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INTRODUCTION OF SCANDIUM, ZIRCONIUM AND HAFNIUM INTO ALUMINUM ALLOYS. DISPERSION HARDENING OF INTERMETALLIC COMPOUNDS WITH NANODIMENSIONAL PARTICLES

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The state of intermetallic compounds Al_3Sc, Al_3Zr, Al_3Hf and slag shots introduced by high-temperature exchange reactions of corresponding fluoride-chloride salts with liquid aluminum has been studied. The particle size and segregation direction during centrifugation and filtration of melt have been examined by microscopy and local X-ray analysis methods. The dispersoids formed during decomposition of solid solution are strong phase reinforcers.

Keywords: Aluminum, scandium, zirconium, hafnium, alloy, intermetallic compounds (IMC), slag, inclusions, microstructure.

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1. Introduction

Small additions of scandium, as well as zirconium and hafnium to aluminum and aluminum-based alloys abruptly increase their strength characteristics. For example, introduction of 0.3%Sc into AMg5 alloy (Al–5%Mg) increases the tensile strength of annealed sheets from 260 to 400 MPa. The structure of scandium-free alloy remains completely recrystallized, while that of scandium-containing alloy is nonrecrystallized [1]. In the presence of zirconium, the modifying effect of master alloy manifests itself at lower scandium concentrations. Aluminum grain nuclei in the presence of zirconium are $Al_3(Sc_xZr_{1-x})$ particles, in which zirconium substitutes for 50% scandium, the lattice type (LI_2) remaining the same [2,3]. Modification of cast alloy Al–Zn–Cu–Mg with a master alloy (0.48%Sc+Zr) leads to grain size refinement to 23 μm [4]. At the same time, the dendritic grain structure disappears. Al_3Sc, Al_3Zr and $Al_3(Sc_{1-x}Zr_x)$ dispersoids formed by secondary segregation have dispersity of <10 nm and are coherent with the aluminum matrix. Hafnium in aluminum alloys has a stronger refining effect than zirconium, which is explained by its more pronounced metallic properties; additionally, hafnium is a good absorber of thermal neutrons. Addition of 1% hafnium in aluminum leads to the production of aluminum superalloys with metal grain size of 40–50 nm. Here, not only alloy reinforcement, but also considerable relative elongation is achieved, the shear and torsional strength is increased and the vibration resistance is improved [5].

Production of light alloys containing expensive rare metals is economically more sound by their synthesis using high-temperature exchange reactions between fluoride-chloride salt melts containing one or several compounds of rare metals and liquid aluminum or its alloys with magnesium [6–8]. With this method of alloy production, liquid aluminum was found to contain inclusions of intermetallic compounds (IMC) and slag shots. Usually, the methods for removal of inclusions include kiln deposition followed by filtration through glass net with a high content of alumina or passing through a layer of coke, carbon, flux etc. The materials used for such refining of melts often become clogged up and are washed out by metal, whereas the inclusions pass through the partitions. Some refractory materials are able to contaminate the filtered metal. The presence of large inclusions leads to sheet stock and stamping rejects, as well as to reduction of the durability of articles because of crack formation and failures, especially under vibrational loads. In this work, we examine the behavior of some solid inclusions during centrifugation.

The performed laboratory-scale experimental studies allowed us to establish that aluminum alloys with required content of alloying additions (scandium, zirconium, hafnium), taken in different ratios, can be produced by the injection method. This method provides uniform distribution of doping metals in the whole bulk of the alloy, the duration of the operation decreases in comparison with other methods of alloying, small amounts of available salts are used, and some impurities are removed into the slag.

2. Analysis of inclusions in aluminum alloys

2.1. Sedimentation theory

In accordance with the Stokes law, during centrifugation of aluminum melt with rotating velocity f until its hardening, the IMC and slag particles move to the bottom or to the top of the crucible with rate υ determined by equation:

$$\upsilon = \frac{2\pi^2}{9} \cdot \frac{d^2 f^2 (\rho_{Al} - \rho_p)\alpha r}{\eta} \tag{1}$$

where η is the aluminum viscosity coefficient; d is the spherical diameter; r is the distance between the rotation axis and particle; ρ_{Al} and ρ_p are the densities of Al and particle; and α is the relative velocity of particle with respect to the velocity of spherical particle of equal volume (α is a constant value depending on the particle profile; for round particles including disk-shaped and rod-like forms, the values of α lie within 0.8–1.0; for film forms, for example, thin oxide films, the values of α can range in the region of 0.25–0.35 depending on the film orientation).

