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GREEN ALUMINUM: TRENDS AND PROSPECTS

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Summary. Due to its properties aluminum is a vital resource for circular economy and zero waste technologies, recycling and sustainability. Recycling aluminum provides an opportunity to decrease carbon dioxide emissions by replacing primary aluminum. Recycling of aluminum requires nearly 5% of energy needed for primary production, that results in greenhouse gases emissions of 0,5 tons of CO_{2e}. Recycled aluminum's main route is for production of casting alloys. With proper metallurgical processing scrape and aluminum waste can be used to make almost any product: wheels, chassis, transmissions in transport sector; facades, windows, doors in construction; cans, foil in packaging; solar panels, wind farms, aluminum-ion batteries in renewable energy and so on. For alloys made from secondary raw materials, beside the creation of a protective layer on the surface of the melt, which prevents its saturation with hydrogen and oxides during contact with the furnace atmosphere, it is important to ensure effective chemical destruction of oxides on the surface of microvolumes of aluminum melt and decrease the content of hydrogen and other dissolved gases. High efficiency in treatment of aluminum alloys made from scrape and waste has shown the modification, which is carried out to improve the structure (grinding grains, dendritic branches, structural components, dispersing particles of the secondary phases, giving them a favorable shape, etc.) and obtain the material with necessary mechanical and service properties.

When choosing a composition for both flux refining and modification, it is necessary to take into account not only materials science aspects of the problem, but also the impact of their composition on the health and safety of production personnel, city residents and the environment.

Keywords: green aluminum, sustainability, environmentally friendly, refining, modification, recycling.

Introduction. Aluminum alloys are one of the most claiming and forward-looking materials. Aluminum is a material of future for such key sectors as transport, renewable energy, construction, packaging etc.. Nowadays the annual production of aluminum is about 100 Mt per year; nearly 40% of Al is obtained by recycling. The level of aluminum consumption in the world averages 8.8 kg per capita [1]. According to the estimates, the amount of aluminum available for recycling will more than double by 2050 (nearly 18 million tons of aluminum will be used) [2].

One of the main advantages of aluminum is that it is a circular material capable of being recycled over- and over again. It is known, that nearly 75% of all the amount of aluminum has been produced ever (about 1 billion metric tons) is still under use. Aluminum is a circular material [3] and does not lose its original properties such as lightweight, conductivity, durability, formability etc., and with the appropriate technologies of collecting, sorting and recycling technologies aluminum can assure output of high quality (fig. 1).

