

Electrochemical synthesis of nickel-aluminium oxide system from metals obtained by ore processing

V V Korobochkin^{1,2}, N V Usoltseva^{1,3}, K G Shorokhov^{1,4} and E V Popova¹

¹ Department of Chemical Engineering, National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk, 634050, Russia

E-mail: ² vkorobochkin@tpu.ru, ³ usolceva@tpu.ru, ⁴ shorohof@hotmail.com

Abstract. Separate and combined electrochemical oxidation of aluminium and nickel has been conducted by alternating current of industrial frequency. Concentration increase of electrolyte solution (sodium chloride) in the range from 3 to 25 wt. % and current density from 0.5 to 1.5 A/cm² was found to result in the increasing metal oxidation rate, excluding aluminium oxidation which oxidation rate is independent of the electrolyte solution concentration. At the current density of 1.5 A/cm² the products of separate oxidation of nickel and aluminium are nickel oxyhydroxides, nickel hydroxides and aluminium oxyhydroxide (boehmite), respectively. In addition to these compounds, the nickel-aluminium oxide hydrate is included in the products of nickel and aluminium co-oxidation. Its content grows with the increasing electrolyte solution concentration. Varying the concentration and current density within the limits indicated, the nickel-aluminium oxide system with nickel oxide content from 3 to 10 wt. % is produced.

1. Introduction

Metal oxides are widely used in industry. Industrial use of natural metal oxides (quartz, corundum, hematite, rutile, cassiterite, magnetite, spinel and others) is limited due to their phase heterogeneity and the presence of impurities and other compounds, as well as varying ore composition of different deposits. Some metals are found in nature mostly as compounds, not containing oxygen. For example, nickel and copper ores consist of metal sulphides. Based on above-mentioned facts, non-ferrous metal ores could be considered as raw materials in producing metals and metal compounds recycled as metal oxides suitable for industrial use. The formation of highly dispersed oxides having improved operating characteristics is promoted by their synthesis in non-equilibrium conditions [1, 2]. Products of electrochemical metal oxidation by alternating current (AC) are characterized by both high specific surface area and high purity because of extremely low content of impurities. This method can be used in producing metal oxides and metal oxide systems. Previously, the AC electrochemical metal oxidation was investigated for the synthesis of copper oxides [3], tin oxides [4] and double copper-containing oxide systems: copper-titanium, copper-cadmium [5], copper-aluminium [6]. Highly-developed aluminium oxide pore structure and its wide application in catalytic and sorption processes determine perspective investigation of the synthesis of alumina-based oxide systems. Nickel-based catalysts are effective in the catalytic partial oxidation of methane in synthesis gas (syngas) [7]. NiO/Al₂O₃ can be used as an oxygen carrier during chemical looping combustion (CLC) of fuels [8]. The absence of direct contact between fuel and air during combustion prevents CO₂ emission into the atmosphere with unreacted oxygen, therefore, avoiding the negative impact on the environment.



Mesoporous nickel-aluminium oxide system can be obtained in several ways. It was established that the bulk NiO-Al₂O₃ catalyst is characterized by higher activity and selectivity in the partial methane oxidation to synthesis gas than supported catalyst due to the fact that nickel is distributed not only on the carrier surface, but also within its framework [9]. In this case, Ni content in the sample affects both the conversion of methane and the amount of generated carbon [10].

The research target is to study the possibility of producing nickel-aluminium oxide system during combined electrochemical oxidation of nickel and aluminium under the action of alternating current.

2. Experimental part

AC electrochemical metal oxidation with soluble electrodes was conducted in solutions of sodium chloride of analytical grade with concentrations of 3, 5, 15 and 25 wt. % at the temperature of 100 °C and current densities of 0.5, 1.0 and 1.5 A/cm². Sodium chloride is used as the electrolyte because this compound meets most requirements for electrolytes. It has high electrical conductivity and does not chemically react with metals and their oxides. Furthermore, chloride ions contribute to the formation of oxide film on the electrode surface that does not create significant difficulties in the electrolysis process. It is due to both the formation of metal hydroxochloride complexes transforming into a liquid phase and the decomposition of loose oxides that are easily removed from the metal surface. The lower concentration limit is due to high energy consumption and instability of the process, while the upper one – solubility of sodium chloride in water. This process at current density of less than 0.5 A/cm² is not of practical interest because, in this case, metal oxidation rate is not high. At current density of 1.5 A/cm² the oxidation rate is so high that there is an intensive heating of the electrolyte, its boil-off, gas-filling of interelectrode space, resulting in unstable unit performance. The electrodes were nickel plates (mark H-0) and aluminium plates (mark A-0).