The spherical diameter d of finest inclusions moving to the bottom of the crucible in the melt is determined by equation [9]:

$$d = \left[\frac{45\eta \cdot \ln\left(R_b/R_g\right)}{8\pi^2 \alpha \cdot f^2 \left(\rho_{Al} - \rho_p\right)\left(t - \frac{7}{12}t_1\right)} \right]^{1/2} , \tag{2}$$

where f is the rotating velocity; t is the period of time when the melt is in the liquid state during centrifugation; R_b is the distance from the rotation axis to the top of the melt in the crucible; R_g is the distance from the rotation axis to the bottom of the melt in the crucible; η is the viscosity coefficient of liquid at starting temperature; and $t = t_1$.

2.2. Experiment conditions

Aluminum alloy ingots were melted, heated to 850°C and centrifuged in cylindrical alundum crucibles with chamotte thermal isolation using an S–6UHL4.2 centrifuge. Centrifugation was carried out with rotating velocity from 600 to 3000 rev/min until hardening of metal. Depending on the alloy mass, the time before crystallization varied from 6 to 10 min (Fig. 1).

The duration of crystallization of samples until complete hardening was 5–8 min. The samples' liquid state time was enough for large particles to settle on the crucible bottom (Fig. 2).

The oxide agglomerates, of lower density than that of the melt, move towards the rotation axis. The samples were divided along the cylindrical axis. The inclusions were analyzed using microscopic, chemical and X-ray phase methods. The centrifuge and samples parameters are as follows: the distance from the rotation axis to the melt upper level in the crucible is R_b=120–150 mm, the same to the crucible bottom is $R_g = 200$ mm, the crucible diameter is $\varnothing_{id} = 40$ mm and the viscosity of aluminum is $\eta_{Al} = 3 \div 5$ Poise.

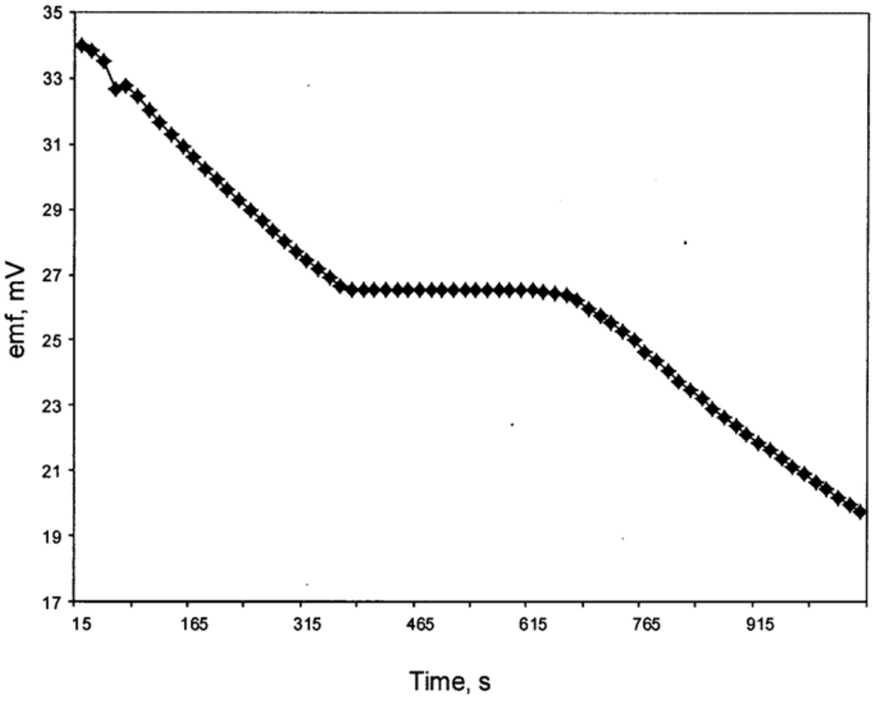

FIG. 1. Crystallization diagram

2.3. Results and discussion

The Al_3Sc phase in aluminum is formed by a peritectic reaction at 1427°C. It has a cubic lattice with four atoms in the cell and the parameter $a = 4.106 \times 10^{-10}$ m and is isomorphous with aluminum with $a = 4.100 \times 10^{-10}$ m [10]. The density of isolated crystals determined by the bottle method is 3.00 g/cm^3.

