Scientific Background for Processing of Aluminum Waste

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Abstract. Changing the source of raw materials for producing aluminum and the emergence of a huge number of secondary alumina waste (foundry slag, sludge, spent catalysts, mineral parts of coal and others that are formed in various industrial enterprises) require the creation of scientific and theoretical foundations for their processing. In this paper, the aluminum alloys (GOST 4784-97) are used as an aluminum raw material component, containing the aluminum component produced as chips in the machine-building enterprises. The aluminum waste is a whole range of metallic aluminum alloys including elements: magnesium, copper, silica, zinc and iron. Analysis of the aluminum waste Al- Zn-Cu-Si-Fe shows that depending on the content of the metal the dissolution process of an aluminum alloy should be treated as the result of the chemical interaction of the metal with an alkaline solution. It is necessary to consider the behavior of the main components of alloys in an alkaline solution as applied to the system Na_2O - Al_2O_3 - SiO_2 - CO_2 - H_2O.

1 Introduction

The urgency of the waste disposal problem is realized by the society, but the methods of processing of many kinds of aluminum waste have not yet been developed or have inefficiently elaborated. According to Rosprirodnadzor, Russia annually produces about 35-40 million tons of solid industrial waste and almost the entire amount of it is placed on landfills, sanctioned and unsanctioned dumps and only 4-5 % are involved in recycling.

2 Materials and methods

The papers [1, 2, 3] present the theoretical and thermodynamic fundamentals of alkaline aluminate solutions using $Na_2O–CaO–Al_2O_3–SiO_2–H_2O$ system obtained at the Russian industrial enterprises processing the Kola nepheline concentrate and other aluminosilicate materials. The process of interaction of aluminum or aluminum oxide α,γ-$Al_2O_{3тв}$ and hydroxides: gibbsite γ-Al $(OH)_3$, bayerite α-Al $(OH)_3$, boehmite γ-AlO (OH), diaspore α-AlO (OH) is

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carried out according to the reactions (1-6) with a transformation OH^- of alkali solution group to the complex ion $Al(OH)^-_{4\,aq}$ and is shown in Table 1.

On the basis of thermodynamic calculations of the Gibbs energy value ΔG^0_T, there was identified a number of energies of aluminum metal and aluminum hydroxide compounds relative to 1 molar solution of NaOH:

Aluminum [Al] (-435,13 kJ/mol)] → gibbsite [$Al(OH)_{3}$] (-5,9 kJ/mol) → bayerite [α-Al $(OH)_3$ (-2,75 kJ/mol)] → boehmite [AlOOH] (0,54 kJ/mol) → diaspore [AlOOH (2,28 kJ/mol)] → corundum [α, γ-Al_2O_3 (5,24 kJ/mol)].

Table 1. The theoretical and thermodynamic fundamentals of alkaline aluminate solutions using Na_2O–CaO–Al_2O_3–SiO_2–H_2O system.

No.	Compound name	Chemical reaction
1	Aluminum	$Al_{solids} + OH^- + 3H_2O = Al(OH)_4^-{}_{aq} + 1{,}5H_2$
2	$Al(OH)_{3amorphous}$	$Al(OH)_{3amorphous} + OH^-_{aq} = Al(OH)_4^-{}_{aq}$
3	bayerite Al $(OH)_3$	$Al(OH)_{3solids} + OH^-_{aq} = Al(OH)_4^-{}_{aq}$
4	boehmite AlOOH	$AlOOH + OH^-_{aq} + H_2O = Al(OH)_4^-{}_{aq}$
5	diaspore AlOOH	$AlOOH + OH^-_{aq} + H_2O = Al(OH)_4^-{}_{aq}$
6	corundum α, γ-$Al_2O_{3solids}$	α, γ-$Al_2O_{3solids} + 3H_2O + 2OH^- = 2Al(OH)_4^-{}_{aq}$

The values obtained for the Gibbs energy indicate a high probability of interaction of aluminum, amorphous hydroxide, bayerite with an alkaline solution at a temperature of 298K.

Table 2. The chemical reactions 3-6 are also possible, but they are less likely as they can only execute with increasing temperature, as evidenced by the calculated standard enthalpy of the reactions.

