SYNTHESIS OF AL_3ZR PRECIPITATES IN ALUMINIUM AND ITS ALLOY BY MEANS OF COMPRESSION PLASMA FLOWS

N.N. Cherenda[1], N.V. Bibik[1], J.V. Amyaga[1], V.V. Uglov[1],
V.M. Astashynski[2], A.M. Kuzmitski[2]

[1]Belarusian State University, Minsk, Belarus, bibiknv@mail.ru
[2]Institute of Physics of the National Academy of Sciences of Belarus, Minsk, Belarus
ast@imaph.bas-net.by

Introduction

Small additions of zirconium can significantly improve mechanical properties of aluminium alloys due to the formation of an intermetallic compound Al_3Zr. This compound has a stable tetragonal $D0_{23}$ structure and a metastable cubic $L1_2$ structure [1]. However, in [2] it was shown that metastable Al_3Zr with a tetragonal $D0_{22}$ structure could also be formed. A high cooling rate during crystallization of the alloy and the presence of alloying elements stabilizing $D0_{22}$ structure can be the main reasons for its formation.

The previous investigations have shown that compression plasma flows (CPF) can be effectively used for mixing of a "coating/substrate" system, thus leading to alloying of a substrate at a depth of tens of micrometers with atoms of coatings [3-4]. This approach is used in the present work to form composite surface layers containing Al_3Zr precipitates in aluminum and an aluminum based alloy.

Experimental

Pure aluminum and silumin (12,9 Si; 3,0 Mg; 0,7 Cu; 0,4 Ni; 0,1 Fe; at. %, Al - balance) samples were the object of investigations. Zr coating with the thickness of 2,5 μm was formed on the samples surface by cathodic arc vapor deposition with the following process parameters: arc current of 100 A, bias voltage of -120 V, deposition time of 10 min. CPF treatment of the coating-substrate system was carried out in the discharge magnetoplasma compressor of compact geometry. The experiments were performed in a ''residual gas'' mode in which the vacuum chamber was filled with nitrogen up to the preset pressure of 400 Pa. The plasma flow parameters were as follows: pulse duration ~100 μs, flow velocity $(5 \div 6) \cdot 10^6$ cm/s and electron concentration $(4 \div 7)\ 10^{17}$ cm^{-3}. By means of changing the distance between the cathode and the sample from 10 cm to 16 cm the energy density absorbed by the surface (Q) varied in the range of 4-19 J/cm^2. Treatment was carried out by a series of three pulses.

The phase composition of the samples was investigated by X-ray diffraction (XRD) in Bragg-Brentano geometry using monochromatic Cu Kα radiation. The surface morphology of the samples was studied by scanning electron microscopy (SEM) using a LEO1455VP device. Microhardness was tested by means of a Wilson Instruments 402MVD hardness testing instrument with Vickers indentor.

Results and discussion

Impact of plasma pulses with the "coating/substrate" system leads to melting of the coating and substrate surface layer, liquid-phase mixing and subsequent crystallization in conditions of a fast cooling rate (10^5 - 10^7 K/s). Treatment of pure aluminum with pre-coated zirconium with Q=4 J/cm^2 resulted in the formation of intermetallic Al_3Zr according to the XRD data (Fig. 1). The formed phase can be attributed either to a tetragonal $D0_{23}$ or cubic $L1_2$ structure because diffraction peaks corresponding to these types of structures are close enough. The increase of the absorbed energy density resulted in the reduction of the diffraction peaks intensity of Al_3Zr because of zirconium concentration per unit volume decrease which occurred due to the increase of the alloying layer thickness.