The compound Al_3Zr in aluminum is melted congruently at 1577°C. At 660.3°C, in the aluminum-rich region, a peritectic reaction takes place, during which Al_3Zr interacts with the melt containing 0.03 at.% Zr and forms an α_{Al}-solid solution. The metastable modification

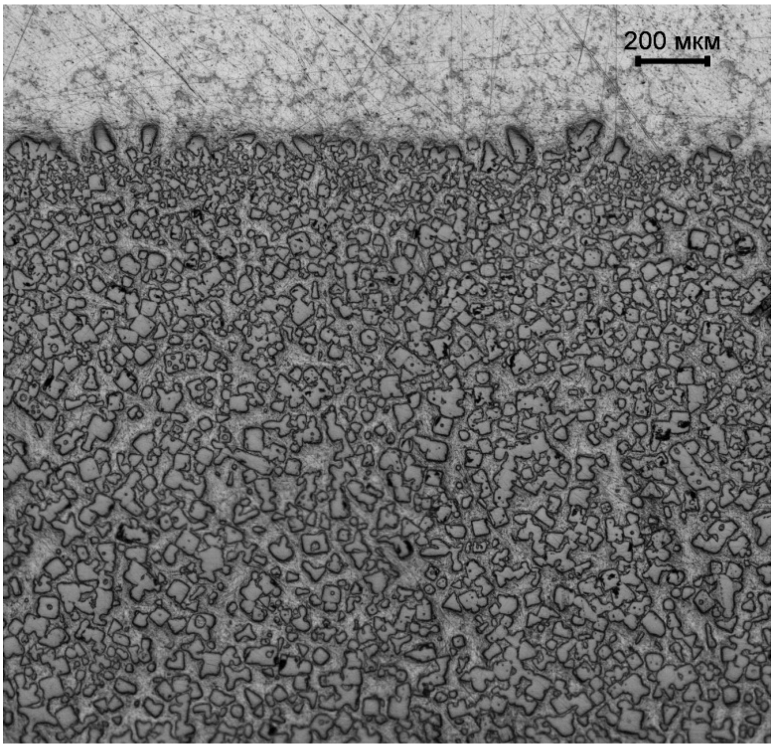

FIG. 2. Large-size IMC particles on the boundary of bottom sediment

of the phase, formed by annealing from supersaturated aluminum solid solution, has a cubic Cu_2Au-type crystal structure with lattice parameters $a = 4.050 \times 10^{-10}$ m [10]. The density of isolated crystals was also determined by the bottle method to be 4.10 g/cm^3.

The compound Al_3Hf is melted congruently at 1590°C, and at 662°C, as a result of a peritectic reaction with the melt containing 0.073 at.% Hf, it forms an α_{Al}-solid solution having the maximum solubility at this temperature, 1.2 mass %. The lattice parameter increases to the maximum, $a = 4.051 \times 10^{-10}$ m [11, 12]. The density of these crystals determined by the bottle method is 6.18 g/cm^3.

Additions of transition metals to the binary alloy Al–2%Sc appreciably affect the strengthening value. The best strengthening during decomposition of the solid solution in the experimental alloy is achieved when the Sc and Zr contents are equal. Additions of Hf produce an analogous effect in character, but of slightly lower magnitude [13].

Depending on the initial content of metals introduced into aluminum and on the alloy cooling rates, the Al_3Me crystals have different sizes and shapes. Without centrifugation (settling) of the alloy containing 10 mass% Sc, the microstructure of the sediment is characterized by round 10–140 μm particles and needles of size to several millimeters. The inclusions of Al_3Sc particles in the ingot volume without centrifugation are predominately 5 μm in size. Large needles are not observed over the sediment from the melt containing 4–5% Sc. In the ingot volume, the particles are under 5 μm in size. At the initial Sc concentration of 2.0%, the major part of the particles in the ingot volume have a rectangular shape and a size of less than 4 μm, while 5–7 μm particles are not more than 10%. Centrifugation of Al–2%Sc master alloy at a rate of 1000 rev/min results in deposition of large IMC particles on the bottom, whereas the nanoparticles of size < 400 nm remain in the bulk. The microstructure of 1.8–2.0% Sc-containing alloy ingots, with crystallization in cast-iron molds and a melt cooling rate from 800°C of minimum 100°C/s, is represented by crystals and plates under 5 μm in size. The composition of α_{Al}-solid solution and IMC particle inclusions was examined with the use of quantitative MS analysis. The content of elements (mass %) was determined for the upper boundary of the bottom layer particles: Al–62.57 and Sc–32.43 (Al_3Sc), and a lower content of scandium was found for the dark particles and for the center of the particles: 16.62–17.78 and 20.77–24.05, respectively. Depending on the temperature, the scandium content of scandium (mass %) in the α_{Al}-solid solution is 0.38 (660°C), 0.22 (600°C), 0.07 (500°C) and 0.03 (400°C).