Reaction Nr.	1	2	3	4	5	6
Thermicity, kJ/mol	-409,2	15,79	33,52	12,57	3,21	6,16

Currently, the secondary processing of aluminum-containing raw materials (aluminum alloys) is essential, because they contain a significant amount of very valuable items: Al - Mg - Ca - Sc - Zn - Cu - Sc - Cr - Zr - Fe - Hf.

Production of recycled aluminum requires fewer energy costs and substantially lower emission of toxic substances into the environment than in the production of primary aluminum. According to forecasts, the proportion of recycled aluminum in the total consumption in 2030 could rise to 22 - 24 million tons per year [4].

Study of the problem of aluminum waste recycling for various enterprises shows that aluminum waste containing aluminum are classified according to their properties: nonrigid and cast alloys [5].

3 Results and discussion

Aluminum waste is a whole range of metallic aluminum alloys with the inclusion of significant amounts of elements of the D.I. Mendeleyev Periodic System of Elements: calcium, magnesium, copper, manganese, silica, zinc, iron [GOST 1639-2009].

Changing the technological properties in comparison with the state diagram shown in Fig.1 shows that the alloys containing alloying component less than the solubility limit have the highest ductility and the lowest strength at high temperature. Analysis of the chemical composition of the aluminum waste containing Al-Zn-Cu-Si-Fe shows that depending on the

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content of the metal the dissolution process of an aluminum alloy should be treated as the result of the chemical interaction of the metal with an alkaline solution containing ionsOH^-.Aluminum alloys should be regarded as a uniform distribution of elements in the crystal lattice of aluminum alloy. From the reactivity point of view, aluminum alloys are local galvanic cells which arise when exposed to water and alkali.

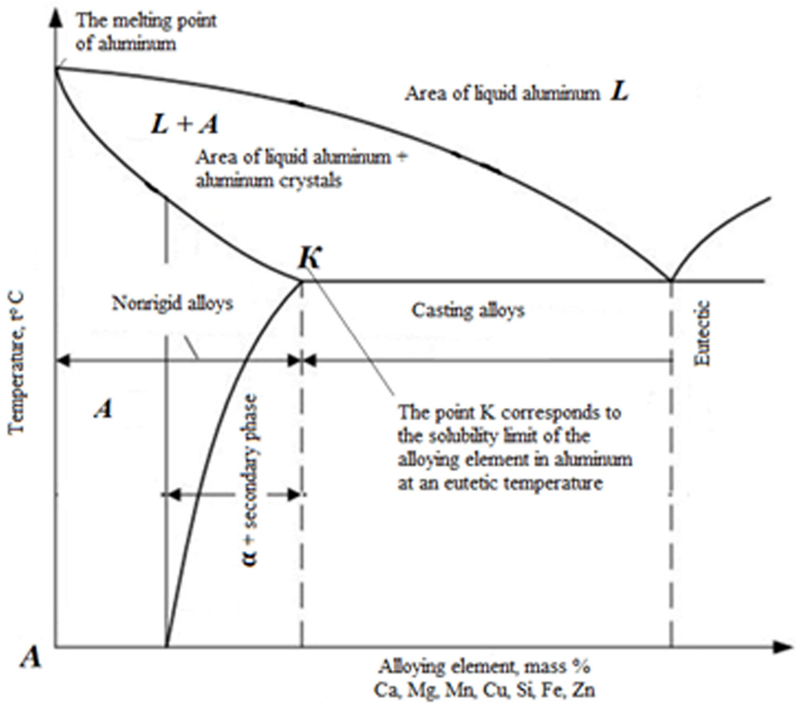

Fig. 1. The circuit diagram of a typical aluminum - alloying element.

The reactions of aluminum alloy components in water and the alkaline solution of the molar concentration (NaOH) used for preparing the aluminate solution are shown in Tab. 3.

Table 3. Gibbs energy and reaction potentials of the dissolution of aluminum waste components in an alkaline solution.

