EAST EUROPEAN JOURNAL OF PHYSICS. 4. 135-139 (2021)
DOI: 10.26565/2312-4334-2021-4-17 ISSN 2312-4334

POSITIVE DEVIATION OF THE HALL-PETCH RELATIONSHIP FOR ALUMINUM CONDENSATES ALLOYED WITH IRON†

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Received July 23, 2021; revised November 17, 2021; accepted November 19, 2021

The structure and strength properties of vacuum aluminum condensates alloyed with iron in the concentration range of 0.1 – 3.2 at. % is studied in the paper. It is shown that up to a concentration of about 2 at. % Fe, the grain size decreases, the strength properties increase and the lattice parameter values of these objects remain unchanged. It is found that at an iron concentration of up to ~ 2 at. % its atoms are concentrated in the grain boundaries of the aluminum matrix metal in the form of grain boundary segregation. At high concentrations, the structure of condensates is a supersaturated solution of iron in the FCC crystal lattice of aluminum. Highly dispersed $Al_{13}Fe_4$ intermetallic compounds are present at the grain boundaries and within the volume of grains. It has been found that the Hall-Petch coefficient for one-component aluminum condensates is 0.04 MPa·m$^{1/2}$, which is typical for this metal. For Al-Fe condensates, a positive deviation from the Hall-Petch dependence is observed and the coefficient k increases to 0.4 MPa·m$^{1/2}$ for a structure with grain boundary segregations and to 0.14 MPa·m$^{1/2}$ for condensates containing intermetallic compounds. The obtained experimental results are explained by the different structural-phase state of the grain boundaries of the aluminum matrix.
Keywords: Grain boundary segregation, vacuum condensate, intermetallic compound, Al-Fe, grain size.
PACS: 61.66.Dk, 64.75.Op, 68.35.Fx, 68.55.Ln, 81.05.Ni, 81.10.Fq, 81.15.Kk

The level of strength properties of nanostructured metals is mainly determined by grain boundary hardening. Its value depends on the grain size and the state of the grain boundaries. A large number of theoretical and experimental studies are devoted to the problem of dispersing the grain structure of metallic materials. Less attention has been paid to the study of the chemical composition and structure of grain boundaries. First of all, this was due to the problems of testing grain boundaries at the atomic level. As a result, it became possible to purposefully influence the properties of grain boundaries by varying their chemical composition and structural-phase state, which can lead to a dramatic increase in various properties of nanostructured metals. For example, alloying of aluminum films, foils, or coatings obtained by physical vapor deposition in vacuum (PVD-technology) with iron allows reducing the grain size of these materials to nanoscale dimension, increasing their strength properties and recrystallization temperature. As a result, these objects are widely used in the aviation and aerospace industries, primarily in parts exposed to thermal effects [1-3]. At the same time, the physical mechanisms of the modifying effect of iron on aluminum are currently controversial and insufficiently studied.

In this regard, the purpose of this work is to study the effect of iron concentration on the structure and strength properties of vacuum Al-Fe condensates.

LITERATURE REVIEW

The grain boundary hardening of metallic materials is described by the Hall-Petch strengthening [4, 5], which for the yield strength has the following form

$$\sigma_y = \sigma_0 + kd^{-1/2}$$

where σ_y is the yield strength, σ_0 is the resistance to the motion of dislocations in a single crystal, k is the Hall-Petch coefficient, d is the grain size.

The authors of various studies use the Hall-Petch equation to describe various strength properties: tensile strength, yield strength, hardness, however, the most correct is to use the yield stress in order to avoid veiling effects associated with strain hardening, brittleness, plasticity, etc. [6].

