ISSN 1392–1207. MECHANIKA. 2014 Volume 20(3): 317–326

Research of Ni-Al-O system catalytic coatings developed for gasification and steam reforming processes

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crossref http://dx.doi.org/10.5755/j01.mech.20.3.4614

1. Introduction

The depletion of fossil fuel reserves, global warming and environmental pollution are serious issues raising major concerns worldwide and as such it is necessary to solve these complex problems holistically [1].

Growing support for local renewable energy sources has made the public much more aware of the significance of environmental pollution and energy security. Biomass is one of energy sources that could play a major role in the development of local energy mix. Forests, agricultural crops and in particular their residues are prominent examples of biomass sources that could be utilized. Other biomass sources include industrial and municipal waste, which have a high percentage of food waste and synthetic or natural fibers in their mass [2].

The use of biofuels such as biodiesel, bioethanol or biogas would assist in solving global challenges because such fuels are a renewable and sustainable answer to our energy needs. As an additional benefit, ecological waste disposal issues are addressed through the use of small and medium capacity plants that convert waste into energy sources (such as methane production via gasification) [3].

Biogas that is obtained via gasification is typically composed of 55-70 vol% CH_4, 27-44 vol% CO_2, < 1 vol% H_2, and <3 vol% H_2S as well as traces of NH_3 [4]. Next, such biogas is converted into syngas (H_2 + CO) using the steam reforming method. Hydrocarbon reforming is defined as steam reforming and dry reforming of methane.

The associated reversible reactions are steam reforming reactions [5]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = +206 \text{ kJ / mol}, \quad (1)$$

water gas shift reactions

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ / mol}, \quad (2)$$

and dry reforming reactions with CO_2

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H^0_{298} = +247 \text{ kJ / mol}. \quad (3)$$

These reactions occur under certain conditions inside of special converters that employ group VIII metal catalyst, usually nickel. Converter consists of an oven with the pipes placed inside. Pipes are filled with catalyst in the form of perforated pellets. The conditions in the reactor pipe for Eqs. (1) and (3) reactions are: temperature, 700 - 900°C, pressure – 2 - 4 MPa, the molar steam-to-carbon ratios P (H_2O) / P (CH_4) ≈ 3, gas flow in a pipe ≈ 1.0 m/s [6].

The second technological step performs (2) reaction and is carried out at temperature of 200 - 400°C.

Petroleum and natural gas reforming is carried out under similar reactions [7, 8]. Ni catalysts are used in many industrial processes, such as hydrogenation, hydrotreating, hydrogenolysis, methanation and steam reforming of hydrocarbons [9].

The other example where Ni catalyst is utilized for similar purposes is solid oxide fuel cell (SOFC) [10]. One of the advantages of SOFC systems is that methane and other hydrocarbons have a broad internal reforming possibility in order to extract hydrogen [11]. SOFC is a triple-layer, solid state type of coating device, constructed from ceramic material and placed in a tank under conditions of high temperature and pressure [12]. One of the ceramic layers is cermet anode that usually is made of Ni-YSZ (thickness 500 µm).

The requirements for Ni catalysts are usually as follows: it must be effective with respect to dross removal, have fine methane reformation, form the required ratio of syngas, be resistant to deactivation due to agglomeration of carbon on the catalyst surface, be resistant to sulphur poisoning, regenerate easily, resist degradation, remain durable, be inexpensive. Haldor Topsoe catalyst R 67-7H could be mentioned as a practically used example: it is used for dross and methane gas reforming. R 67-7H has 12-14% Ni carried out on Al_2O_3 support, and its surface area is 12-20 m^2g^{-1} [13]. Catalytic supports can be obtained from aluminium hydroxide while thermal treatment to γ-Al_2O_3 form containing large surface area [14].

Research has shown that Ni catalysts are active and stable when Ni is placed on nanometric ZrO_2 (15-20 nm), MgO (10-20 nm) and γ-Al_2O_3 (5-19 nm) supports [15]. The reason for such characteristics and coal formation on a catalyst surface is related to Ni particle size and distribution on a layer as well as its electron density. The more active the catalyst surface area, the greater the amount of molecules reacted per unit of time. Preferably, produced catalyst should have surface area of 100 – 400 m^2g^{-1}. Atoms of the moving metal should be precipitated into micro pores of a surface by a dispersion method with the derivative size of 10 - 100 Å.

