GENESIS OF ELEMENTS AT PRIMARY ALUMINUM PRODUCTION

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Abstract: *The characteristic of the elements present in the primary aluminum at electrolytic method of production is given. Based on elemental analysis of aluminum on regulated and unregulated impurities, with accordance of their initial content and effect on operational characteristics of cast billets, in this paper we describe groups of useful elements, neutral and harmful impurities at production of materials for functional purposes (sacrificial, composite, electrotechnical, etc.).*

KEYWORDS: *PRIMARY ALUMINUM, IMPURITIES, SACRIFICIAL ALLOYS, ANTIFRICTION COMPOSITE ALLOYS*

1. Introduction

Aluminum finds broad application as a base metal for functional and constructional alloys, such as sacrificial, antifriction, electrotechnical, etc. Functional alloys differ from other by design of properties at a stage of their creation, and achievement of set value of any special property which has crucial significance. For example, in sacrificial alloys used for protection of metal constructions from corrosion this property is stationary electrochemical potential [1]. For composite alloys depending on the purpose of material is possible to achieve various operational characteristics, such as wear resistance, heat resistance, thermal expansion coefficient, thermal conductivity, etc. [2]. For electrotechnical materials critical characteristics are electrical conductivity and specific electrical resistance. Regardless of the destination of manufactured products, at the achievement of predetermined characteristics of alloys for functional purpose on the aluminum base content of regulated and unregulated impurities plays an important role.

In grades of primary aluminum used for production of aluminum alloys the content of iron, silicon, copper, manganese, magnesium, zinc and other impurities is limited [3]. Raw aluminum produced by electrolysis of cryolite-alumina melts contains substantial amounts of metal impurities, non-metallic inclusions and gases. Sources of presence of various elements in primary aluminum are composition of raw materials and conditions of metal production. In bauxites, which are the main raw materials for production of alumina and then metallic aluminum, about 40 elements are revealed. Additional source of impurities is various constructive elements of electrolyzer. For example, the carbonaceous materials (anode paste, baked anodes, cathode products) applied at electrolysis are sources of such impurities as vanadium, titanium, manganese, zinc, etc.

2. Elements in primary aluminum: genesis and interaction

Based on the results of spectral analysis of aluminum produced by different factories in the Russia and abroad, in Fig. 1 in form of matrix of Mendeleev's Periodic Table are listed elements found in the aluminum ingots. Classification of the elements with their allocation to different groups carried out under consideration of the nature of interaction of aluminum with elements in accordance with their influence on the formation of various phases in aluminum alloys. At the same time we take into account the concentration of the impurity element in aluminum and its impact on the operational properties of the cast products.

Data on nature of interaction of elements of various groups of Periodic system with primary aluminum are given below.

Elements of group I. In the aggregate of considered criteria and properties for various types of functional materials the influence of these impurities can be shown differently. For instance, in sacrificial alloys copper will be most harmful impurity and its content reaches 0.01 - 0.02%. Sodium and lithium at concentrations

Elements in primary aluminum									
I	II	III	IV	V	VI	VII	VIII		
H	-	-	-	-	-	-			
Li	Be	B	C	-	O	F			
Na	Mg	Al	Si	P	S	Cl			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	Zn	Ga	Ge	As	-	-			
-	Sr	Y	Zr	-	-	-			
-	Cd	-	-	Sb	-	-			
-	Ba	La	-	-	-	-			
-	-	-	Pb	-	-	-			

Fig. 1. Matrix of Mendeleev's Periodic Table indicating the elements found in aluminum ingots

of a few hundredths or thousandths of a percent have the property to activate the surface of alloy during its operation and can serve as activators of sacrificial alloys. At production of antifriction aluminum matrix composites sodium and lithium also play a positive role reducing the surface tension of matrix melt and facilitating wettability of exogenous reinforcing phase.