Name of alloying element	Chemical reaction	ΔG^0_{298}, kJ/mol	Standard potentials of metals, V
Beryllium	$Be_{solids} + 2OH^- + 2H_2O = Be(OH)_4^{2-} + H_2$	-309,38	-1,847
Aluminum	$Al_{solids} + OH^- + 3H_2O = Al(OH)_4^{--} + 1,5H_2$	-337,77	-1,66
Manga-nese	$Mn_{solids} + OH^- + 2H_2O = Mn(OH)_3^- + H_2$	-97,32	-1,18
Chromium	$Cr_{solids} + OH^- + 2H_2O = Cr(OH)_3^- + H_2$	49,27	-0,852
Zinc	$Zn_{solids} + 2OH^- + 2H_2O = Zn(OH)_4^{2-} + H_2$	-74,05	-0,763
Cadmium	$Cd_{solids} + 2OH^- + 2H_2O = Cd(OH)_4^{2-} + H_2$	46,76	-0,403
Iron	$Fe_{solids} + 2OH^- + 2H_2O = Fe(OH)_4^{2-} + H_2$	35,64	-0,037
Silicon	$Si_{solids} + 2OH^- + 2H_2O = H_2SiO_4^{2-} + 2H_2$	-398,63	-
Copper	$Cu_{solids} + 2OH^- + 2H_2O = Cu(OH)_4^{2-} + H_2$	152,09	+0,337

To evaluate the dissolution of aluminum waste components in an alkaline solution the free Gibbs energy was selected as a criterion ΔG^0_{298}, which is connected to the electromotive force of the element with an equation $\Delta G^0_{298} = n \cdot F \cdot E^o$, where n - the charge of the ions; F - Faraday constant, equal to 96485 C/mol; E^o - EMF of the element, V.

Thus, when analyzing the reactivity of the aluminum alloy elements, it must be kept in mind that these compounds release hydrogen from the water molecules as a result of a chemical reaction and the role of alkali is reduced to the dissolution of the corresponding hydroxide. For example, the chemistry of the process for aluminum is carried out as follows:

1. Stage $Al + H_2O = Al(OH)_3 + 3/2\ H_2$;
2. Stage $Al(OH)_3^+ + OH^- = Al(OH)_4$

Therefore, it reacts with water to form aluminum hydroxide which being an amphoteric compound further exhibits acidic properties sufficiently and easily neutralized with alkali (NaOH) to form the aluminate complex anion.

The element silica has similar properties. Other elements such as Mg, Ti, Mn, Ni, Fe and Cu exhibit basic properties and even in the case of their dissolution, they will be presented only by hydroxides. The possibility of their dissolution in an alkaline solution can be evaluated using the solubility data for the corresponding hydroxyl compounds. For example, if an aluminum alloy contains iron and copper, that may form local galvanic element copper - iron - (NaOH solution).

In this case, the iron elements become Fe^{2+} ions and then pass into the solution due to the fact that the formation of $Fe(OH)_2$ on the surface robs free electrons from the copper $2Fe \rightarrow 2Fe^{2+} + 4e$; $2H_2O + O_2 + 4e = 4OH^-$. The presence of oxygen leads to the formation of different versions, for example, FeO(OH).

Thus, a variety of different elements in the aluminum alloy results in the need to approach the thermodynamic analysis of the behavior of all the components when they are dissolved in an alkaline solution.

To develop the technological process of processing of aluminum alloys it is necessary to determine what amount of aluminum oxide can be converted into an alkaline aluminate solution, so the dissolution of the aluminum alloy should be seen as a heterogeneous system $Na_2O - Al_2O_3 - SiO_2 - CO_2 - H_2O$, which is shown in Fig. 2.