There are many technologies for catalytic layer formation from the liquid phase, such as suspension, sol-gel deposition, hybrid method between suspension and sol-gel, deposition on structured objects from suspension, sol-gel or hybrid methods, electrophoretic deposition, electrochemical deposition and electroless plating, impregnation. Other methods are chemical vapour deposition, physical vapour deposition, flame assisted vapour deposition, flame spray deposition, powder plasma spraying and synthesis of zeolites [16].

The most common method used in catalyst manufacture is as follows: metal salt water solution is impregnated into the support material with a large surface area, e.g., γ-Al_2O_3, α-Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, ZrO_2, TiO_2. Another method is called co-precipitation. According to the previously discussed method, metal salt solution is mixed together, in the constant pH environment and placed onto desired product. Normally, Ni/γ-Al_2O_3 catalyst contains 15-20% of Ni. Finally, Ni/γ-Al_2O_3 is thermally treated in reducing hydrogen atmosphere under 700 °C temperature [17].

Samples of ceramic catalysts D16 x L14 which are filled with convertering oven pipes are presented in Fig. 1.

Fig. 1 Samples of ceramic catalysts

Other effective and promising method to produce stable and active catalysts is an application of hydrotalcites (HT) [8]. HT- like compounds are defined by general formula $[M(II)_{1-x}\ M(III)_x\ (OH)_2]^{x+}\ A^{z-}{}_{x/z}\ mH_2O$. Such compounds have CdI_2 type of structure with partial M(II) / M(III) substitution where the corresponding positive charge is balanced by interlayer anions. The Ni-Al type of hydrotalcite, often referred to as takovite, has formula of $[(Ni_6Al_2)\ (OH)_{16}(CO_3)\ 4H_2O]$ [18]. The typical thermal behaviour of HT is that under low temperatures, the interlayer crystal water is lost with no indication of structural degradation. HT-like compounds are stable under temperature of 400°C [19]. If higher temperature is applied, hydroxyl groups form the brucite-like layer and the anions which transform into oxides or spinels, characterized by high stability and homogeneous distribution of introduced cations.

Thermal degradation of HT is accompanied by dispersion of metal oxides with metal components that contain a large surface area [20]. These mixed oxides are promising materials in various fields and applications of catalysis [21]. An interesting example of Ni-Al type hidrotalcite production is a case where precursors were prepared by coprecipitation at constant pH. The precipates were filtered, dried at 80°C and then treated hydrothermally in a teflon coated autoclave at 180°C for 48 h [22]. But in this case, HT was produced as a powder, but not as a coating. Hydrotalcite type coating with good adhesion on a steel substrate would be a very complex difficult problem.

In addition to the selection of catalytic material and the verification of its manufacturing technology, the other important issue is to reduce the catalysts' volume. In our opinion, thin catalytic layer formation on the several times larger volume of pallets is economically inefficient. A catalyst with a large support structure occupies a lot of space. On the other hand, the catalytic steam reforming process is endothermic and requires high energy consumption. It also requires high temperature operating furnaces that are expensive and technically complex equipment.

Catalyst formed on metal supports will significantly reduce this problem; however it has to ensure efficient gas flow intermixture inside the whole volume of the reaction tube. Such catalysts will be relatively lighter than the industrial-ceramic and will be lower in terms of volume, thus reducing expensive reaction tube technical specifications. Heat transfer in the system "coat-support", as well as in all the reaction tube cross-sections will be more efficient and smooth. The geometric surface area of the catalytic zone will occupy from 5 to 10 times less space inside the same volume of the reactor tube compared to the ceramic-type catalyst, thus also lowering size of the high temperature furnace and energy costs of the process. It is expected that when using an effective catalyst on metal supports, the catalytic process temperature will be reduced. Finally, the process energy demand will be reduced and the technological equipment will be cheaper. All those improvements will reflect in gas price reduction.

The major problem of the technology of efficient catalyst on a metal support is the difficulty to form repetitive, reliable catalytic coating that is durable thermodynamically, chemically stable and at the same time is sufficiently catalytically effective for entire product lifetime.

Research goal: to form reliable catalytic surface (i.e. corresponding to the adhesion, thermal, chemical, and catalytic requirements) on a metal support when applying activated thermal-chemical condensate deposition method.