As a result of centrifugation of zirconium-rich (10 mass %) aluminum alloy, 50 μm and smaller particles are observed in the microstructure of the bottom phase, and on the boundary with the bottom phase also needles of 200 μm and less in length are found. As distinct from Al–Sc ingots, slag inclusions in the form of black shots are seen in the bottom sediment layer. Without centrifugation, the IMC particles in the ingot volume are chiefly 5–15 μm in size. Depending on the initial content of zirconium in the aluminum melt, the dissolution of large-sized particles at 750°C is slow. At 0.3 mass % Zr content, at least 30 min are required for their dissolution at this temperature. After centrifugation of the melt, the content of zirconium in the α_{Al}-solid solution was found to be 0.28–0.30 mass %. The intermetallic particles contain 36.18–56.38 mass % of Zr. Iron (0.07–0.08) and silicon impurities (0.55–1.63), as well as an enhanced zirconium content (0.33 mass %) are found in some samples of α_{Al}-solid solution of the master alloy. In the aluminum angle of the phase diagram Al–Zr–Sc, the only nonvariant peritectic transformation is found at a temperature of 659°C, $L + Al_3Zr \rightarrow (Al) + Al_3Sc$ [9].

For the initial concentration of 12 mass % Hf in aluminum, round particles of a maximum 60 μm in size are deposited on the bottom during centrifugation. At the initial concentration of 5 mass % Hf in the melt, no needle-shaped inclusions are found over the sediment. The size of IMC particles in the ingot volume did not exceed 2 μm. The bottom sediment, like for the alloys with zirconium, is found to contain round slag inclusions.

Thus, it was shown that depending on the initial concentration of alloying component (Sc, Zr, Hf), crystallization conditions and the presence of other alloying components, IMC of different forms are obtained and large IMC particles can be formed, which slowly dissolve at the temperature of master alloy introduction into the alloy.

3. Chemical alloying of aluminum and alloys based thereon

In the light of the above discussion, alloying of aluminum and aluminum-based alloys (both cast alloys and wrought alloys) using aluminothermic methods holds much promise. These methods can be used for introduction of refractory, scattered and rare metals into alloy and for improvement of properties (such as heat resistance, corrosion resistance, weldability, mechanical strength etc.). In particular, the case in point is alloying of aluminum with small additions of scandium, zirconium and hafnium. The application of aluminothermic methods for the production of master alloys and alloys by blowing (injection) through aluminum melt using a gas-powder suspension consisting of inert gas (argon Ar or carbon dioxide CO_2) and a ground salt mixture of sodium fluoride and potassium chloride with aluminum fluoride that contains oxides and fluorides of metals introduced into the alloy at 700–900°C is described in detail in Ref. [14]. Production of aluminum-scandium alloys in industrial kilns of KUMZ OJSC is described elsewhere [15].

The new method, developed by the authors, allows alloying of aluminum and aluminum-based alloys with scandium, zirconium and hafnium with the use of a salt composition consisting of a mixture of potassium chloride and potassium and aluminum fluorides (or only potassium, sodium and aluminum fluorides), which contains oxides of the corresponding metals introduced by injection into melted aluminum. During melting, the ground mixtures of these salts dissolve the oxides forming complex compounds, which easily interact with melted aluminum; for example, the application of a mixture of sodium and potassium fluorides can hold promise for dissolution of scandium oxide (Fig. 3).

