X-ray studies of aluminum alloy of the Al-Mg-Si system subjected to SPD processing

V D Sitdikov$^{1,2}$, M Yu Murashkin$^{1,2}$, M R Khasanov$^3$, I A Kasatkin$^2$, P S Chizhov$^3$, E V Bobruk$^{1,2}$

$^1$ Ufa State Aviation Technical University, Ufa, Russia
$^2$ Saint Petersburg State University, Saint Petersburg, Russia
$^3$ Moscow State University, Moscow, Russia

E-mail: svil@mail.rb.ru

Abstract. Recently it has been established that during high pressure torsion dynamic aging takes place in aluminum Al-Mg-Si alloys resulting in formation of nanosized particles of strengthening phases in the aluminum matrix, which greatly improves the electrical conductivity and strength properties. In the present paper structural characterization of ultrafine-grained (UFG) samples of aluminum 6201 alloy produced by severe plastic deformation (SPD) was performed using X-ray diffraction analysis. As a result, structure features (lattice parameter, size of coherent scattering domains) after dynamic aging of UFG samples were determined. The size and distribution of second-phase particles in the Al matrix were assessed with regard to HPT regimes. Impact of the size and distribution of the formed secondary phases on the strength, ductility and electrical conductivity is discussed.

1. Introduction

By the present moment SPD techniques such as equal-channel angular pressing (ECAP) and high pressure torsion (HPT) have been actively developed [1, 2]. These methods enable fabricating nanostructured and UFG states in bulk billets of different metals and alloys. These states are characterized by enhanced properties and high potential for industrial application. Unusual mechanical properties of bulk nanostructured materials are of special interest. It was shown [1] that materials subjected to SPD could demonstrate a very high strength in combination with sufficient ductility, high fatigue strength, low-temperature or high-strain-rate superplasticity. An extremely small grain size, high density of crystalline defects in grain boundaries and their strongly non-equilibrium state are specific features of bulk nanostructured materials [1, 2].
New approaches to improvement of mechanical and electrical properties of Al-based alloys via processing by SPD techniques have been recently proposed in a number of published papers [3-5]. In particular it was established that dynamic aging (DA) took place in these alloys during SPD. As a result nanosized particles of strengthening phases formed in the Al matrix. The DA process consists in material hardening during SPD at the expense of supersaturated solid solution decomposition as a result of interaction of impurity and alloying atoms with mobile dislocations. DA should occur faster than during conventional thermomechanical treatments due to activation of diffusion processes. The experiments demonstrated that alongside with UFG structure formation DA significantly improved electrical conductivity and strength properties of alloys of the Al-Mg-Si system [3-5]. However, the mechanisms of second-phase nanosized particles formation during DA in the course of SPD have not been studied yet. At the same time managing the formation of nanosized phases can make it possible to more effectively influencing physical and mechanical and service properties of Al-based alloys.

X-ray diffraction (XRD) analysis is widely used to characterize structure of materials. The XRD analysis is an irreplaceable method applied for studies of DA, as it allows controlling all the changes in the microstructure (phase composition, dislocation density, lattice parameter, size of coherent scattering domains and microdistortions of a crystalline lattice) [6, 7].

This paper deals with the results of studies on UFG structure produced in Al-based alloy 6201 by 10 high pressure torsion rotations in the temperature range from 130 °C to 230 °C. The aim is to establish the influence of the size and distribution of particles of the strengthening phase in the volume of Al matrix on its strength, ductility and electrical conductivity.

2. Experimental procedure
Al-based alloy 6201 was used as material to study DA. The chemical composition of the alloy was Mg: 0.6-0.9 wt.%, Si – 0.5-0.9 wt.%, Fe ≤ 0.5 wt.%, Cu ≤ 0.1 wt.% Zn ≤ 0.1 wt.% Cr ≤ 0.03%, Mn ≤ 0.03 wt.%. The material was supplied by Ludinovocable. In order to fabricate a UFG structure the initial Al-based alloy was subjected to HPT with a number of rotations equal to 10. The HPT was conducted at 130 °C, 180 °C, 200 °C and 230 °C, as according to the TEM data active DA is observed in the mentioned range of temperatures.