Research purposes:

1. Research and investigate the Ni-Al-O-type coatings designed for steam reforming gasification and steam reforming catalytic processes, carried out at 700-900°C.
2. Modify the catalytic Ni-Al-O-type coatings, by transferring them from the oxide into the partially oxide-hydrotalcite and then to the final oxides, oxide-spinel phase formation and to investigate their properties.

2. Experimental

In order to obtain a catalytic Ni-Al-O coating, the activated chemical vapour deposition method was used [23]. The coatings were placed on 40 μm thickness ferritic Sandvik 0C-404 strip steel, without underlayer. The composition of the steel is presented in Table 1. The thickness of the formed coating was 30 μm at both sides of the strip. During the coating formation process, the temperature did not exceed 250 °C [24].

Table 1

Chemical composition of Sandvik 0C-404steel strip [25]

C	Cr	Al	Si	Mn	P	S
0.02	20.5	5.50	0.50	0.35	0.02	0.005
max			max	max	max	max

The described system of coating (Ni-Al-O) – support was evaluated with regard to following characteristics: adhesion and chemical stability, surface morphology, structure, crystallites' size, chemical and phase composition. The properties of the formed coatings were investigated under three different technological methods:

- Th- Thermal treatment;
- Ht- Hydrothermal treatment;
- Ht-Th- Hydrothermal- thermal treatment.

Thermal treatment (Th). Coating samples were treated at temperatures between 100-1200°C at a pressure of 1 bar. Thermal treatment was performed by furnace SNOL 1.6.1-11 at a heating rate of $10°C{\cdot}min^{-1}$. The sample was kept inside the furnace for 4 hours, and it cooled inside the equipment.

Hydrothermal treatment (Ht). Samples used were a series of small samples that were taken from the Th method and thermally treated at 300°C. Hydrothermal treatment was carried out using a 2.5L autoclave constructed for the exact specifications of the test (Fig. 2). The lower chamber of the autoclave A (≈ 1/3 volume) was filled with a carbonized water before heating.

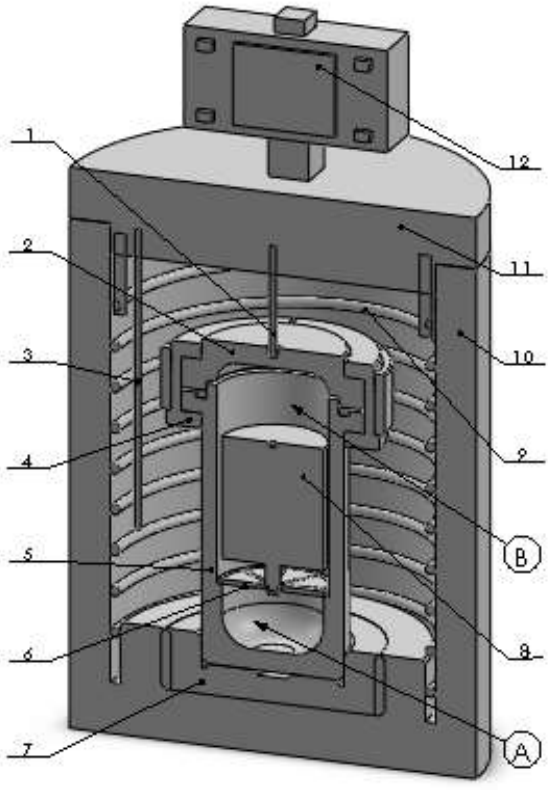


Fig. 2 Hydrothermal device (autoclave). Principal scheme: *1* - autoclave thermocouple, *2* - autoclave lid, *3* - furnace thermocouple, *4* - gasket, *5* - autoclave housing, *6* - tablemat, *7* - metal plate, *8* - samples container, *9* - heating elements, *10* - furnace insulation shell, *11* - furnace lid, *12* - module of device power and the control parameters, *A* - zone A, *B* - zone B

The samples together with catalytic units were placed in the upper part B of the autoclave that was above the liquid phase. While heating the autoclave, supercritical steam phase was formed in the chamber. The desired pressure inside the autoclave chamber was obtained by selecting the heating temperature using the empirical relationship presented in the following graph (Fig. 3).