For the majority of one-component metals and alloys in a wide range of grain sizes from several to hundreds of micrometers, the constancy of the values of the exponent (-1/2) and the k value is maintained [7]. At the same time, in a number of studies [8, 9] facts of deviation from dependence (1) are noted both due to the change in the value of k and the exponent from -1/2 to -1. To explain these experimental results, many theoretical models have been proposed [6], among which the most famous are the following. 1. Compositional model of the grain structure, suggesting different properties of grain boundaries and intragranular volume, predicting changes in the exponent depending on grain size [10]. 2. Dislocation mechanisms, which involve changes in the value of k due to various ways of transferring deformation through the grain boundary [11]. 3. Models providing various options for the transition of translational

† ***Cite as:*** E. Lutsenko, A. Zubkov, M. Zhadko, and E. Zozulya, East. Eur. J. Phys. **4**, 135 (2021), https://doi.org/10.26565/2312-4334-2021-4-17

deformation mechanisms to rotational [12]. For nanostructured aluminum and its alloys, these circumstances are enhanced due to a significant spread in the values of the Hall-Petch coefficient, even for a single-component metal, the value of which is in the range of 0.02 – 0.29 MPa·m$^{1/2}$, depending on the production methods [11, 13], the method of the grain size measurement [6, 13], chemical purity of metal [14], etc. The authors of some studies have noted both positive [7] and negative deviations from the Hall-Petch dependence [15]. It should be noted that there is no unambiguous interpretation of the observed experimental results in the available literature [6]. An important feature of these studies is the underestimation or ignoring of impurities, alloying elements or modifiers, which can radically change the structural-phase state of grain boundaries. Suffice it to note that the content of the second component constituting ~ 1·10^{-4} at. % in the volume of a matrix metal with a grain size of about 100 μm is capable of covering the entire area of grain boundaries with a monoatomic adsorption layer [16]. This state of the adsorption layers provides for the formation of strong interatomic bonds between the segregating substance and the matrix metal. As a result, the cohesive strength of grain boundaries increases, the tendency to brittle intercrystalline fracture increases and other properties improve. Depending on the combination of physical and mechanical properties of the constituent components of the metal, such grain boundary segregation can significantly change the strength and other properties of metals in general [17, 18].

RESEARCH METHODOLOGY

The objects of study were Al and Al-Fe condensates up to 50 μm thick, obtained by the PVD method, by evaporation of the constituent components from different sources and subsequent condensation of a mixture of their vapors on a non-orienting substrate in vacuum. The substrate temperature was 200–250°C. The concentration of alloying elements was monitored by the X-ray spectral method. Mechanical tests were carried out at room temperature in the active tension mode with a strain rate of 0.36 mm/min on a TIRATEST-2300 setup. The samples had the following geometry: width – 3 mm, thickness – 30 μm, length – 30 mm. Thus, the test conditions and geometric dimensions of these objects correspond to the methodology developed in [19]. The structure of the condensates was studied by X-ray diffractometry, light and transmission microscopy using DRON-3M, OptikaM XDS-3Met, and JEM-2100 devices, respectively.

RESULTS

Fig. 1, 2, 3 shows the concentration dependences of the grain size (d), lattice parameter (a) and yield strength (σ_y) of the aluminum matrix on the iron content in the condensates. It can be seen that up to a concentration of about 2 at. %, the value of d decreases and the value of a remains. It should be noted that the observed increased solubility of Fe is characteristic of such objects and exceeds the equilibrium solubility at room temperature, which is 0.025 at.% [20].

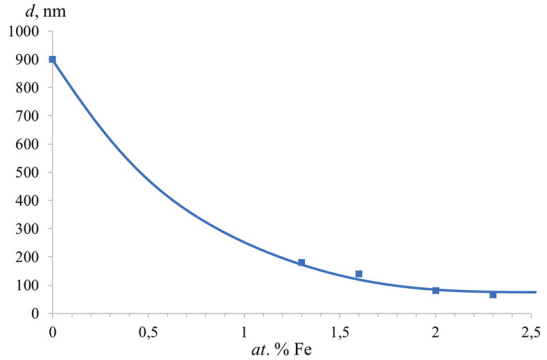


Figure 1. Dependence of the grain size of aluminum on the concentration of Fe.

