa Rao, *Mater. Sci. Forum*, **710**: 132 (2012).
3. V. A. Shalomeev, N. A. Lysenko, E. I. Tsivirko, V. V. Lukinov, and V. V. Klochikhin, *Metal Sci. Heat Treatment*, **50**, No. 1: 34 (2008).
4. Sri Lathabai and P. G. Lloyd, *Acta Mater.*, **50**, Iss. 17: 427 (2002).
5. C. J. Silva, A. Kula, R. K. Mishra, and M. Niewczas, *J. Alloys Compd.*, **687**, No. 5: 548 (2016).

6. Somjeet Biswas, Satyaveer Singh Dhinwal, and Satyam Suwas, *Acta Mater.*, **58**: 3247 (2010).
7. F. I. Nohrin, *Pis'ma v ZhETF*, 13, No. 38: 71 (2012).
8. A. Maurel, V. Pagneux, D. Boyer, and F. Lund, *Proc. R. Soc. London, Ser. A*, **462**: 2607 (2006).
9. A. Maurel, V. Pagneux, F. Barra, and F. Lund, *Phys. Rev. B*, **72**: 174111 (2005).
10. A. Maurel, V. Pagneux, F. Barra, and F. Lund, *J. Acoust. Soc. Am.*, **121**: 3418 (2007).
11. A. K. Gupta, A. Gupta, S. Tripathi, V. Bhalla, and J. M. Singh, *Universal J. Mater. Sci.*, **1**, No. 2: 63 (2013).
12. V. S. Postnikov, *Vnutrenneye Treniye v Metallakh* [Internal Friction in Metals] (Moscow: Metallurgiya: 1974), p. 301 (in Russian).
13. V. N. Chuval'deev, *Neravnovesnyye Granitsy Zeren v Metallakh. Teoriya i Prilozheniya* [Nonequilibrium Grain Boundaries in Metals. Theory and Application] (Moscow: Fizmatlit: 2004) (in Russian).
14. V. N. Chuval'deev, *Vestnik Nizhegorodskogo Universiteta*, **5**, No. 2: 124 (2010) (in Russian).
15. G. Wilde and S. Divinski, *Mater. Transactions*, **60**, Iss. 7: 1302 (2019).