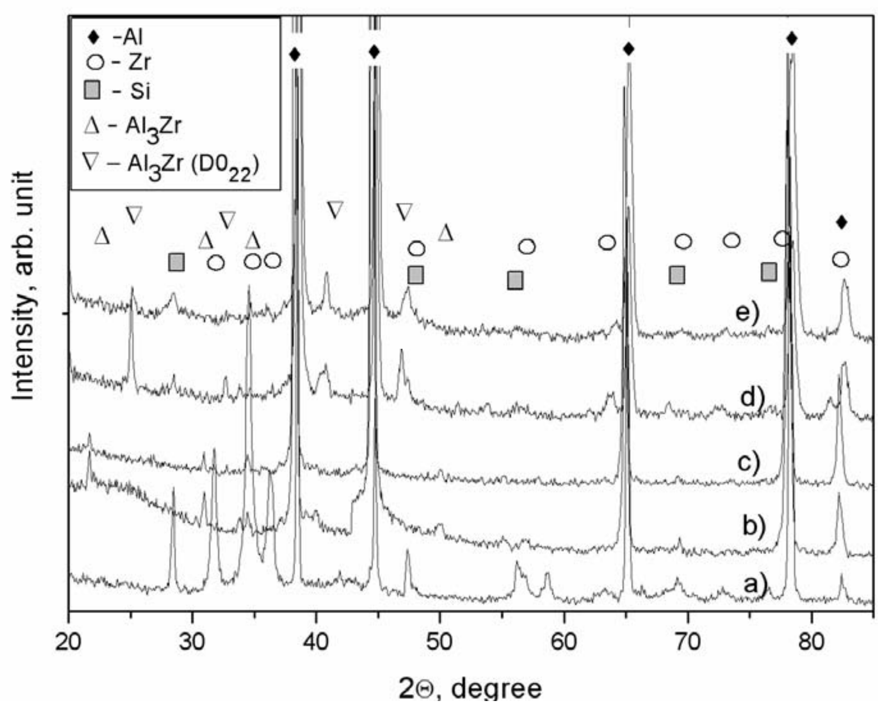


Fig. 1. XRD patterns of untreated Zr/silumin sample (a) and samples of Zr/silumin (b,c) and Zr/aluminum (d,e) treated by CPF with Q=4 J/cm^2 (b, d) and Q=19 J/cm^2 (c, e).

Plasma treatment of the Zr/silumin system led to formation of metastable phase Al_3Zr with a tetragonal $D0_{22}$ structure with the lattice parameters of a=0,389 nm and c=0,885 nm. $D0_{22}$ Al_3Zr formation can be explained by the presence of silicon atoms in the samples stabilizing this type of structure [2].

The samples treated with a lower absorbed energy density did not have a uniform distribution of zirconium along the surface (Fig. 2). The areas enriched with zirconium were characterized by the formation of intermetallic compounds with the size of 0,5-1,0 μm (Fig. 2c). The concentration of zirconium in the areas was 9,7 ± 2,1 at.%. The areas with a smaller zirconium concentration possessed a cellular structure with the cells size of 0,5 μm. The boundaries of cells were enriched with heavy alloying elements (Zr, Ni, Cu, Fe). The concentration of zirconium in this area was 2,2 ± 0,5 at.%, which is greater than the zirconium solubility limit in aluminum in equilibrium conditions. Zirconium atoms could take part in the formation of a supersaturated aluminum solid solution.

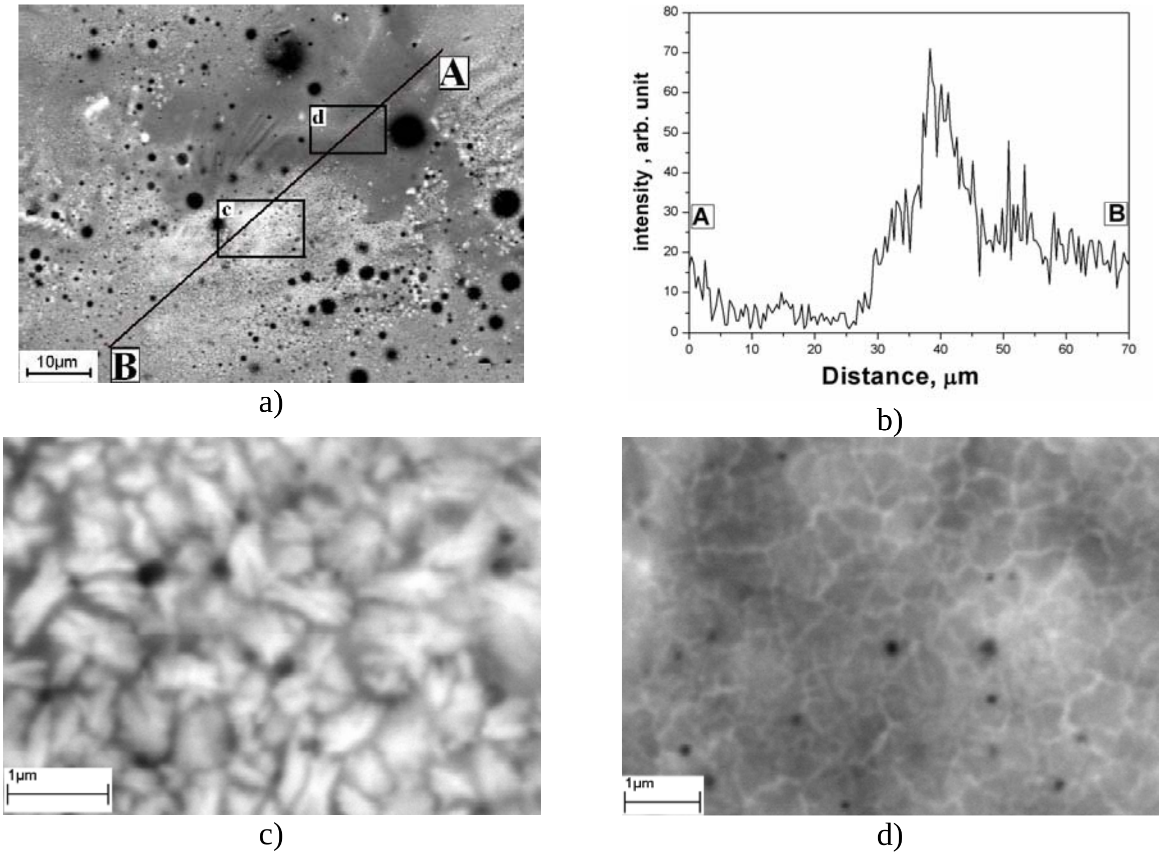
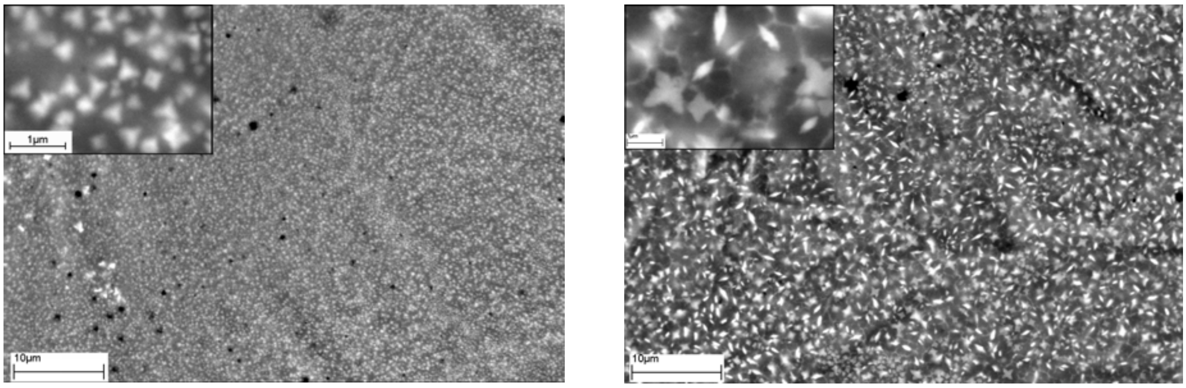