XRD analysis was conducted using Bruker D8 Discover diffractometer, equipped with Goebel mirror and secondary collimator. Unfiltered copper radiation was used to reveal peaks of secondary phases on an X-ray pattern. X-ray measurements were performed at a voltage 40 kV and a current 40 mA.
The wavelength $\lambda_{\text{K}a1}=1.54060$ Å was used for calculations. The general view of X-ray patterns was taken with a scanning step of 0.05° and exposure time in every point equal to 5 seconds in the range of 2θ angles from 20° to 155°. Precise measurements of the chosen X-ray peaks were performed with a step of 0.02° and collection time of 4 seconds/point. The quantitative phase analysis, evaluation of the lattice parameter $a$, sizes of coherent scattering domains (CSD) $d$, mean-square microdistortions $\langle \varepsilon^2 \rangle$ were fulfilled using PDXL software (www.rigaku.com). A Rigaku Ultima IV diffractometer with a small-angle scattering system was used to measure the size and distribution of particles of the strengthening phase in the Al matrix volume. Cu $K\alpha$ radiation was used for the measurements. The beam path between the studied sample and the detector was evaluated. The investigations were done in the 2θ angle range from 0.08° to 1.4° with exposure time equal to 5 seconds with a step of 0.002°. Small-angle XRD patterns were processed using “Nano-Solver” software (www.rigaku.com). The investigation of electric conductivity will be conducted at room temperature by an eddy-current method using a VE-27NC device.

3. Results and their discussion

Four states of the Al-based alloy are shown on the chosen part of the X-ray pattern (Fig. 1). One can identify the strongest X-ray peaks of Cu $K\alpha$ radiation and less intensive peaks of Cu $K\beta$ and Cu $L\alpha$ radiation. These peaks, corresponding to Al, are strongly widened and almost blend in the scattering diffusion background. Increase of the HPT temperature leads to the narrowing of the considered X-ray peaks (Fig. 1), accompanied with decreasing of full width at half maximum (FWHM) for peaks (111) and (200), presented in Table 1. Besides, low-intensity peaks are observed on X-ray patterns. These peaks are related to $\text{Mg}_2\text{Si}$ with hcp lattice ($c/a=1.128$) as the results of qualitative phase analysis showed. Basing on the TEM studies, authors demonstrated [3-5] that globular-shaped $\text{Mg}_2\text{Si}$ particles with a size 20-40 nm formed as a result of dynamic aging are dispersed precipitates of the strengthening phase. It was mentioned that the content of the $\text{Mg}_2\text{Si}$ had a strong influence on the strength, ductility and electric conductivity.

The quantitative phase analysis showed that the volume fraction of $\text{Mg}_2\text{Si}$ in the Al matrix did not change monotonously (Table 1.). X-ray phase analysis conducted by RIR technique showed that when the HPT temperature increased from 130 °C to 200 °C, the volume fraction of the Mg$_2$Si phase grew from 1.36% to 1.57%. Further increase of the temperature up to 230 °C results in saturation of the fraction of the considered phase to 1.59%. At the same time other microstructural characteristics change monotonously, when the HPT temperature increases. For example, the lattice parameter $a$
quickly achieves saturation ($a=4.05009\pm0.00008$), when the HPT temperature reaches 200 °C. This value of the lattice parameter is very close to that typical of coarse-crystalline Al ($a=4.049$ Å) [8].

The latter testifies to the fact that the Al matrix became free of impurities as a result of dynamic aging. The results of electrical conductivity measurements showed that this value increased significantly. Thus, the electrical conductivity in the state after HPT at 200 °C increased 1.07 times as compared to the state after HPT at 130 °C.

Table 1. 6201 alloy parameters after treatment

| State       | FWHM  | FWHM  | Volume   | $a$, Å  | IACS, % | $<\varepsilon^2>$, | CSD,  |
|-------------|-------|-------|----------|---------|---------|-------------------|-------|
|             | (111), deg. | (200), deg. | fraction of Mg$_2$Si, % |         |         | %             | nm    |
| HPT at 130 °C | 0.122(2)   | 0.1218(15)   | 1.36     | 4.05124(7) | 55.7    | 0.034         | 66.6  |
| HPT at 180 °C | 0.118(2)   | 0.1177(16)   | 1.42     | 4.05115(7) | 58.1    | 0.027         | 68.4  |
| HPT at 200 °C | 0.111(2)   | 0.1108(14)   | 1.57     | 4.05009(8) | 59.9    | 0.023         | 74.6  |
| HPT at 230 °C | 0.107(2)   | 0.1055(14)   | 1.59     | 4.04998(8) | 60.1    | 0.017         | 77.1  |
On the other hand, microdistortions of the crystalline lattice $\langle \varepsilon^2 \rangle$ reduce from 0.034% to 0.017%, and the coherent scattering domain size connected with the average grain size increases from 67 nm to 77 nm as a result of HPT temperature increase. The mentioned changes of the XRD parameters also reflect the changes in mechanical properties. Thus, in [9] increase of HPT temperature from 130 °C to 230 °C leads to reduction of the ultimate tensile strength from 412 MPa to 275 MPa, and the ductility enhances from 4.9 % to 19.1 %. It should be noted that in the initial coarse crystalline state the ultimate tensile strength is 95 MPa, and the ductility is 20.4%. Thus, by comparing the XRD parameters and mechanical properties, one should expect that the state after HPT at 200 °C is optimal from the point of view of combination of electrical conductivity and mechanical properties.