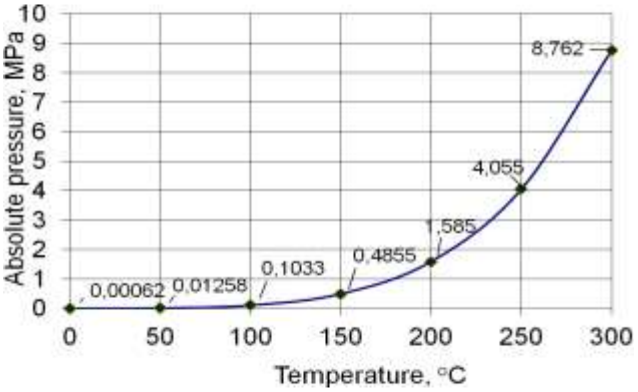


Fig. 3 Temperature and pressure dependence of supercritical steam in the autoclave

The selected hydrothermal process parameters were as follows: temperature 200°C, pressure 15 bar, 6 hours of sample preservation time inside the autoclave. The equipment heating rate was $10°C{\cdot}min^{-1}$. The samples were cooled inside the autoclave until the pressure was reduced to atmospheric level.

Hydrothermal thermal treatment (Ht-Th). After being removed from autoclave, samples were then treated at process-specific temperatures of 700°C and 900°C. The rest of the thermal treatment conditions were the same as in the Th method.

The samples for catalytic tests were prepared of 2 types of coated strips: the first type of a stretched die-punched strip, and the second of a solid-perforated strip (Fig. 4). Both first and second type of coated strip should be placed on top of each other. In this research, the combined strip was rolled with a diameter of 0.04 m and a height of 0.1 m. The stretched – stamping method rather than longitudinal corrugating method was carried out in order to make the contact of the gas molecules more efficient and ensure their migration along all possible block lengths of the reactor tube. The material was perforated to ensure smooth migration across the entire cross-section of potential catalytic units. Such technological solutions should work for any industrial catalyst placed on a metal support.

Fig. 4 Pressed-perforated structure of the catalytic unit: *1* - stamped punching-coated perforated strip, *2* - covered with perforated strip

Coating adhesion (critical scratching load) was tested while applying the "scratching" method, using a specially designed device for this type of coating adhesion testing [26]. The technically clean 20% HCl and HNO_3 solution (3:1 ratio) and in the other a case-1M NaOH solution were used in order to investigate their effect on coating-support systems over a 300 hour test period. The material phase composition was determined via X-ray diffractometer DRON-6 while using the PDF-2 database [27]. The surface morphology and elemental composition was studied by applying SEM EV0-50 (energy dispersion spectrometry, and elemental analysis) tool. The analytical results were obtained in INCAx – sight detector with EDS (energy dispersion spectrometer) support. Experimental results are presented in mass units. The size of the system crystallites was determined by Sherrer's equation and studied using X-fit program with pseudo Voight functional simulation [28].

3. Results

The adhesive relationships within the coating and the plate (method Th) consistently increased when the heat treatment temperature was raised up to 1100°C and reached a value of 46.0 N (Fig. 5). Above temperature point of 1200 °C, adhesion decreased. This variation exists because Sandvik 0C-404 strip steel, which is suitable both for this experimental work and as a heating element, itself becomes crisp at such high temperature and thus degrades. At heat treatment temperature of 300°C, the coating adhesion for Th and Ht methods were 27.0 and 25.3 N, respectively. Hydrothermal treatment of the coating adhesive contacts decreased slightly compared with the method of thermal treatment alone, because the surface layer was formed from the vapour phase at relatively low energies. The coating adhesion at 900°C, the maximum operating temperature of the catalyst, was 34.0 N for the Th method, while in Ht-Th method it almost did not decrease at all and was 33.8 N.

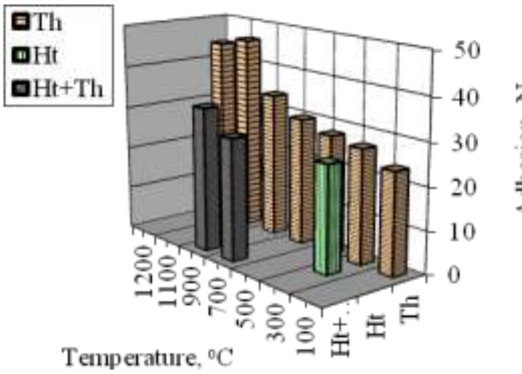


Fig. 5 Critical load of Ni-Al-O coating in the scratch testing depending on thermal treatment method and temperature

Under the Th method, the system "coating-support" resistance of 20% HCl and HNO_3 acid (ratio 3:1, same as aqua regia) solution consistently increased when heat-treatment temperature of samples was increased to 1100°C for 156 hours (Fig. 6). At 1200°C the system "coating-support" resistance to acid solution decreased due to high temperature support degradation.