Electrolysis products were washed with distilled water and air-dried at a temperature of 110 °C for 6 hours. The remove of electrolyte ions is conditioned by high mobility of sodium ions that significantly accelerate sintering, as well as by the formation of different sodium-containing compounds of aluminium oxide. At the same time, the formation of nickel-aluminium spinel is prevented [11].

X-ray diffraction (XRD) measurements were performed using DRON-3M diffractometer under the following conditions: CuK_α-radiation ($\lambda=1.5418 \text{ \AA}$) at 25 mA and 35 kV, counting rate of 40/min and angle scan region (2θ) from 10 to 70°. PDF 2 database was used to identify the phase composition.

3. Results and discussion

The combined electrochemical oxidation of copper and aluminium intensifies the copper oxidation and insignificantly affects the aluminium oxidation rate [3], while above-mentioned nickel reaction is visa versa: rate of combined nickel oxidation is preferably lower than the rate of separate one. On the contrary, combined oxidation of metals accelerates the aluminium oxidation. The dependence of the aluminium oxidation rate from the second metal property substantiates the assumption of interprocess in the combined oxidation of metals with different properties.

Irrespective of synthesis conditions, aluminium oxidation rate (q_{Al}) significantly exceeds nickel oxidation rate (q_{Ni}) (figure 1): 5-20 times in combined oxidation of nickel and aluminium, and 3-7 times in separate oxidation of metals. This can be explained by the hydrogen depolarization at electrochemical oxidation of metals with negative electrode potentials (in this case, aluminium), promoting higher current efficiency, therefore, the predominance of aluminium compounds in electrolysis products [12]. Nickel oxides have significant true density, surface tension and solubility. Moreover, such processes as coagulation, recondensation and coalescence are more typical for nickel resulting in the degradation of the porous structure [1]. As a result, well-developed boehmite porous structure and prevailing of this compound in the electrolysis product predetermine its primary role in the formation of the material porous structure.

Figure 1 shows that the dependence of nickel oxidation rate from electrolyte solution concentration is linear at all current densities. Nickel oxidation rate increases to 2.1-2.3 times at electrolyte solution

concentration growth from 3 to 25 wt. %. The concentration influence on the oxidation rate increases when current density grows. At all solution concentrations the increase of current density from 0.5 to 1.5 A/cm² accelerates metal oxidation in 3.5-6.0 times.

Comparable to nickel, aluminium oxidation rate does not depend on the sodium chloride solution concentration and increases 3.8 times when current density increase from 0.5 to 1.5 A/cm².

Irrespective of current density at combined metal oxidation, the oxidation rates of both metals increase linearly with the growth of electrolyte solution concentration from 3 to 25 wt. %. Depending on the current density the oxidation rate of nickel and aluminium increase to 1.6-5.7 and 1.5-2 times, respectively. Increasing current density from 0.5 to 1.5 A/cm² accelerates electrochemical oxidation of nickel to 1.7-6.0 times and aluminum to 1.4-1.7 times.