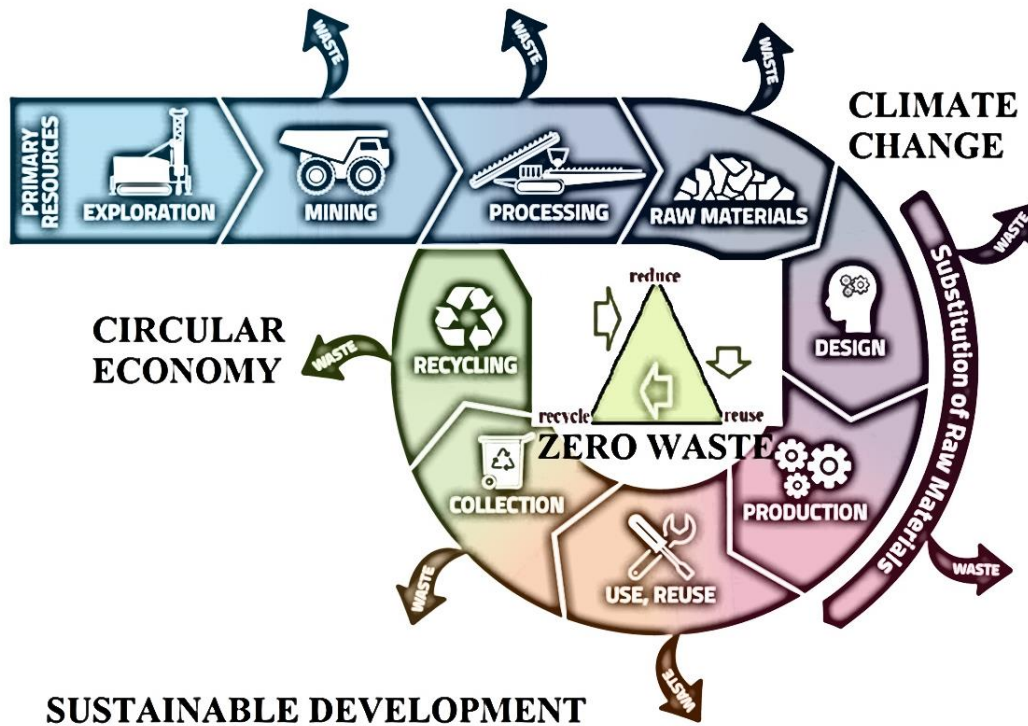


Fig. 1. The 3W approach for producing of aluminum

Body (the main part). Casting aluminum alloys are classified as primary (made from mineral resources) as secondary (based on recycled aluminum) alloys. Primary aluminum is obtained by using electrolytic method, which provides output of high quality, but is accompanied by emissions of greenhouse gases and large amounts of energy consumption. Thus depending on the region of origin aluminum can have different carbon footprint. When using coal, the carbon footprint from production of aluminum is nearly 12... 22 tons of CO₂e; when using gas it is nearly 5... 8 tons of CO₂e; when using hydropower - 2... 4 tons of CO₂e per 1 ton of primary aluminum [4]. In the EU countries the carbon footprint is about 7 tons of CO₂e (for comparison in China - 20 tons of CO₂e). Carbon dioxide emissions are one of the main criteria to define whether aluminum is "green", environmentally friendly.

The need for large amounts of energy for the electrolytic method determines the location of enterprises in areas provided with cheap electricity. The region of largest amount of primary aluminum production is North America (nearly 20% of all aluminum produced in the world). Further follow China - 19%, Western Europe - 16%, Asia and South America - nearly 8% for each region, Africa - 5%, East Europe - 2% and the rest 22%. When aluminum producers rely primarily on a renewable energy source (e.g. hydropower) to produce the metal it also can be considered sustainable and green.

The production of 1 ton of primary aluminum requires about 13.000 ... 15.000 kW·h of electricity, while the production of recycled aluminum - about 200 ... 550 kW·h of electricity [5], which determines not only the price of aluminum alloys, but also the level of greenhouse gases emissions. The level of carbon footprint for aluminum recycling is nearly 0.5 CO₂e/t. That's why the part of green aluminum

alloys is constantly growing. The world leaders of aluminum recycling are the U.S.A., Japan, Germany, France, Britain and Italy.

Aluminum and its alloys tend to interact with gases due to the high chemical activity of aluminum. Aluminum alloys contain hydrogen, oxygen, nitrogen, carbon monoxide, etc. (the main part belongs to hydrogen and oxygen). Hydrogen is present in alloys as in dissolved state as in the form of gas bubbles. Oxygen forms solid slag inclusions - oxides of aluminum and other metals. Hydrogen in the structure is bound into complexes with oxide inclusions ($H_2-Al_2O_3$).

The amount of hydrogen and aluminum oxides increases with an increase of their quantity in raw materials, which especially concerns recycled metal. The process of refining is carried out to reduce the content of hydrogen and aluminum oxides in casting aluminum alloys. Refining fluxes based on sodium and potassium chlorides and fluorides, potassium cryolite, aluminum fluoride, sodium and potassium silicon fluoride, lithium fluoride and chloride are widely used in foundry production. The other substances with positive effect on non-metallic impurities and gases of aluminum alloys are hexachloroethane C_2Cl_6 , barium chloride $BaCl_2$ as well as mixtures of KBF_4+KCl , $NaF+NaCl+KCl+Na_3AlF_6$ and others.