Immediately after the hydrothermal treatment, the Ht method with the system "coating-support" resistance to acidic environment was studied. At this temperature the result was similar to the Th method: 20.5 and 22 h, respectively.

For comparison, in this method coated stainless Sandvik 0C-404 strip steel was used as a support and it passed acid treatment about 4 times longer than the uncoated one.

Resistance to acid solution under the maximum catalyst operating temperature of 900°C was 71h for the Th method and 71.8h for Ht-Th method. Thus, hydrothermal treatment influenced the final result and increased the "coating-support" resistance to acid solution.

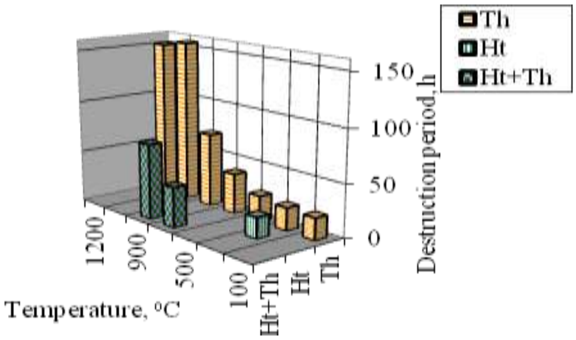


Fig. 6 Resistance of the system "coating Ni-Al-O – substrate" to 20% acids HCl and HNO_3 (ratio 3:1)

The use of 1M NaOH solution has made absolutely no impact on the "coating-support" system after the entire 300 hours test period.

From adhesion and chemical aspects perspective, these results reveal a reliable, long-term activity of the catalyst under relatively high temperature, high pressure and, at the same time, aggressive chemical media conditions. It is important to note that the gas flow through the catalyst is less than 1 $m \cdot s^{-1}$ in industrial conditions and, therefore, the process experiences abrasion.

After XRD studies (Th method) it was found that the system heat treated at 100-1200°C discrete (100°C) temperature range had phases: phase substrate Fe-Cr oxide and five phases (Fig. 7). Depending on the heat treatment temperature it was: γ-Al_2O_3, NiO, $NiAl_{32}O_{49}$, $NiAl_2O_4$ and α-Al_2O_3phase.

It was observed that after the thermal treatment at any temperature system the "coating-support" had no metallic Al and Ni phases. γ-Al_2O_3 and partially NiO phase transformation into spinel Al-Ni phases, which is also a catalyst, only started at 1000 °C. The beginning of the transition phase was characterized by the appearance of $NiAl_{32}O_{49}$. A catalytic carrier γ-Al_2O_3 phase, with a large surface area, partially began to shift to corundum α-Al_2O_3 only at 1000°C. This means that the large surface area containing catalytic coating was formed. This coating, in terms of phase, is functional and can work even at higher temperatures.

After XRD studies (Th, Ht and Ht-Th methods), it was found that the system "coating-support" after heat treatment at 300°C and hydrothermal treatment with autoclave (Ht method) contained the following phases: substrate phase Fe - Cr and oxide phases (Fig. 8).

Oxide phases were bunsenite–NiO, γ-$Al_2O_3$and vapour phase formed plohmite- AlO(OH) and hydrotalcite-takovite- $[(Ni_4Al_2)(OH)_{12}CO_3(H_2O)_3]_{0,5}$.

After the hydrothermal treatment hydrotalcite and oxide structure were formed on the coating surface. At the regular catalyst performance temperature of 700°C, (900°C for method Ht-Th) after heat treatment, the coating had the same phase as after the usual heat treatment at the same temperature, except the XRD peaks were lower than for Th method. This means that the phase degree of crystallization is lower for the Ht-Th method than for Th method.