Hydrogen actively interacts with aluminum forming with it endothermic interstitial solid solution. Solubility of hydrogen at transition of aluminum from liquid to solid state is reduced from 0.69 to 0.039 cm^3/100 g, whereby gas porosity in castings appears. The presence of pores in cast metal results in its macroinhomogenity therefore hydrogen in aluminum must be considered as one of harmful elements at using of primary aluminum for production of sacrificial, tribotechnical and other alloys for functional and construction purposes. Moreover, in primary aluminum of various grades content of hydrogen can reach 2.85 cm^3/100 g.

Due to the low concentration of potassium in the primary aluminum his influence on properties of castings from aluminum alloys can be neglected.

Elements of group II. From the elements of group II which are found in primary aluminum any can't be attributed to group of harmful elements. Conversely, such elements as Mg and Zn on combination of properties are the main alloying elements in sacrificial alloys. At producing of aluminum matrix composites magnesium acts as surface-active element improving the wettability of exogenous ceramic particles.

Beryllium which is present at concentrations to 0.001% has the refining effect and significantly reduces harmful impact of iron in aluminum, and also suppresses a possibility of oxidation of aluminum-magnesium alloys. Calcium, strontium, barium and cadmium practically not change properties of alloy due its low concentrations.

Elements of group III. Due to very low concentrations of Sc, Y, La, B and Ga in aluminum these elements should be regarded as neutral. Boron has a refining and modifying effect on aluminum alloys. In the electrotechnical alloys based on aluminum boron neutralizes the harmful effects of vanadium, chromium, zirconium

and titanium on the electrical conductivity. At production of antifriction metal matrix composites boron along with titanium, zirconium and some other elements which forms insoluble hard-melting compounds used as initial component-precursor for formation of new endogenous reinforcing phases (TiB_2, ZrB_2, MoB and others) in conditions of liquid-phase reactionary synthesis [4].

Elements of IV group. Titanium and zirconium forms with aluminum limited solid solutions and intermetallic compounds Me_mAl_n. Solid solution of titanium in aluminum (Al + 0,1% Ti) has stationary potential almost identical with aluminum. Taking into account that in A85 aluminum grade (Russian Standard 11069-2001) content of titanium and zirconium less than 0.04%, these metals will be completely in solid solution with aluminum without changing of its properties and without decreasing quality of sacrificial alloys. The carbon presented in aluminum at amounts $1…2\cdot10^{-4}$ % is in type of thinnest carbide inclusions which won't make essential changes to electrochemical properties of alloy. Silicon at concentrations up to 0.19% does not change stationary potential of aluminum in positive direction. It can be assumed that silicon as impurity in aluminum in amounts up to 0.1-0.2% is not harmful. It should be noted that at production of aluminum matrix composites silicon promotes decrease the contact angle of wetting and improves assimilation of exogenous reinforcing particles by matrix melt [5]. Content of germanium in aluminum is negligible so its influence can be neglected. Solubility of lead in solid aluminum doesn't exceed 0.2% at monotectic temperature. As the content of lead in aluminum, as a rule, not more than $1\cdot10^{-3}$ %, this element can be considered as neutral for sacrificial alloys and antifriction composite alloys.

Elements of group V. Aluminum may contain thousandths of a percent of vanadium and phosphorus and up to 0.015% arsenic and antimony. Insignificant concentrations of elements of this group in primary aluminum and nature of their interaction with it won't change electrochemical properties of sacrificial alloys that allow attributing them to group of neutral elements. At production of metal matrix composites these elements will also not have a negative effect on operational properties due to their low content in primary aluminum.

Elements of group VI. Chrome, oxygen and sulfur differently interact with aluminum. Presence of chromium in solid solution based on aluminum practically does not alter its stationary potential. Whereas chromium content in primary aluminum is thousandths of a percent it is possible to expect formation only of solid solution in structure of such alloy and to consider chrome as neutral impurity. Oxygen is present at primary aluminum in the form of insoluble oxide in amount of 0.02-0.07%. Aluminum oxide mixed into the melt influences on the physical-mechanical and technological properties of aluminum alloys and also on their gas content. At production of sacrificial alloys their electrochemical properties will be determined by content of oxides and gases, whereby oxygen in the form of oxide inclusions should be attributed to group of harmful elements. However, at producing of aluminum matrix composites finely-divided oxide Al_2O_3 by using of special processing methods in the conditions of exogenous or endogenous reinforcing can be a reinforcing phase [6]. Sulfur and its compounds with aluminum are unstable in the melt and don't influence on structure and properties of castings.