High efficiency in the processing of casting aluminum alloys was shown by modification, which is carried out in for improvement of the structure (grinding of grains, dendrite branches, structural components, dispersing particles of the secondary phases, giving them a favorable shape, etc.) and increasing the mechanical and service properties. Fine powders of silicon carbides, niobium, tantalum, titanium carbides, titanium nitrides, vanadium, hafnium, zirconium, etc. and salts K_2TiF_6 , K_2ZrF_6 , KBF_4 , Na_2CO_3 , $BaCO_3$ are quite widespread as modifiers of recycled aluminum alloys.

On the one hand refining and modification are effective, simple, technological and economically efficient methods of aluminum alloys processing and can be recommended for the treatment of recycled alloys; on the other hand substances that are used for flux refining and modification can lead to the release of particularly toxic products, that are dangerous as for production personnel and citizens as for the environment. The other important issue that despite the production of aluminum alloys by recycling is considered green, the furnace treatment of the melt can include processing with chemicals that adversely affect the temperature regime of the planet and ozone layer thickness.

For instance, according to the classification of the International Agency for Research on Cancer [6], hexachloroethane is a potential carcinogen (dose-dependent neoplasms occur in the human body), affects the central nervous system and belongs to group 2B. Concentrations of hexachloroethane under chronic inhalation exposure are taken into account when assessing risks to public health from atmospheric air pollution. Barium chloride, barium carbonate, sodium fluoride, barium-titanium-zirconate, barium tetratitanate belong to the 2nd class of danger; potassium carbonate, calcium fluoride, titanium nitride, potassium, sodium and calcium chlorides - up to the 3rd class of danger; strontium carbonate - up to the 4th class of danger [7]. Features of the biological action of the components of refining fluxes can be fibrogenic, irritating, allergenic, carcinogenic, etc.. Thus, potassium chloride is characterized by high mutagenic activity, is fire- and explosion-dangerous.

Calcium chloride can cause acute poisoning. Fluoride leads to a violation of the functioning of the main regulatory systems of human body (the immune, nervous, endocrine systems) and directly affects the organs and tissues (dental fluorosis, bone mineralization disorders etc.).

The use of sulfur is of great interest to neutralize the harmful effects of iron (the most harmful impurity in the structure of secondary aluminum alloys). The orientation of iron-rich phases during crystallization is related to the predominance of covalent type of interatomic bonds. To reduce the anisotropy of the force fields of valence electrons in the nucleus of crystallization, it is necessary to change the nature of the interatomic interaction. When sulfur is added to the melt and its atoms are dissolved in the growing crystal, the strength of the covalent component of the bond between the atoms of iron-containing phases decreases and the orienting effect of the crystal on the adjacent liquid surface is weakened. Alloying of the iron-containing phase with sulfur, which has four valence electrons on the outer electron shell, causes an increase in electron density, uniformity of electron distribution, and loss of directionality of interatomic interaction bonds. As a result, the chemical bond changes to a non-directional metal bond and crystallization formations of iron-containing phases acquire a favorable morphology, which results in proper structure and properties of the material. At the same time the use of sulfur is limited for packaging and requires specific occupational safety measures while it is used in the technological process.

Sulfur belongs to the 4th class of danger for humans; the maximum permissible concentration (occupational exposure limit) of sulfur in working zone air is 6 mg/m. Sulfur can cause inflammation of mucous membranes of the eyes and upper respiratory tract, skin irritation and diseases of gastrointestinal tract. Sulfur is flammable. Dust suspended in the air is fire and explosive dangerous. Production premises and laboratories in which work with sulfur are carried out must be equipped with general and exhaust ventilation. Air control of the working area should be carried out. All workers must be provided with individual protection means (clothes, equipment).

Conclusions. Aluminum can be considered green when its production and alloys processing are low-carbon (as well as associated with the reduced amount of other greenhouse gases, hazardous chemicals and environmental pollutants), include recycling of scrape and waste, involve zero waste approach and eventually assume to be used for the purposes of circular economy and ecologically friendly solutions. High efficiency in the processing of recycled aluminum alloys was evidenced by the refining and modification. Formulation of refining and modification chemical components that do not have a hazard class or are classified as low hazard is an urgent issue of modern material science of recycled aluminum alloys.

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