In all three methods a nano crystal coating was obtained. In the Th method, the substrate crystal size in-

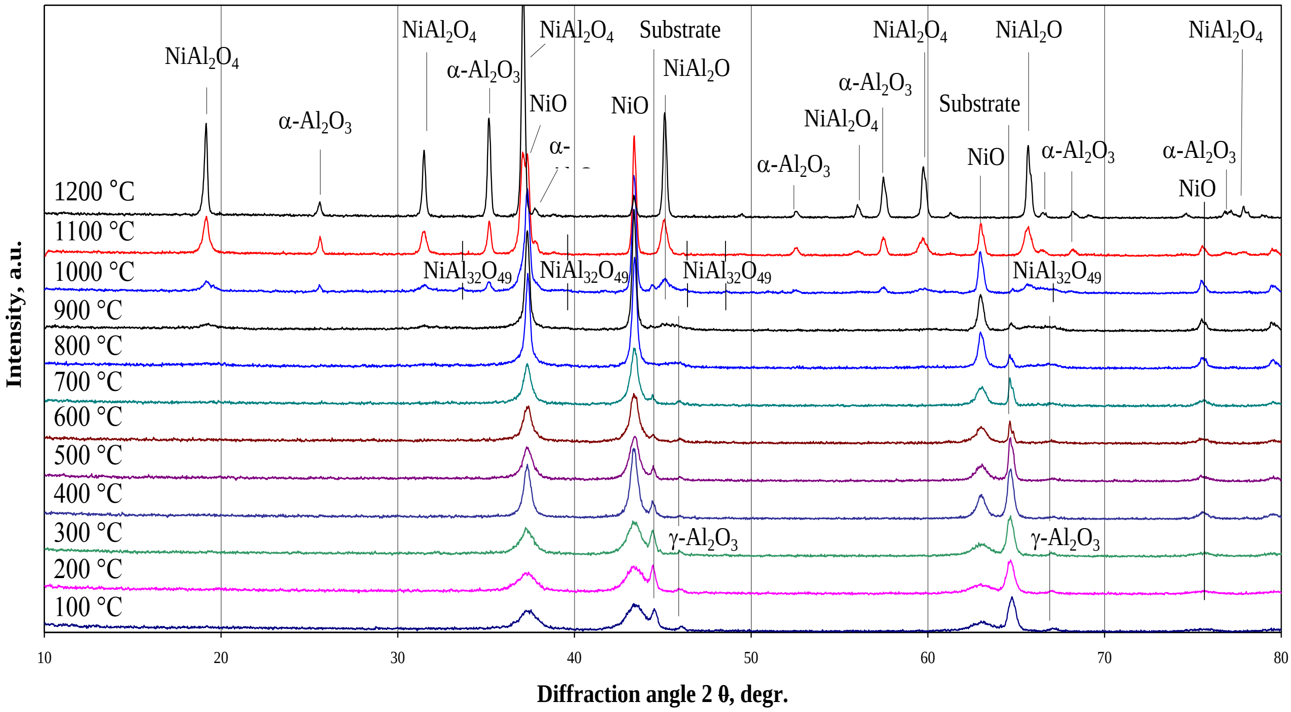


Fig. **7** XRD patterns of a system “Ni-Al-O coating - substrate” after thermal treatment (Th method)