Elements of VII group. Manganese content in aluminum is in range from 0.001 to 0.05%. At such concentrations manganese practically always is in solid solution with aluminum and does not deteriorate alloy properties. Sources of fluorine and chlorine in aluminum are electrolyte of electrolysis cells and different fluxes. However, due to the high activity of these elements relative to aluminum at their interaction formed low-boiling halides of aluminum which are removed from the melt in the form of gas bubbles. It should be noted a positive role of aluminum purging with gaseous fluorine and chlorine for removal hydrogen from the melt. For these reasons and due to the low concentration of fluorine and chlorine in primary aluminum their impact on properties of functional alloys can be neglected.

Elements of VIII group. According to experimental data [7], increasing of iron content results in monotonous decreasing of potential and electrochemical capacity of aluminum. Presence of iron impurity in aluminum sacrificial alloys promotes formation of Fe_nAl_m type compounds, which are cathodes in relation to aluminum [8]. For these reasons, iron must be attributed to the group of harmful impurities in sacrificial alloys. At production of aluminum matrix composites by mechanical stirring there are examples of use of iron powder as a reinforcing phase for improving of tribological properties [9]. Presence of nickel and cobalt in aluminum worsens electrochemical characteristics of alloys owing to formation of a number of chemical compounds like Ni_nAl_m and Co_nAl_m. At production of aluminum matrix composites nickel powder has been successfully tested as a precursor for the endogenous intermetallic compounds. Reactions of synthesis of these compounds are exothermic and promote wetting and assimilation of entered exogenous ceramic particles, including nanosized components [10].

3. Classification of elements in primary aluminum

Taking the foregoing into consideration, in Table 1 is provided classification of elements which are present in aluminum ingots by their influence on operational properties of castings from functional alloys.

Table 1. Classification of elements in primary aluminum by their influence on the operational properties of alloys for functional purposes

Groups of elements according to their influence on operational properties	Sacrificial alloys	Antifriction composite alloys
Useful	Mg, Zn, Mn, Be, Na, Li, K, Ca, Ba, Zr, Ti	Mg, Si, Cu, Na, Li, Be, B, Ti, Zr, C, V, Cr, O, Fe, Ni, Co
Neutral*	Sr, Cd, Sc, Y, La, B, Ga, C, Si, Ge, Pb, V, P, As, Sb, S, Cr, F, Cl	K, Ca, Zn, Sr, Ba, Cd, Sc, Y, La, Ga, Ge, Pb, P, As, Sb, S, Mn, F, Cl
Harmful	Cu, Fe, Ni, Co, H, O	H

* Assignment of elements to the neutral category in most cases caused by their low content in the primary aluminum.

4. Conclusions

1. Depending on the desired complex of properties of functional alloys, impurities in primary aluminum can be assigned to different groups on influence on operational properties of products.
2. In addition to regulated by Russian standards harmful impurities of iron and copper, at production of sacrificial alloys it is necessary to additional attribute hydrogen, oxygen, nickel and cobalt to harmful elements, that testifies to expediency of application for preparation of such alloys of high grades of aluminum.
3. In aluminum matrix composites for tribotechnical purposes as harmful element from attendees in primary aluminum it is necessary to consider only the hydrogen promoting formation of gas porosity and worsening assimilation of the reinforcing phase. Therefore for their manufacturing use of aluminum of lower grades is allowed.
4. At production of aluminum-based functional alloys for ensuring of high quality of castings it is necessary to

include operation of melts refining from dissolved hydrogen in technological process.

5. Literature

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