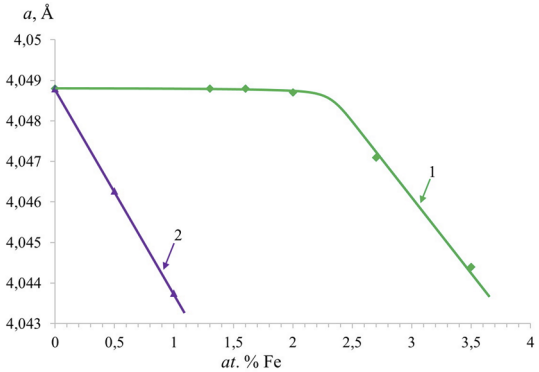


Figure 2. Dependence of the crystal lattice parameter of aluminum on the concentration of Fe
1 – lattice parameter, 2 – Vegard's law.

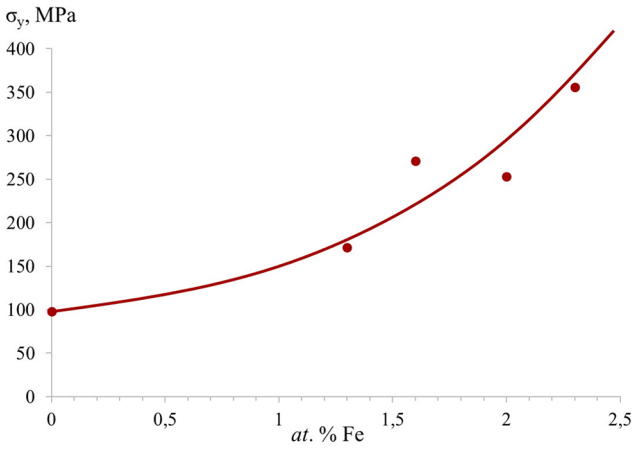
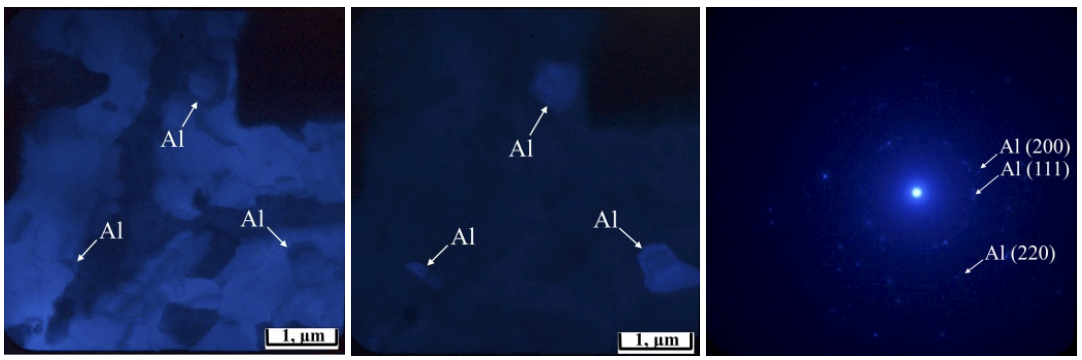


Figure 3. Dependence of the yield strength of aluminum on the concentration of Fe.

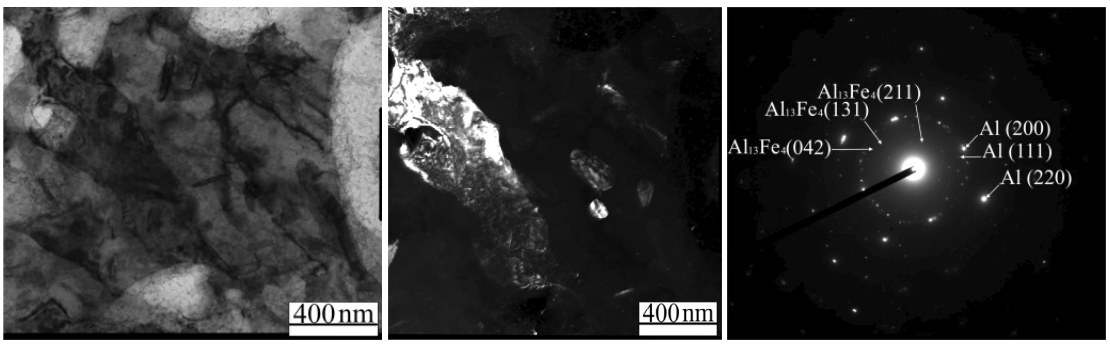
The electron diffraction patterns contain only diffraction reflections belonging to the FCC lattice of aluminum (Fig. 4). With a further increase in the iron content, the diffraction reflections of the intermetallic compound with the stoichiometric composition $Al_{13}Fe_4$ appear in the electron diffraction patterns (Fig. 5).



