Influence of additional severe plastic deformation at elevated temperatures on microstructure and physical-mechanical properties of ultrafine grained Al-0.4Zr alloy

T A Latynina, M Yu Murashkin, R Z Valiev and T S Orlova

1ITMO University, 49 Kronverkskiy pr., St. Petersburg 197101, Russia
2St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg 199034, Russia
3Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 K. Marx str., Ufa 450000, Russia
4Ioffe Institute, 26 Politekhnicheskaya str., St. Petersburg 194021, Russia

E-mail: t.latynina13@yandex.ru

Abstract. The effect of high pressure torsion (HPT) at room temperature and subsequent HPT at elevated temperatures on the microstructure, mechanical and electrical properties of the Al-0.4Zr alloy has been investigated. It has been shown that the HPT treatment of the alloy with an ultrafine grained structure at elevated temperatures led to a drastic increase in strength, which is accompanied by an increase in conductivity. Experimental values and theoretical estimations of the yield stress and electrical resistivity at 77 K are compared. Possible reasons for the observed strengthening effect are discussed.

1. Introduction

For electrotechnical alloys, which are used for power transmission lines, it is especially important to combine high values of electrical conductivity and strength for operation at elevated temperatures of 150-200 °C [1]. Nowadays, Al-based alloys with 0.1-0.4 wt.% Zr are considered promising materials to meet these requirements [1]. However, Al-Zr alloys have low strength, hence increasing their strength while keeping a high level of heat resistance and conductivity is a challenge. Methods of severe plastic deformation (SPD) are efficient to drastically increase mechanical properties of different metals and alloys due to the formation of an ultrafine grained (UFG) structure and the introduction of an enhanced defect density in the crystal lattice. By using a two-stage processing by SPD, first at room temperature (RT) and then at an elevated temperature, a good combination of strength (365 MPa) and conductivity (58.4% IACS – International Annealed Copper Standard) has been achieved for Al-Mg-Si alloys due to the grain refinement and the nanoscale precipitate formation [2]. But secondary phase nanoparticles in this alloy did not provide any reasonable thermal stability of the strength. In this paper, the influence of two-stage processing by high pressure torsion (HPT) on microstructure and physical-mechanical properties of the Al-0.4 wt.% Zr alloy has been investigated.

2. Materials and experimental procedures

The initial Al-0.4 wt.% Zr alloy was processed by the method of combined casting and rolling [3], and then subjected to HPT under a hydrostatic pressure of 6 GPa at room temperature (RT) to 10
revolutions (\(n=10\)) (hereinafter referred to as HPT_RT state). As a result of such treatment, samples were obtained in the shape of discs with a diameter of 20 mm and a thickness of approximately 1.2 mm. The true strain at a distance of 5 mm from the center of the disc was \(\varepsilon \approx 6.6\). Then, some HPT_RT samples were subjected to additional HPT processing at elevated temperatures, \(T_{\text{HPT}}=230\) and 280 °C, to \(n=1, 5, 10\) and 20. The microstructure of the alloy in all the studied states was examined by X-ray diffraction (XRD), electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM), as described in [4]. EBSD studies were performed using a Zeiss Merlin scanning electron microscope with a scan step of 0.2 µm on an area containing at least 2000 grains. To perform mechanical tests, blade-shaped samples with a gauge width of 2 mm and a gauge length of 6 mm were cut from HPT-processed disks at a distance of 5 mm from the disk center [5]. Uniaxial tensile tests were performed on a Shimadzu AG-XD Plus machine with a constant strain rate of \(5 \times 10^{-4} \text{s}^{-1}\) [5]. Vickers microhardness \((H_V)\) was measured using a Shimadzu HMV-G tester with a load of 1 N during 15 s, the indentations being performed along the gauge [6]. Electrical resistivity \((\rho)\) was measured by a standard four probe technique at 77 K for comparison with theoretical estimates and at 293 K for calculation of conductivity \(\omega\) at RT \((\omega=1/\rho_{293})\), more detailed data of these measurements are provided in [6].

3. Results and discussion
The effect of a substantial increase in the strength of UFG Al-0.4 wt.% Zr (preliminary treated by HPT at RT) by its short-term annealing in the temperature range of 90-280 °C was earlier revealed [7]. Therefore, in the present work, temperatures of 230 and 280 °C were chosen for the second HPT treatment. Figure 1 shows the dependences of microhardness and resistivity at 77 K for the UFG Al-0.4Zr alloy on the number of HPT revolutions at 230 and 280 °C. For further investigation, the states after HPT at 230 °C with \(n=10\) and at 280 °C with \(n=5\) (indicated in figure 1 by a dashed circle and hereinafter referred to as HPT_RT-HPT_230_10 and HPT_RT-HPT_280_5, respectively) were chosen, which demonstrated a significant increase in microhardness and a decrease in electrical resistivity compared to the HPT_RT state.