Fig. 2 displays an X-ray pattern obtained on a diffractometer with a small-angle scattering system. XRD patterns were exposed through X-ray transmission.

\[ I(q) = |F(q)|^2 S(q) \]

**Fig. 2. Part of the SAXS pattern of Al alloy 6201 in different structural states.**

Computer modeling within the approach was used to analyze X-ray patterns taken in the areas of low-angle reflections [10]. In particular the dependence of intensity of reflected X-ray quanta was determined as

\[ I(q) = |F(q)|^2 S(q) \]
where the value \( F(q) \) stands for the shape and size of particles, and \( S(q) \) – the parameter responsible for the so-called structure factor responsible for similarity between the particles and considering the contribution of exposure parameters in a diffraction pattern, \( q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \) - the scattering vector.

Such parameters of Mg\(_2\)Si particles as atomic density, mass absorption coefficient were used for modeling. The shape was taken as a sphere according to the TEM results [3-4]. The computer modeling of the specified X-ray patterns enabled stating the size and distribution of Mg\(_2\)Si particles in the Al matrix in different structural states (Fig. 3).

![Particle size Analysis](image)

![Particle size Distribution/Vol%(Vol%)](image)

**Fig. 3.** Experimental and simulated SAXS patterns (a), size and distribution of Mg\(_2\)Si particles in the Al matrix (b). High pressure torsion at 180 °C.

As the modeling results showed the average size of Mg\(_2\)Si particles was (18±4) nm at 130 °C. When the HPT temperature increased up to 180 °C, the particle size grew up to 28±6 nm, and at 200 °C and 230 °C they enhanced up to (38±4) nm and (51±8) nm respectively.

**Conclusions**

The XRD technique has enabled for the first time establishing the quantitative characteristics of the structure in Al alloy 6201. It is shown that activation of dynamic aging takes place during SPD temperature increase, which is confirmed by enhancement of the volume fraction of the Mg\(_2\)Si second phase and the alloy crystalline lattice parameter tendency to the values typical of pure
aluminum. The small-angle diffraction technique enabled for the first time measuring the size and distribution of Mg$_2$Si particles in the Al matrix. When the HPT temperature increases, the average size of particles and the distance between their centroids grow.

Acknowledgements

The research has been conducted under the financial support provided by RFBR within the project № 14-03-00943_a. The X-ray studies were fulfilled at the XRD Center of Saint-Petersburg State University. The authors gratefully acknowledge the Russian Ministry for Education and Science for the financial support of this study: Contract No. 14.B25.31.0017 of June 28, 2013.

References

[1] Valiev R, Islamgaliev R, Alexandrov I 2000 Progress in Materials Science 45 pp 103-189.
[2] Valiev R, Langdon T 2006 Progress in Materials Science 51 pp 881-981.
[3] Sabirov I, Murashkin M, Valiev R 2013 Materials Science & Engineering A560 pp 1–24.
[4] Bobruk E, Murashkin M, Kazykhanov V and Valiev R 2012 Rev. Adv. Mater. Sci. 31 pp 109-115.
[5] Murashkin M, Sabirov I, Kazykhanov V, Bobruk E, Dubravina A, Valiev R 2013 J. Mater. Sci. 48 pp 4501–4509.
[6] Ungár T 2001 Mat. Sci. Eng. A309 pp 14-22.
[7] Alexandrov I and Valiev R 1996 Philosophical Magazine B 73 pp 861-872.
[8] Swanson, Tatge Natl. Bur. Stand. (U.S.), Circ. 539, I11, 1953.
[9] Valiev M, Murashkin M, Sabirov I 2014 Scripta Materialia 76 pp 13–16.
[10] Omote K, Ito Y and Kawamura S 2003 Appl. Phys. Lett. 82 pp 544-546.