a b c

Figure 4. Electron-microscopic images of aluminum condensate
a – bright field image, b – dark field image, c – electron diffraction pattern.

A decrease in the lattice period of the FCC aluminum matrix is also observed, which indicates the formation of a supersaturated solution of iron in aluminum (Fig. 2).



a b c

Figure 5. Electron-microscopic images of Al-3.2 at. % Fe condensate
a – bright field image, b – dark field image, c – electron diffraction pattern.

In the entire range of concentrations, an increase in the yield stress occurs (Fig. 3). It should be noted that the yield stress of unalloyed condensates is an order of magnitude higher than that of single-component aluminum obtained by crystallization from a melt, which strongly depends on the chemical purity of the matrix metal. For example, for aluminum A99 the yield stress is 10 MPa, for A8 is 20 MPa, and for A6 is 30 MPa [20].

These experimental results and the data of [17] allow us to conclude that in the concentration range of 0.1 - 2 at. % iron atoms are located in grain boundaries in the form of grain boundary segregation. At such iron content within the

grain, the structure is uniform, the grain size changes due to the blocking effect of monoatomic segregation of iron atoms during the condensate formation. According to the Seah theory [21], such grain boundary segregation of Fe in aluminum should increase the cohesive strength of grain boundaries. With a further increase in the iron content (over 2 at. %), a fundamental change in the structural state of the condensates occurs. The aluminum matrix is a supersaturated solution of iron in the FCC lattice of aluminum, as evidenced by a decrease in the lattice parameter (Fig. 2). Simultaneously, first at the grain boundaries, and then in the volume of the aluminum matrix, the formation of highly dispersed intermetallic compounds $Al_{13}Fe_4$ occurs (Fig. 5) [17].

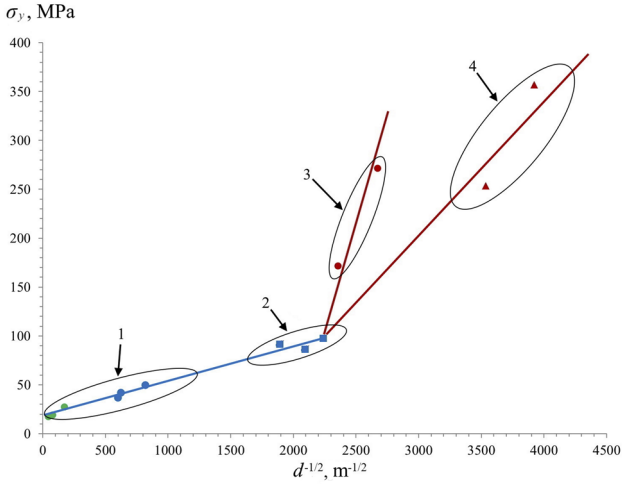


Figure 6. Hall-Petch dependences: 1 – [7, 22], 2 – Al condensates, 3 – Al-Fe condensates (up to 2 at. % Fe), 4 – Al-Fe condensates (over 2 at. % Fe).