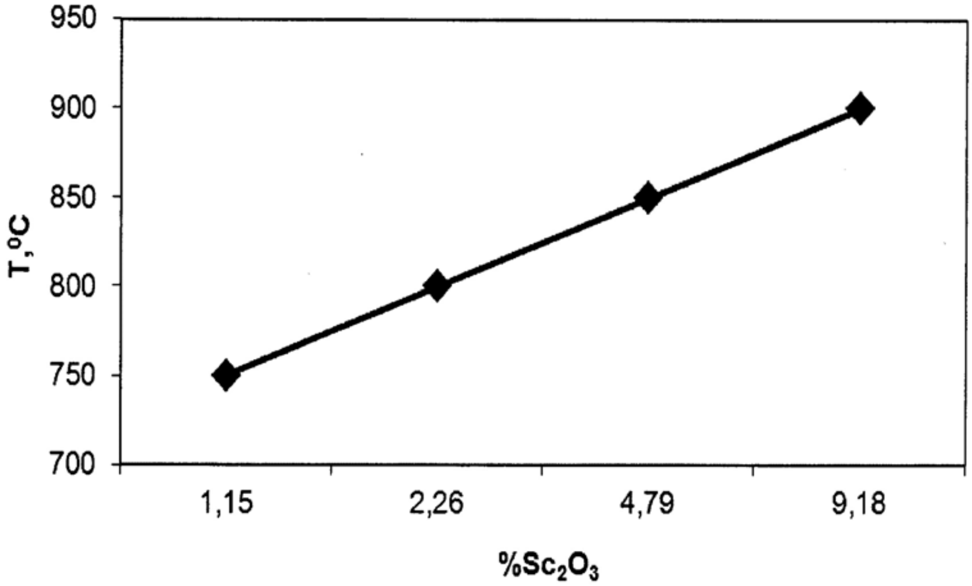

FIG. 3. The liquidus curve piece of a salt system with scandium oxide (0.4NaF + 0.6KF) – Sc_2O_3

From the X-ray phase analysis data presented in Fig. 4 it was established that during melting with sodium and potassium fluorides, scandium oxide is dissolved forming sodium dipotassium hexafluoroscandiate (scandium cryolite-elpasolite) K_2NaScF_6.

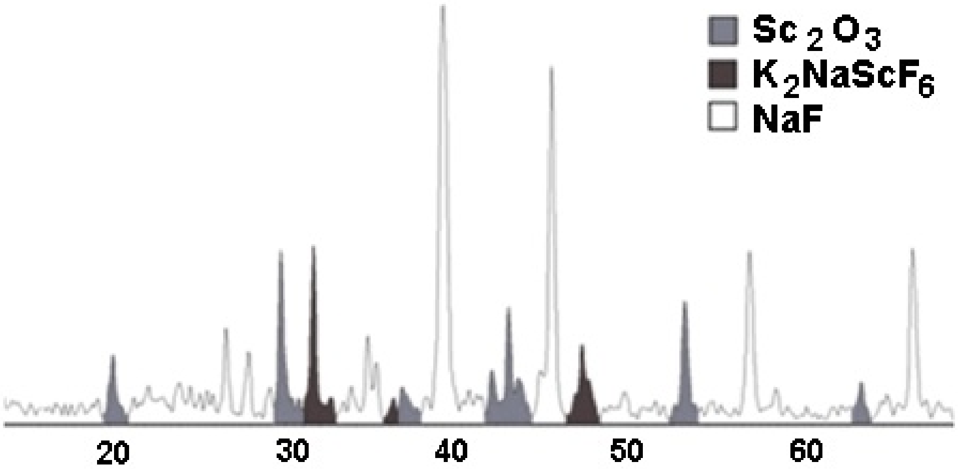

FIG. 4. The X-ray diffraction pattern of a salt system with scandium oxide (0.4NaF + 0.6KF) – Sc_2O_3

Alloying of aluminum with scandium, zirconium and hafnium allows new-generation alloys to be produced (for example, 1570, 1975 etc.). After blowing of aluminum melt with a gas-powder suspension, the slag is easily removed and the finished product can be poured into moulds if other alloying additions, for example lithium, are not introduced. The laboratory-scale experimental studies performed showed that the injection method can be used for obtaining aluminum alloys with required content of alloying additions (scandium, zirconium, hafnium) taken in different ratios. This method provides uniform distribution of doping metals in the whole bulk of the alloy, the duration of the operation decreases in comparison with other methods of alloying, small amounts of available salts are used, and some impurities are removed into slag. So, it is established experimentally that the content of sodium decreases by 15% (if a salt mixture without sodium fluoride is used), silicon – by 25% and copper – by almost 80%. In order to obtain a satisfactory ratio of dopants during complex alloying of aluminum, the concentrations of the compounds of introduced metals in the salt mixture should be maintained with allowance for the yield of alloying metals into the alloy at the temperature of the process. In case of deviation from the necessary concentration of salts of metals reduced by the aluminothermic method, the required ratios in the alloy cannot be attained.