**Figure 1.** Dependences of microhardness \(H_V\) (a) and electrical resistivity \(\rho_{77}^{\text{exp}}\) at 77 K (b) for the Al-0.4Zr alloy preliminary treated by HPT at RT on the number of revolutions of additional HPT at 230 °C (1) and 280 °C (2). The values of \(H_V\) and \(\rho_{77}^{\text{exp}}\) for the initial state are also presented.

Quantitative changes in mechanical properties (microhardness \(H_V\), conventional yield stress \(\sigma_{0.2}^{\text{exp}}\), ultimate tensile strength \(\sigma_{UTS}\) and relative elongation to failure \(\delta\), electrical resistivity at 77 K \(\rho_{77}\)
and electrical conductivity at RT ($\omega = 1/\rho_{\text{RT}}$) for the alloy due to HPT at RT, and then at elevated temperatures are given in table 1. HPT processing at RT leads to a significant increase in strength, however, the electrical conductivity significantly decreases. As a result of the additional HPT processing at 230 and 280 °C, the strength properties further drastically increased ($\sigma_{0.2}$ by 89 and 65%, $\sigma_{\text{UTS}}$ by 43 and 21%, respectively), and $\omega$ at RT also significantly increased (by 3.5 and 8% IACS).

| State                        | $\sigma_{0.2}^{\text{exp}}$ (MPa) | $\sigma_{0.2}^{\text{th}}$ (MPa) | $\sigma_{\text{UTS}}$ (MPa) | $\delta$ (%) | $\omega$ (% IACS) | $\rho_{\text{RT}}^{\text{exp}}$ (n$\Omega$·m) | $\rho_{\text{RT}}^{\text{th}}$ (n$\Omega$·m) |
|-----------------------------|----------------------------------|----------------------------------|----------------------------|--------------|-------------------|---------------------------------------------|---------------------------------------------|
| Initial                     | 120±2                            | 108                              | 130±1                      | 25.9±0.2     | 50.7              | 9.5±0.1                                     | 9.5                                         |
| HPT_RT                      | 140±1                            | 137                              | 192±1                      | 23.2±0.6     | 43.9              | 13.5±0.1                                    | 9.9                                         |
| HPT_RT-HPT_230_10           | 264±4                            | 110*                             | 276±5                      | 7.7±0.6      | 47.3              | 10.0±0.4                                    | -                                           |
| HPT_RT-HPT_280_5            | 229±2                            | 104*                             | 232±2                      | 15.7±0.9     | 52.0              | 7.9±0.5                                     | -                                           |

* Estimations were made without contribution to strengthening from the precipitates.

To reveal the microstructural changes, which are responsible for the obtained changes in properties, the microstructural characterization was performed. The results of EBSD (average grain size $d_{\text{av}}$, fraction of high angle grain boundaries (HAGBs) $f_{\geq 15}$, average misorientation angle $\theta_{\text{av}}$) and XRD (the lattice parameter $a$, the size of coherent-scattering domains $D_{\text{XRD}}$, the elastic microdistortion level $<\varepsilon^2>^{1/2}$ and the dislocation density $L_{\text{dis}}$) analyses are shown in table 2. The dislocation density strongly increases after HPT at RT. The subsequent HPT at 230 and 280 °C causes its decrease by approximately 4 and 7.5 times respectively. The EBSD investigation of the microstructure shows that HPT at RT results in a refinement of the grain structure, an equiaxed grain structure is formed with an average grain size $d_{\text{av}}=840$ nm (figure 2a and table 2). Most grain boundaries (GBs) are HAGBs with misorientations $\geq 15^\circ$.

![Figure 2](image_url)

**Figure 2.** Typical EBSD maps and TEM images with diffraction patterns obtained for the HPT_RT (a, d), HPT_RT-HPT_230_10 (b, e) and HPT_RT-HPT_280_5 states (c, f).