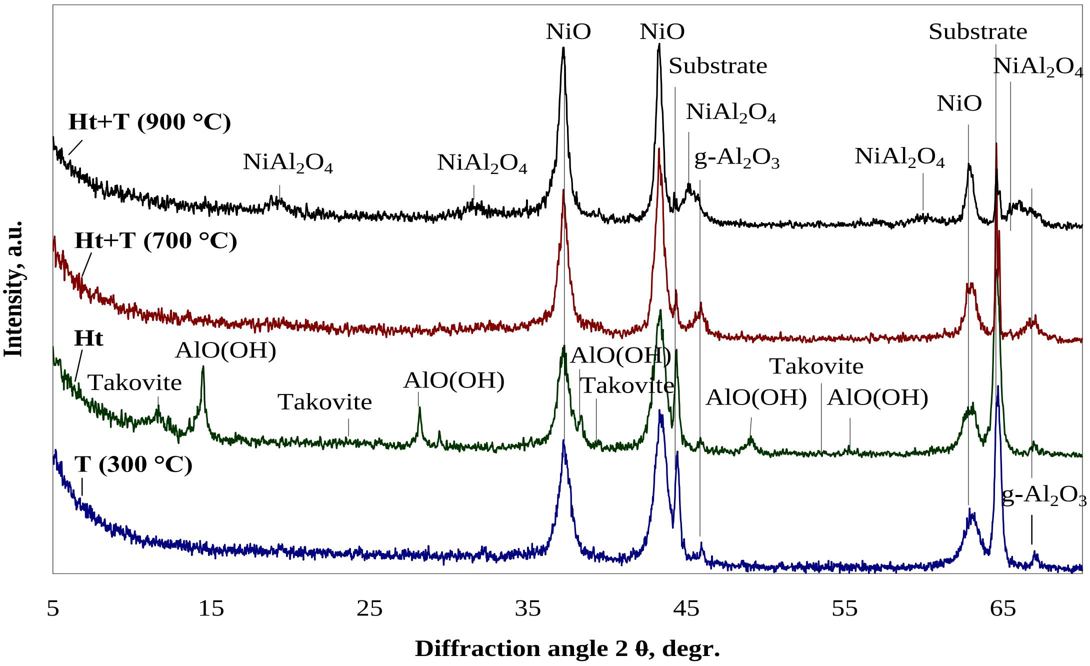


Fig. 8 XRD patterns of a system “Ni-Al-O coating- substrate” after thermal treatment at 300°C temperature (Th method), hydrothermal treatment (Ht method), hydrothermal- thermal treatment at 700°C and 900°C temperatures (Ht-Th method)

creased steadily from 30.3 nm at 100 °C to 102.0 nm at 800 °C (Fig. 9).

A catalytic carrier phase γ-Al_2O_3 with a large surface area existed at 100-900°C temperature range and the crystal size did not exceed 20.0 nm. This result perfectly correlates with the other author’s [15] experimental results in terms of fairly good catalytic carrier settings. An interesting fact is that the most active catalytic NiO phase existed over the temperature range from 100°C to 1200°C and no fully spinel derivatives were observed. The size of the crystallites increased from 10.2 nm at 200°C to 72.0 nm at the maximum operating 900°C temperature.

The decrease of NiO crystallites size over 1100°C is due to the gradual predominance of spinel phase $NiAl_{32}O_{49}$, $NiAl_2O_4$ and corundum α-Al_2O_3 occurrence at 900-1000 °C temperature range, on the coating. After hydrothermal treatment (Ht method), the newly formed plohmite crystallite’s size was 28.3 nm and hydrotalcite-takovite was only 4.4 nm. In comparison to the Th method, the appearance of new phases formed relatively large

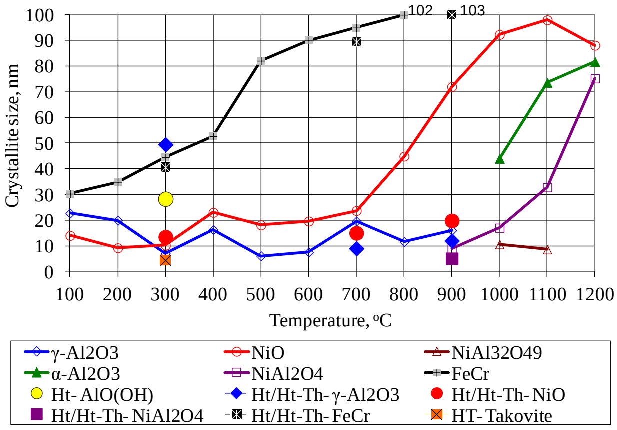


Fig. 9 The distribution of crystallite size of the system “Ni-Al-O coating – substrate”

49.5 nm γ-Al_2O_3 crystallites. Support and nickel crystallites of oxide remained by the same size.

In the Ht-Th method, the plohmite phase has been completely transformed to the case of aluminium oxide γ-Al_2O_3 at 700°C temperature. The same phase has been determined in the Th method. According to theory [14], this transformation was supposed to take place at 400°C. However, it is important that the crystallite size decreased from 3 to 10 units for all phases in the “coating-support” system. That means thermal structure stabilization of the system was carried out. Such stabilization is obvious under 900°C catalyst operating temperature. Support crystallites were the same size as in Th method under 800°C. Catalytic carrier γ-Al_2O_3 and spinel phase $NiAl_2O_4$ crystallites are also reduced and, even more importantly, the maximum size of catalytically active NiO phase crystallites was only 19.6 nm, instead of the former 72.0 nm in the Th method. In most of the cases, large crystallites reduce the catalytic activity and made it difficult to deal with them. However, crystallites can always be grown up to the required size by raising the heat treatment temperature. That would result in a catalyst operating temperature margin. From the entire complex of new data, hypothetical assumptions can be made: the catalyst operating temperature should be reduced and this reduction should be within 100°C temperature range. This is another improvement that would significantly reduce the price of the process and the cost of produced gas.