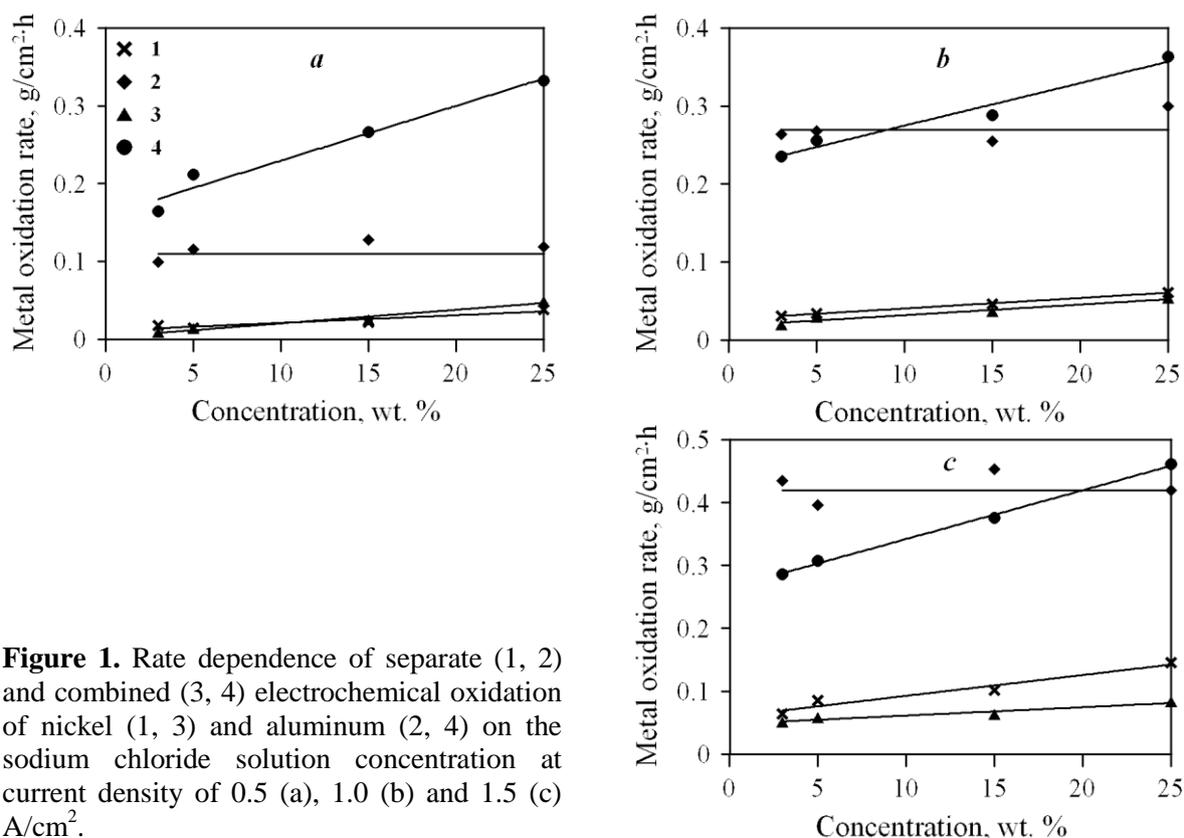


Figure 1. Rate dependence of separate (1, 2) and combined (3, 4) electrochemical oxidation of nickel (1, 3) and aluminum (2, 4) on the sodium chloride solution concentration at current density of 0.5 (a), 1.0 (b) and 1.5 (c) A/cm².

The cell voltage is greatly determined by the resistance of electrolyte solution and also depends on oxide film resistance on the electrode surface. Voltage stability in time during electrochemical nickel oxidation at all values of solution concentrations and current densities indicates that formed oxide film does not show significant resistance. Increasing voltage in time during aluminum oxidation results in the formation of a dense oxidation product layer, the thickness of which increases in time and requires additional voltage to overcome the resistance of this layer.

The increase of sodium chloride solution concentration increases electrical conductivity, thus, the voltage required to overcome solution resistance decreases. Measured cell voltage decreases with increasing concentration of the electrolyte solution in both separate and combined metal oxidation (figure 2).