Thus, there are three concentration regions with the following structural states: one-component condensates; two-component single-phase condensates with an iron concentration of up to 2 at. %, the grain boundaries of which contain segregation of iron, presumably in an atomic form, the so-called 2D structures; and finally condensates containing more than 2 at. % Fe, having a different intragranular structure and state of grain boundaries. These distinctive circumstances are reflected in the Hall-Petch dependence shown in Fig. 6. The value of the Hall-Petch coefficient determined for one-component aluminum is 0.04 MPa·m$^{1/2}$, which is in good agreement with the literature data for high-purity aluminum obtained by crystallization from the melt. For condensates containing grain-boundary monolayer segregation, the Hall-Petch coefficient increases significantly to 0.4 MPa m$^{1/2}$ (plot 3, Fig. 6). A further increase in the iron concentration leads to a decrease in the slope of the Hall-Petch dependence and the value of the coefficient k is 0.14 MPa m$^{1/2}$. Thus, in the concentration range from 0.1 to 3.2 at. % Al-Fe condensates have different states of grain boundaries and intragranular volume, resulting in a change in the value of k. Grain-boundary segregation of iron in the form of monoatomic layers increase the value of the k from 0.04 MPa·m$^{1/2}$ to 0.4 MPa·m$^{1/2}$, that is, there are positive deviations from the Hall-Petch dependence. It should be noted that a similar effect was observed by the authors of [8], who paid no attention and did not study the possibility of the formation of grain boundary segregation of iron.

Intermetallic compounds formed during condensation of a vapor mixture of aluminum and iron in the grain boundaries lead to the destruction of the adsorption layers and, as a result, the value of k decreases. For these objects, the level of strength properties is determined by the total action of solid solution, dispersion and grain boundary hardening.

CONCLUSIONS

1. The structure and strength properties of one-component and alloyed with iron aluminum condensates have been studied.

2. It was found that for one-component aluminum condensates the Hall-Petch dependence is observed. The Hall-Petch coefficient is 0.04 MPa m$^{1/2}$. This is in good agreement with the literature data obtained for high-purity aluminum crystallized from the melt.

3. Alloying with iron up to 2 at. % of aluminum condensates leads to a positive deviation from the Hall-Petch dependence and increases the Hall-Petch coefficient to 0.4 MPa·m$^{1/2}$.

4. Al-Fe condensates containing more than 2 at. % Fe, which is located within the grain boundaries of the matrix metal in the form of intermetallic compounds, have a Hall-Petch coefficient of 0.14 MPa·m$^{1/2}$. This value is higher than the analogous value for single-component aluminum, but less in comparison with condensates with grain-boundary segregations of iron in the form of monolayers.

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ПОЗИТИВНЕ ВІДХИЛЕННЯ СПІВНОШЕННЯ ХОЛЛА-ПЕТЧА ДЛЯ КОНДЕНСАТУ АЛЮМІНІЮ, ЛЕГОВАНОГО ЗАЛІЗОМ

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В роботі вивчено структуру і характеристики міцності вакуумних конденсатів алюмінію, легованих залізом в діапазоні концентрацій 0,1 – 3,2 ат. %. Показано, що до концентрації приблизно 2 ат. % заліза відбувається зниження розміру зерна, підвищуються характеристики міцності і зберігається значення періоду кристалічної решітки даних об'єктів. Встановлено, що при вмісті заліза до ~ 2 ат. % Його атоми зосереджені в границях зерен матричного металу – алюмінію у вигляді зернограничних сегрегацій. При великих концентраціях структура конденсатів є пересиченим розчином заліза в ГЦК кристалічній решітці алюмінію. На границях і всередині об'єму зерен присутні високодисперсні інтерметалліди $Al_{13}Fe_4$. Виявлено, що для однокомпонентних конденсатів алюмінію виконується залежність Холла-Петча. Величина коефіцієнта Холла-Петча становить 0,05 МПа·м$^{1/2}$, яка характерна для цього металу. Для конденсатів Al-Fe спостерігається позитивне відхилення від залежності Холла-Петча і коефіцієнт k збільшується до 0,4 МПа·м$^{1/2}$ для структури з зернограничною сегрегацією і до 0,14 МПа·м$^{1/2}$ для конденсатів, які містять інтерметалліди. Отримані експериментальні результати пояснюються різним структурно-фазовим станом границь зерен алюмінієвої матриці.

Ключові слова: Зернограничная сегрегація, вакуумний конденсат, інтерметалід, Al-Fe, розмір зерна