TEM studies did not reveal the formation of secondary phases (figure 2d). Additional deformation at elevated temperatures only slightly increases $d_{\text{av}}$, $f_{\geq 15}$ and $\theta_{\text{av}}$ (table 2) and mainly leads to dynamic aging – the formation of nanosized Al$_3$Zr precipitates (figure 2e, f), thereby reducing the
concentration of solute Zr atoms. The amount of precipitates is not high, it increases with HPT temperature growing (figure 2 e,f). The precipitates are non-uniformly distributed in the samples. A rough estimation of the average size of the precipitate from the TEM images gave the values of 18-19 nm for both states after HPT at elevated temperatures. TEM studies demonstrate that the grain interior is mostly free of dislocations in all the three states: HPT_RT and HPT_RT-HPT_230_10 and HPT_RT-HPT_280_5. Hence, a decrease in the $L_{dis}$ after the additional HPT at elevated temperatures is mainly related to the regions at and around GBs, which points to GB relaxation during HPT at elevated temperatures.

### Table 2. Microstructure parameters obtained by EBSD and XRD analysis for the Al-0.4Zr alloy

| State                  | EBSD       | XRD        |
|------------------------|------------|------------|
|                        | $d_{av}$ (nm) | $f_{>15}$ (%) | $\theta_{av}$ (°) | $a$ (Å) | $D_{XRD}$ (nm) | $\theta^{<,>1/2}$ (%) | $L_{dis}$ (m$^{-2}$) |
| Initial                | 1420±20    | 25         | 11.5          | 4.0514±0.00002 | 252±6 | 0.003±0.0001 | 1.4·10$^{12}$ |
| HPT_RT                 | 840±15     | 82         | 33.8          | 4.0515±0.00006 | 212±11 | 0.063±0.0006 | 3.6·10$^{13}$ |
| HPT_RT-HPT_230_10      | 920±15     | 88         | 36.2          | 4.0512±0.00003 | 483±6 | 0.036±0.0007 | 9.0·10$^{12}$ |
| HPT_RT-HPT_280_5       | 930±15     | 89         | 36.5          | 4.0514±0.00007 | 559±25 | 0.022±0.0002 | 4.8·10$^{13}$ |

The contributions from different electron scattering mechanisms to electrical resistivity at 77 K were estimated according to the Matthiessen's rule [8]:

$$\rho_{77}^{th} = \rho_{dis}^{pure} + L_{dis}\Delta\rho_{dis} + S_{GB}\Delta\rho_{GB}^{sol} + C_{Zr}^{sol}\Delta\rho_{Zr} + \Delta\rho^{pt},$$  

where $\rho_{dis}^{pure}$=2.7 nΩ·m [9] is the electric resistivity of single-crystalline defect-free aluminum, $\Delta\rho_{dis}$=2.7·10$^{-25}$ Ω·m$^3$ [10], $\Delta\rho_{GB}^{sol}$=2.6·10$^{-16}$ Ω·m$^2$ [10] are the contributions from unit densities of dislocations and grain boundaries in Al, respectively, $\Delta\rho_{Zr}^{sol}$=15.8 nΩ·m/wt.% [11] is the contribution from a unit concentration of Zr in the solid solution, $L_{dis}$ (m$^2$) is the dislocation density, $S_{GB}$ (m$^3$) is the bulk density of GBs, $C_{Zr}^{sol}$ (wt.%) is the concentration of solute Zr; $\Delta\rho^{pt}$ – the contribution originating from the secondary phase precipitates. The estimated ($\rho_{77}^{th}$) and experimental ($\rho_{77}^{exp}$) values are compared in table 1. HPT at RT led to a substantial increase in $\rho_{77}^{exp}$ caused by changes in the microstructure. The estimation showed that the contribution from the $L_{dis}$ change was negligibly small (~9.4·10$^{-3}$ nΩ·m), the Zr concentration in the Al matrix did not change, the increase in the GB density gives the resistivity increase ~0.38 nΩ·m, which is an order of magnitude smaller than the change in $\rho_{77}^{exp}$ (table 1). It is reasonable to suggest that the specific resistivity of GBs ($\Delta\rho_{GB}^{G}$) in the Al-0.4Zr alloy subjected to HPT at RT is higher than that in coarse-grained Al. This could be caused by two reasons: the formation of mainly HAGBs in non-equilibrium states similarly to the case of commercially pure Al [4] and the possible segregation of impurities at GBs. Additional HPT at 230 and 280 °C results in a substantial decrease in $\Delta\rho_{GB}^{G}$ by ~3.5 and 5.5 nΩ·m, respectively. This is mainly due to the reduction of the Zr content in the Al matrix. An additional decrease in electrical resistivity can be caused by the GB relaxation to a more equilibrium state, however, if the grain-boundary segregation process occurs during additional HPT, this will contribute to the electrical resistivity.