In nickel oxidation the cell voltage reduction is 20 wt. % at current density of 0.5 A/cm². At 1.0 and 1.5 A/cm² the cell voltage is reduced to ~ 3 times, the most significant decline is observed when the solution concentration is higher than 15 wt. %. In aluminium oxidation the cell voltage behavior is somewhat different. The cell voltage decreases with increasing concentration of 3 to 5 wt. %; the

reduction is greater the higher the current density is. At current density of 1.5 A/cm^2 , an increase in concentration of more than 5 wt. % does not cause a significant change in the cell voltage, whereas at current densities of 0.5 and 1.0 A/cm^2 the voltage is reduced to 1.5 to 2 times, during electrolysis in solution concentration increase to 15 wt. %, respectively. Further increase of electrolyte solution concentration does not significantly change the cell voltage. Cell voltage during co-oxidation of metals decreases 4-10 times by increasing the concentration of the electrolyte solution from 3 to 25 wt. %, but rises 5-6 times with increasing current density from 0.5 to 1.5 A/cm^2 .

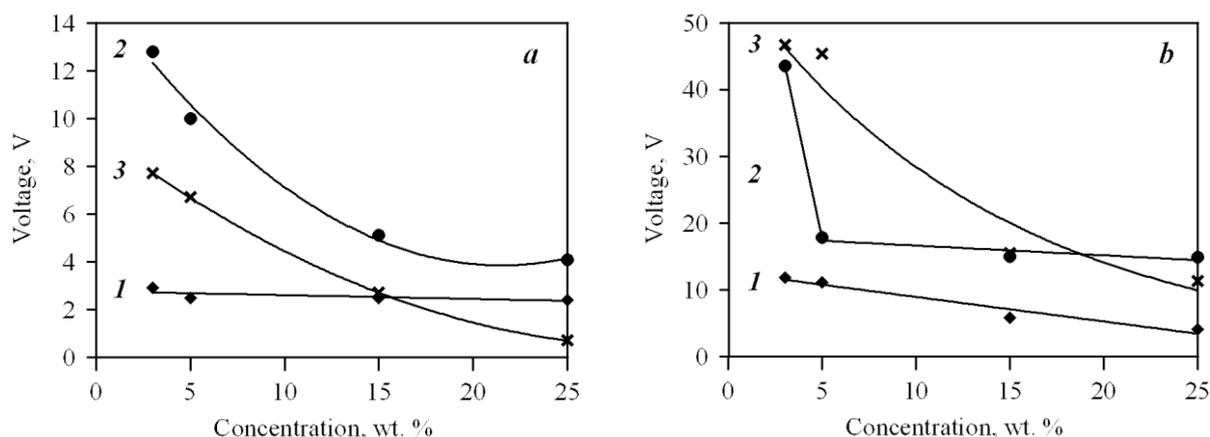


Figure 2. Cell voltage dependence on sodium chloride concentration in separate oxidation of nickel(1), aluminium (2) and nickel and aluminium co-oxidation (3) at current densities of 0.5 (a) and 1.5 (b) A/cm^2 .

Comparing oxidation rates and cell voltage revealed that the highest rate of electrochemical oxidation of nickel and aluminium are achieved by carrying out the process in solutions with high concentration and lowest cell voltage. Increasing current density provides higher oxidation rate, but considerably increases the voltage that must be applied to perform this process.

Figures 1 and 2 show that there is a relationship between the correlation of the metal oxidation rates and the cell voltages in combined and separate metal oxidation. It was established that the rate of combined metal oxidation exceeds the rate of separate metal oxidation when the voltage in combined oxidation is lower than in separate oxidation. This could be associated with the structure of the oxide film on the electrode surface. Intensification in combined oxidation of metals is a result of the formation of oxidation product layer on the electrode surface, which does not create significant resistance.

According to the X-ray diffraction patterns (figure 3), the products of separate nickel and aluminium oxidation in the sodium chloride solution with the concentration of 15 wt. % and current density of 1.5 A/cm^2 (provides the highest metal oxidation rate) consist of the same nickel-containing compounds (anhydrous Ni(OH)_2 (JSPDS card No. 14-0117) and hydrated $\text{Ni(OH)}_2 \cdot \text{H}_2\text{O}$ (JSPDS card No. 22-0444) nickel hydroxides, nickel oxyhydroxides NiOOH (JSPDS card No. 06-0075), $\text{Ni}_2\text{O}_3 \cdot \text{H}$ (JSPDS card No. 40-1179)) and aluminium oxyhydroxide (boehmite AlOOH , JSPDS card No. 17-0940), respectively. Wide indistinct peaks of boehmite indicate that slightly crystallized compound with defective structure is formed in ac-oxidation of aluminium.