The injection method is carried out in the following way:

– Preliminarily preparation of the salt mixture (50–60% KCl, 30-45% KF, 5–10% AlF_3): drying at 150°C, mixing, introduction of the calculated amount of compounds (oxides) of alloying addition (not more than 25% of the total mass of the mixture), grinding with simultaneous mixing and loading into the injection plant (Fig. 5). The reagents are taken in 5–20% excess.

– The necessary amount of alloying aluminum (or aluminum-based alloy) is melted in an L–9/11/B180 Nobertherm furnace to the temperature specified in the process instruction for a particular alloy, for example 750–800°C for pure aluminum.

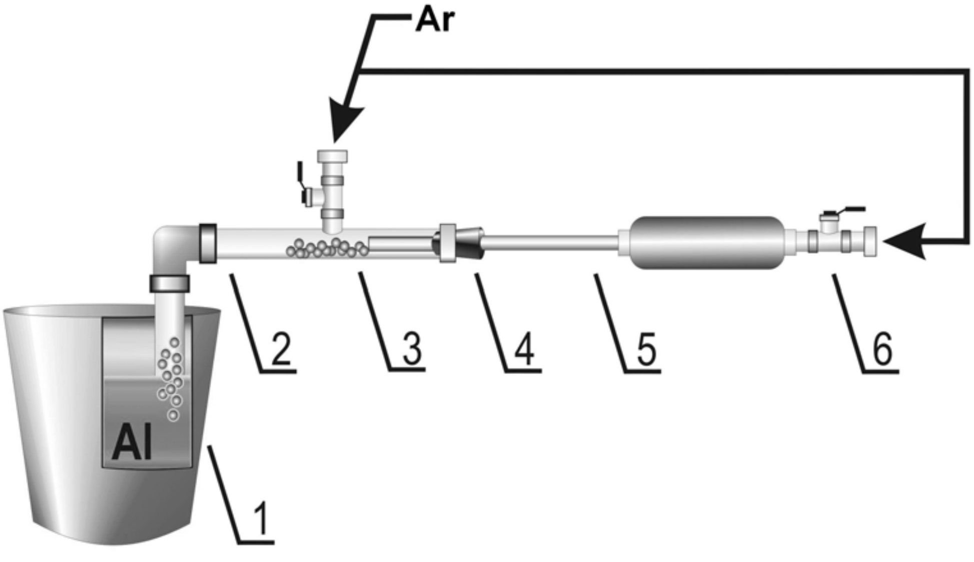

Fig. 5. The diagram of a plant for injection of powdered salts into liquid aluminum. 1 – crucible for aluminum; 2 – single-jet tuyere; 3 – powdered salts; 4 – plug; 5 – accelerating jet; 6 – pulse gate; CO_2 – shielding gas; Al – liquid aluminum

– The powder is injected into aluminum melt with the use of carbon dioxide until all salt mixture is consumed. Gas blowing is carried out for as many again as 1–5 min, after that, the slag is discharged and the metal is poured into a cast-iron mold.
– The content of alloying additions in aluminum is refined analytically in the Laboratory of physicochemical methods of analysis at the ISSC UB RAS using the atomic absorption spectroscopy method (plasma version) on a Perkin Elmer-503 Atomic absorption spectrometer.

The alloying component in the composition of powder mixture is introduced into the melt by blowing the mixture in the carrier gas jet through aluminum melt. The powdered mixture is composed of potassium fluoride, potassium chloride and aluminum fluoride, and the alloying elements are oxides of the corresponding metals taken in the ratio, mass %:
– potassium fluoride (KCl) – 50-60%,
– potassium chloride (KF) – 15-35%,
– aluminum fluoride (AlF_3) – 5-10%,
– oxide of introduced metal (a mixture of metal oxides) – 10-25%.

Carbon dioxide (CO_2) is used as a carrier gas; it is fed with a rate of 0.2–20 ndm^3/min under a pressure of 0.1 atm. The direct metallurgical yield of alloying components, both at individual and joint introduction of dopants, is more than 90%. Alloys with estimated content of alloying elements, from 0.3 to 0.6 mass %, are produced.