Contributions from different mechanisms to the total strengthening, which is their superposition, were also estimated in the same way as was done in [6]:

$$\sigma_{0.2}^{th} = \sigma_0 + \sigma_{GB} + \sigma_{dis} + \sigma_{Or} + \sigma_{sol},$$  

where $\sigma_0$, $\sigma_{GB}$, $\sigma_{dis}$, $\sigma_{Or}$, and $\sigma_{sol}$ are the contributions from dislocations, grain boundaries, stress, and solute, respectively.
where $\sigma_0=10$ MPa is the Peierls-Nabarro stress of the Al crystal lattice, $\sigma_{\text{gb}}$ is grain boundary strengthening, $\sigma_{\text{dis}}$ is strain hardening due to dislocations, $\sigma_{\text{or}}$ is precipitate strengthening by the Orowan mechanism and $\sigma_{\text{sol}}$ is solid-solution hardening.

The experimental ($\sigma_{0.2}^{\text{exp}}$) and theoretical ($\sigma_{0.2}^{\text{th}}$) values of $\sigma_{0.2}$ are in good agreement for the states before and after HPT at RT (table 1). However, for the states after additional HPT at elevated temperatures the values of $\sigma_{0.2}^{\text{exp}}$ are dramatically higher than the estimated values of $\sigma_{0.2}^{\text{th}}$ (table 1), which points to the operation of the additional strengthening mechanism caused by microstructural changes during the second stage of HPT. The amount of nano-sized precipitates is small, and their distributions throughout the samples are non-uniform, hence, the Orowan strengthening could not be efficient. According to a simple estimation, if even the Orowan strengthening takes place, the maximum possible contribution of the Orowan strengthening (if the whole amount of Zr was in the precipitates of 18 nm in size) will not exceed 80 MPa, whereas the obtained difference between $\sigma_{0.2}^{\text{exp}}$ and $\sigma_{0.2}^{\text{th}}$ equals to 154 and 114 MPa for HPT_RT-HPT_230_10 and HPT_RT-HPT_280_5 states, respectively. Then one may conclude that similar to the case of commercially pure Al [5], the achieved dramatic strengthening of the Al-0.4Zr alloy after additional HPT at an elevated temperature is most probably caused by the rearrangement of the HAGBs structure, which is accompanied by a decrease in the dislocation density in them. In addition, in the Al-0.4Zr alloy, the influence of possible GB segregation cannot be excluded [12,13] and needs to be checked in further investigations.

4. Conclusions
A drastic increase in strength was found after additional HPT at elevated temperatures for the Al-0.4Zr alloy, which was preliminary subjected to HPT at RT. The strength enhancement was accompanied by an increase in electrical conductivity. The analysis of different hardening mechanisms to the total strengthening indicates that HPT at elevated temperatures caused an additional strengthening mechanism, which is most likely associated with the rearrangement of the HAGBs structure.

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References
[1] Belyi D I 2012 Cables and Wires 1 8 (in Russian)
[2] Valiev R Z, Murashkin M Yu and Sabirov I 2014 Scr. Mater. 76 13
[3] Machine for the continuous casting of metal rods 1953 US Patent 2659948 A
[4] Orlova T S, Mavlyutov A M, Bondarenko A S, Kasatkin I A, Murashkin M Yu and Valiev R Z 2016 Phil. Mag. 96 2429
[5] Mavlyutov A M, Latynina T A, Murashkin M Yu, Valiev R Z and Orlova T S 2017 Phys. Sol. State 59 1970
[6] Orlova T S, Mavlyutov A M, Latynina T A, Ubyivov E V, Murashkin M Yu, Schneider R, Gerthsen D and Valiev R Z 2018 Rev. Adv. Mater. Sci. 55 92
[7] Latynina T A, Mavlyutov A M, Murashkin M Yu, Valiev R Z and Orlova T S 2018 Collection of Materials of XXIII Petersburg Readings on the Problems of Strength (St. Petersburg: VVM Publishing) p 130 (in Russian)
[8] Rossiter P L 1991 The Electrical Resistivity of Metals and Alloys (Cambridge, Cambridge University Press)
[9] ASM Handbook 1990 Properties and Selection: Nonferrous Alloys and Special-Purpose Materials (ASM International)
[10] Karolik A S and Luchvich A A 1994 J. Phys. Cond. Matter 6 873
[11] Kutner F and Lang G 1976 Aluminium 52 322
[12] Murashkin M Yu, Sabirov I, Medvedev A E, Enikeev N A, Lefèvre W, Valiev R Z and Sauvage X 2016 Materials & Design 90 433
[13] Sauvage X, Enikeev N, Valiev R, Nasedkina Y and Murashkin M 2014 Acta Mater. 72 125