Since the aluminium oxidation rate is significantly higher than the nickel oxidation rate, the samples predominately include aluminium oxidation products. Products of combined electrochemical oxidation of metals contain the same nickel- and aluminium-containing phase as the products of the separate metal oxidation. Besides, nickel aluminium oxide hydrate ($\text{Ni}_5\text{Al}_4\text{O}_{11} \cdot 18\text{H}_2\text{O}$, JCPDS card No. 22-0452) is formed. The contents of $\text{Ni}_5\text{Al}_4\text{O}_{11} \cdot 18\text{H}_2\text{O}$ and nickel oxyhydroxide increases as the concentration of the electrolyte solution, used for the electrochemical oxidation of metals, growth (figure 4).

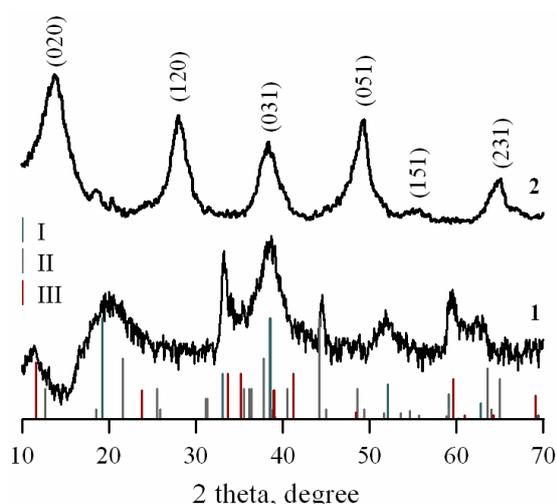


Figure 3. XRD patterns of separate electrochemical oxidation products of (1) nickel and (2) aluminum in sodium chloride solution with concentration of 15 wt. % at current density of 1.5 A/cm² (I – Ni(OH)₂, II – Ni₂O₃H, III – 2Ni(OH)₂·2H₂O).

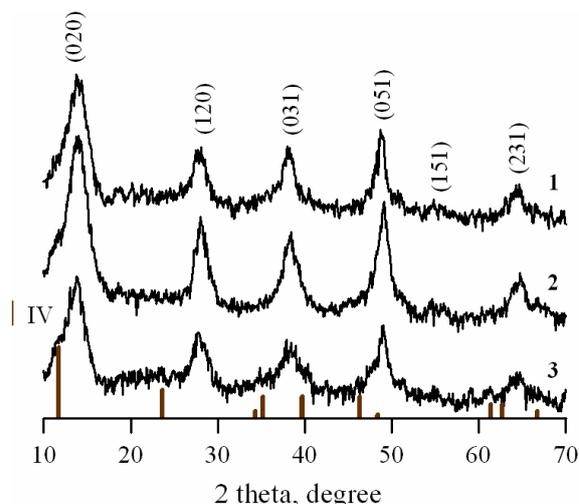


Figure 4. XRD patterns of combined electrochemical oxidation products of nickel and aluminum in sodium chloride solution with concentrations of 3 (1), 15 (2) and 15 (3)wt. % at current density of 1.5 A/cm² (IV – Ni₃Al₄O₁₁·18H₂O).

Regardless of the phase composition of nickel- and aluminium-containing compounds, the nickel oxide NiO and alumina Al₂O₃ are formed during heat treatment of the material [11]. The mass changes of the electrodes were recalculated based on these oxides. The content of nickel oxide in the oxide system increases 2-4 times when the concentration grows from 3 to 25 wt. % and 2-6 times at the changing of current density from 0.5 to 1.5 A/cm² (figure 5). Thus, variation of the process conditions of combined electrochemical oxidation of nickel and aluminium results in oxide system formation with nickel oxide content of 3 to 10 wt. %.