Fig. 2. Surface morphology of the Zr/silumin samples treated by CPF with Q=4 J/cm^2 (a, c and d) and the distribution of the characteristic X-ray intensity of zirconium (b) along the marked line.

The increase of the absorbed energy density led to the increase of melt existence time thus resulting in more uniform zirconium distribution. The findings showed that plasma impact with the samples pre-coated with Zr resulted in the formation of a composite layer containing a supersaturated aluminium solid solution and disperse intermetallic phases on the basis of Al_3Zr. The form and size of Al_3Zr precipitates depended on the samples composition. Treatment of Zr/Al samples with Q=19 J/cm^2 resulted in the formation of Al_3Zr inclusions ($D0_{23}$ or $L1_2$ structure) with a characteristic size of 0.1-0.3 μm (Fig 3a). Treatment of Zr/silumin samples with Q=13-19 J/cm^2 led to synthesis of plate-shaped precipitates ($D0_{22}$ structure) with lateral dimension ~ 1 μm (Fig 3b).



a) b)

Fig. 3. Surface morphology of aluminum (a) and silumin (b) samples precoated with Zr after treatment by CPF with Q=19 J/cm^2 and 13 J/cm^2, respectively.

Structural and phase transformations in the surface layer resulted in improvement of microhardness of the samples. It was found that microhardness of the plasma-mixed Zr/Al and Zr/silumin systems exceeded hardness of the initial untreated samples 2,8 and 1,5 times, respectively.

Conclusions

The findings showed that treatment of aluminum and silumin samples pre-coated with Zr by compression plasma flows led to the formation of a modified composite layer containing a supersaturated aluminum solid solution and intermetallic inclusions of Al_3Zr. In the surface layer of pure aluminum Al_3Zr inclusions had $D0_{23}$ or $L1_2$ structure while in silumin - $D0_{22}$ structure. The synthesized composite layer possessed a high hardness value (up to 2,8 GPa in silumin).

References

1. **Gua J.Q., Ohtera K.** Materials Letters 27 (1996) 343-347.

2. **Dheepa Srinivasan, Chatoopadhyay K.** Materials Science and Engineering. A304-306 (2001) 534-539

3. **Uglov V.V., Anishchik V.M., Cherenda N.N., Stalmashonak A.K., Astashinski V.M., Kuzmickii A.M., Punko A.V.** High Technology Plasma Processes 8 (2004) 605-615.

4. **Uglov V.V., Cherenda N.N., Anishchik V.M., Stalmashonak A.K., Astashinski V.M., Mishchuk A.A.** Vacuum 81 (2007) 1341–1344