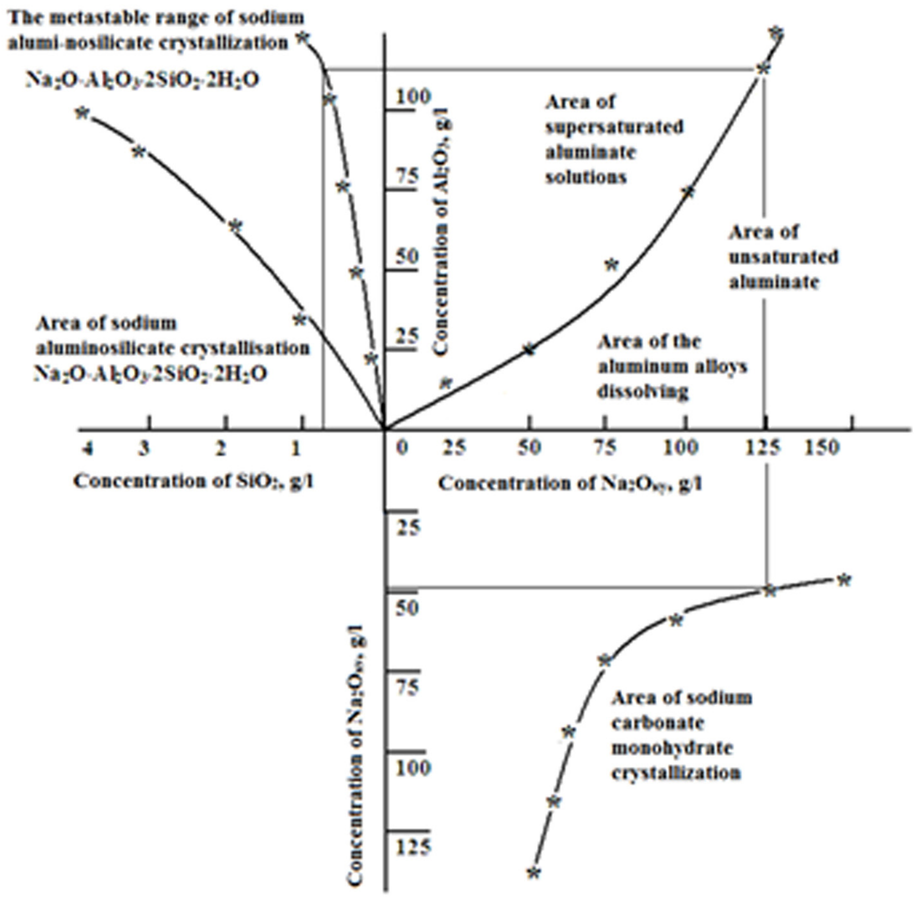

Fig.2. The equilibrium diagram of the system Na_2O - Al_2O_3 - SiO_2 - CO_2 - H_2O in the temperature the interval 80-90 °C.

The dissolution process of aluminum alloy and its components by reaction with an alkaline solution may be carried out only when a free caustic alkali is present in a solution.

As an example, consider the interaction of aluminum $Al_{solids} + OH^- + 3H_2O = Al(OH)_4^- + 1{,}5H_2$ and silicon $Si_{solids} + 2OH^- + 2H_2O = H_2SiO_4^{2-} + 2H_2$ in an alkaline solution and determine the areas of alkaline aluminate solutions, which affect its dissolution.

Since the dissolution of the alloy is performed in reactors with an open surface, the caustic alkali is able to absorb CO_2 from the air. In this case, the neutralization reaction proceeds $2NaOH + CO_2 = Na_2CO_3 + H2_O$ and, consequently, a decrease of free alkali.

These data suggest that the amount of free alkali for the process should be calculated from the formula:

$$Na_2O_{ку} = Na_2O_{total} - Na_2O(NaOH) - Na_2O(Na_2CO_3) - Na_2O_{impurity}, \quad (1)$$

where*:*

$Na_2O_{total.}$ - the total caustic alkali, $Na_2O_{ку}$ alkali connected in NaOH, $Na_2O_{гасн}$ alkali related to sodium hydro aluminosilicates, $Na_2O(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$, $Na_2O(Na_2CO_3)$ - the alkali carbonate is Na_2CO_3, $Na_2O_{impurity}$ - alkali connected to other inorganic compounds.