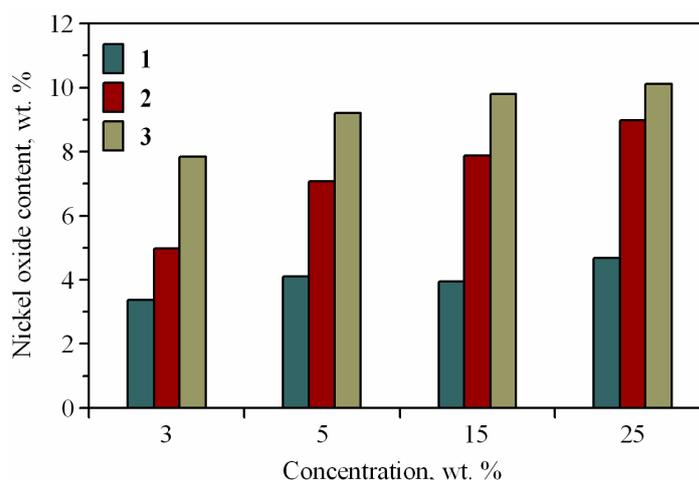


Figure 5. Dependence of nickel oxide content in nickel-aluminum oxide system on concentration of sodium chloride solution at current density of 0.5 (1), 1.0 (2) and 1.5 A/cm².

4. Conclusion

Applying alternating current both individual and combined electrochemical oxidation of nickel and aluminium were performed. It was established that the rate of aluminium oxidation is much higher than nickel oxidation. The rates in combined metal oxidation exceed the rates in separate metal oxidation under conditions when the cell voltage of co-oxidation is less than the voltage of separate oxidation. In electrochemical nickel oxidation, hydrated and unhydrated nickel hydroxides and nickel oxyhydroxides are formed. Electrochemical aluminium oxidation results in aluminium oxyhydroxide (boehmite) formation. Along with indicated compounds of nickel and aluminium the products of combined oxidation of metals include nickel aluminium oxide hydrate. The content of this compound and nickel oxyhydroxide increases with the growth of concentration of sodium chloride solution. Varying the concentration of electrolyte solution from 3 to 25 wt. % and current density from 0.5 to 1.5 A/cm² results in the formation of nickel-aluminium oxide with the content of nickel oxide from 3 to 10 wt. %.

References

- [1] Zyryanov V V 2005 *Inorganic Materials* **41** 378–92
- [2] Merzhanov A G 2012 *40 Years Of SHS: A lucky star of a scientific discovery. A presentation with elements of a scientific lecture* (Bentham Science Publishers) p 104
- [3] Korobochkin V V, Gorlushko D A, Balmashnov M A and Usoltseva N V 2010 *Bulletin Tomsk polytech.univer. Chem.* **317** 13–16
- [4] Korobochkin V V, Balmashnov M A, Gorlushko D A, Usoltseva N V and Bochkareva V V 2013 *Inorganic Materials* **49** 993–99
- [5] Dolinina A S, Korobochkin V V, Usoltseva N V, Balmashnov M and Botyanova I V 2014 *Procedia Chemistry* **10** 369–72
- [6] Usoltseva N V, Korobochkin V V, Balmashnov M A and Dolinina A S 2014 *Procedia Chemistry* **10** 320–25
- [7] Enger B Ch, Lødeng R and Holmen A 2008 *Appl. Catal. A: Gen.* **346** 1–27
- [8] Gayón P, Dueso C, Abad A, Adanez Ju, Diego LF and Garcia-Labiano F 2009 *Fuel* **88** 1016–23
- [9] Horiguchia Ju, Kobayashia Ya, Kobayashia S, Yamazakia Yu, Omataa K, Nagaob D, Konnob M and Yamadac M 2011 *Appl. Catal. A: Gen.* **392** 86–92
- [10] Huang X, Sun N, Xue G, Wang Ch, Zhan H, Zhao N, Xiao F, Wei W and Sunc Yu 2015 *RSC Adv.* **5** 21090–98
- [11] Lazić MM, Hadnadev MS, Bošković GC, Obadović DŽ and Kiss EE *Science of Sintering* **40** 175–84
- [12] Kuksina O Yu, Kondrashin V Yu and Marshakov IK 2004 *Protection of Metals* **40** 581–86