The decomposition of solid solutions with the formation of secondary dispersoids begins below 500°C. The eutectic temperature of the Al–Sc alloy is only 1°C lower than the melting point of aluminum and has a composition of 0.47% Sc (0.38 at.% Sc). The solubility of Sc in solid Al at the eutectic temperature is 0.34%, and at 600°C, it decreases to 0.23% [10]. The size of nucleus in the form of Al_3Sc particle is smaller than 1.8 μm, and Al_3Sc dispersoid formed by secondary segregation, as was already mentioned above, is < 10 nm in size and is completely coherent with the aluminum matrix, which further improves the mechanical properties.

When, besides scandium, cheaper modifying agents (zirconium and hafnium) are introduced into aluminum alloy, the structure of the formed IMC becomes more complicated, which appreciably affects the strength and other properties. According to the dependence proposed by Darken and Gurry [16] that the proximity of atomic radii and electronegativities of melted components promotes the formation of vast regions of solid solutions, it can be suggested that the mechanical properties (hardness) of light aluminum alloys are strengthened.

Examination of alloys containing individually Sc, Zr, Y and Hf or their mixtures and having different compositions shows that the microhardness of the produced materials increases when the element's atomic number and the complexity of the component composition lower (Fig. 6).

The results obtained can be used for predicting the properties after introduction of modifying agents into aluminum alloys. The microhardness of alloys containing Sc, Zr, Y and Hf increases as the element atomic number and the composition complexity lower.

4. Conclusions

The studies performed showed that depending upon the initial concentration of alloying component (Sc, Zr, Hf) and other conditions, IMC crystals of different shape are produced and large IMC particles can be formed, which dissolve slowly at the temperatures of master alloy introduction into the alloy. Segregation of inclusions into a small region of sediment is possible already at a centrifuge rotating velocity of 1000 rev/min. When zirconium and hafnium are introduced by high-temperature exchange reactions into the salt

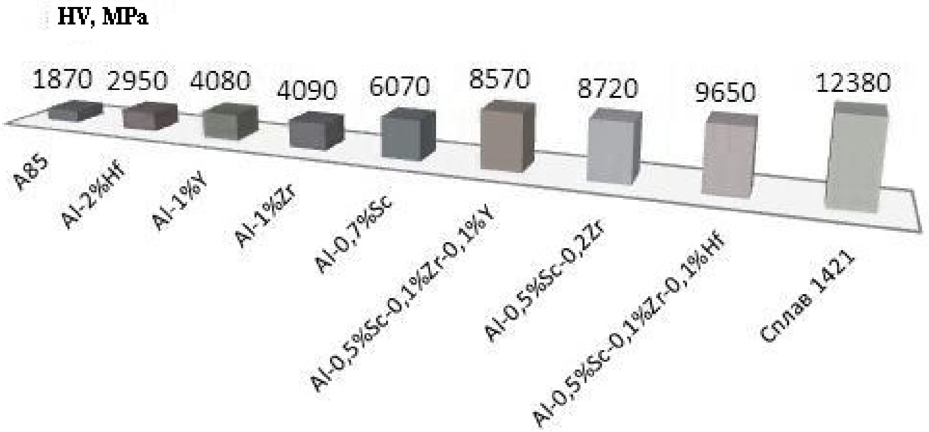

FIG. 6. The microhardness of alloys versus their composition

melts based on fluorides and chlorides of alkaline metals and the corresponding rare metal with aluminum, “heavy” slag shots can also deposit on the bottom. Primary removal of suspended impurities from aluminum alloy can be carried out in settling centrifuges; the diameter of finest inclusion particles removed from the solution is 400–500 nm. The centrifugation method can be used to analyze the particles in the melt and to determine the solubility of phases and the kinetics of particle size as functions of the melt temperature.

The introduction of alloying additions (scandium, zirconium, hafnium) into aluminum and aluminum-based alloys by injecting process powders into aluminum melt has the following advantages over other methods:

1. Cheap compounds (oxides) of alloying metals are used.
2. Low process temperatures.
3. Uniform distribution of dopants in the volume.
4. Easily accessible carbon dioxide is used for injection.
5. Complex alloying is possible.

Owing to segregation of secondary nano-sized IMC located on the grain boundary, at comparable concentrations, dispersion hardening of alloys is superior to solid-solution strengthening.

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