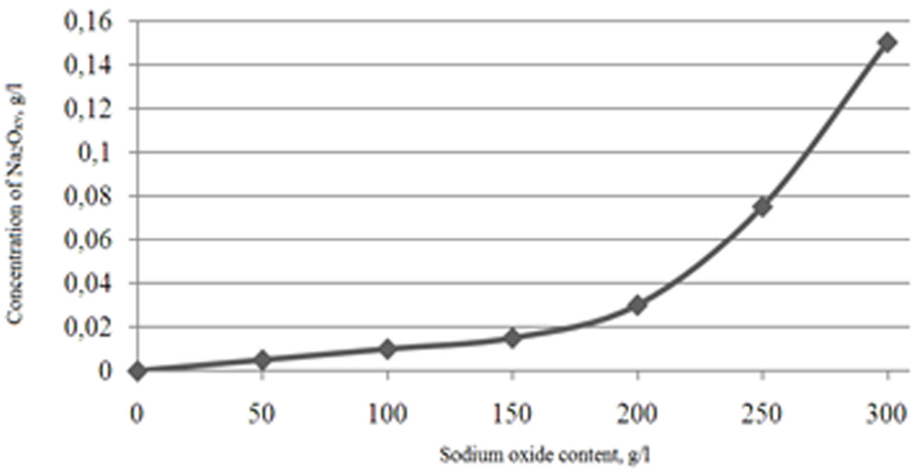

Fig.3. The solubility of iron hydroxide in an alkaline solution of various concentrations of a temperature of 80 – 90°C.

The experimental data on the solubility of iron hydroxide shown in Fig. 3 shows that the alkaline solutions containing Na_2O_{Ky} of 100 - 300 g/l the solubility of iron hydroxide is (0.003 - 0.05) Fe_2O_3 g/l. It should be noted that the solubility of iron hydroxide in alkaline solution at pH = 10 is $2.5 \cdot 10^{-26}$ g/l.

Calcium as an alloying element in aluminum significantly changes its properties, and introduced into a new aluminum gives it special properties and plasticity. When the calcium content is of 5 %, the alloy has the effect of superplasticity [6].It is known that the solubility of the hydroxides of alkaline earth metals depends on an excessive amount of hydroxyl ions in the form of NaOH solution and the temperature rise which causes a decrease in the solubility of calcium hydroxide.

4 Conclusions

1. On the basis of thermodynamic calculations of the Gibbs energy value ΔG^0_{298}, there was identified a number of energies of aluminum metal and aluminum hydroxide compounds relative to 1 molar solution of NaOH:

Aluminum [Al] (-435,13 kJ/mol)] → gibbsite [$Al(OH)_3$] (-5,9 kJ/mol) → bayerite [α-Al $(OH)_3$ (-2,75 kJ/mol)] → boehmite [AlOOH] (0,54 kJ/mol) → diaspore [AlOOH (2,28 kJ/mol)] → corundum [α, γ-Al_2O_3 (5,24 kJ/mol)].

2. Calculated values of ΔG^0_{298} show that only five alloy elements (aluminum, silica, and others) are dissolved during alkaline chemical processing of aluminum alloy. Standard potentials of metals are used to roughly estimate the electrochemical corrosion in alkaline solutions at normal temperatures and to select the contact pairs of dissimilar metals.

3. To determine the dissolution rate of aluminum waste, the experiments were performed with the aluminum alloy specimens of 40x40 mm, which were placed in an alkaline solution of various concentrations (10 - 160 g/l) and temperature (60 - 90 °C) to achieve the same result (4 μm yield on the surface side).

4. The etching equation was obtained based on experimental data that can be written as: $\alpha = k\, C_{NaOH}\, 2^{T-40}\, \tau$, wherein: α - the value by which to determine the number of metal aluminum passed into an alkaline solution, expressed in g/l Al_2O_3, k - the speed constant of

1.5 10^{-4} g/s; C_{NaOH} - NaOH concentration, mol; τ - etching time, s. For example, at a temperature of 70 °C the concentration of 120 g/l of NaOH (3 mol) and a time of 5 seconds, α = 1.5 10^{-4} 3 2 $^{70-40}$ 5; concentration α = 0.018 g/l Al_2O_3.

5. On the basis of literature and experimental data considering the separate sections Na_2O - Al_2O_3 - SiO_2 - CO_2 - H_2O we developed the comprehensive chart with the separate sections Na_2O - Al_2O_3 - H_2O (crystallized $Al(OH)_3$; Na_2O - Al_2O_3 - SiO_2 - H_2O (crystallized $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, sodium hydro aluminosilicate);Na_2O - Al_2O_3 - CO_2 - H_2O (accumulation of CO_2 in alkaline solution, an aqueous sodium carbonate is crystallized in the form of $Na_2CO_3{\cdot}nH_2O$.

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