SEM images (Fig. 10) represent coating morphology, characterized by only Ni-Al-O type of coatings resulting from the heat-activated chemical condensation deposition method (Th method) and heat treated at 900 °C temperature afterwards.

The panoramic image (a) (magnification 5000×) of the heterogeneous coating with a variety of structural defects is seen. The multiple layers of the coating can be seen in image (b). Such defined porosity is similar to membrane or microfilter and ensures the migration of gas molecules inside the coating volume. Therefore, it is an effective design solution, which appears during coating formation process.

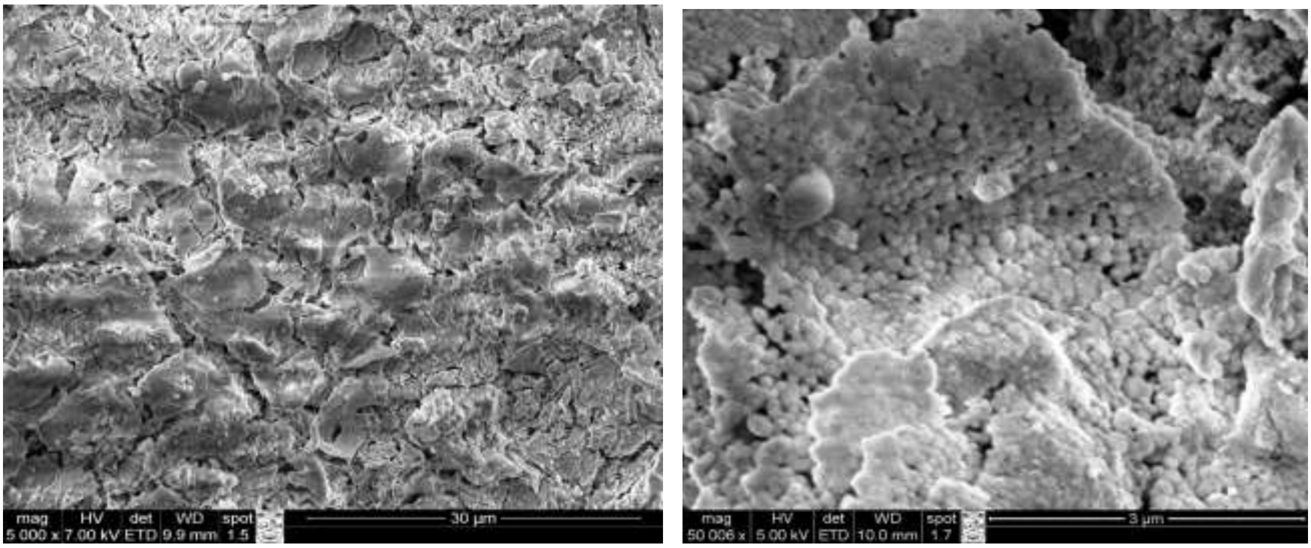
Other SEM images (Fig. 11) present the coating surface after hydrothermal treatment (Ht method).

In the presence of partial hydrotalcitic structure (panoramic view (a), magnification 5000×) the surface is cracked and the material is deposited on the surface in the form of ultra dispersed vapour. In 50000x magnification in (b), the coating looks fine-grained with micro cracks.

In the Ht-Th method (after hydrothermal-thermal processing) at a catalyst operation temperature of 900°C (panoramic view) (a) less cracks can be seen and the vapour phase is deposited and dispersed on the upper layers of the coating (Fig. 12).

With a magnification of 50000× (b) the coating seems to be of two types: one, which is formed of crystallites with clearly geometrically defined shape and second, ultra dispersed formation allusion. In a relatively high coating magnification of 200000×, fine-grained surface is seen, where identifiable objects size is 3-5 nm (Fig. 13).

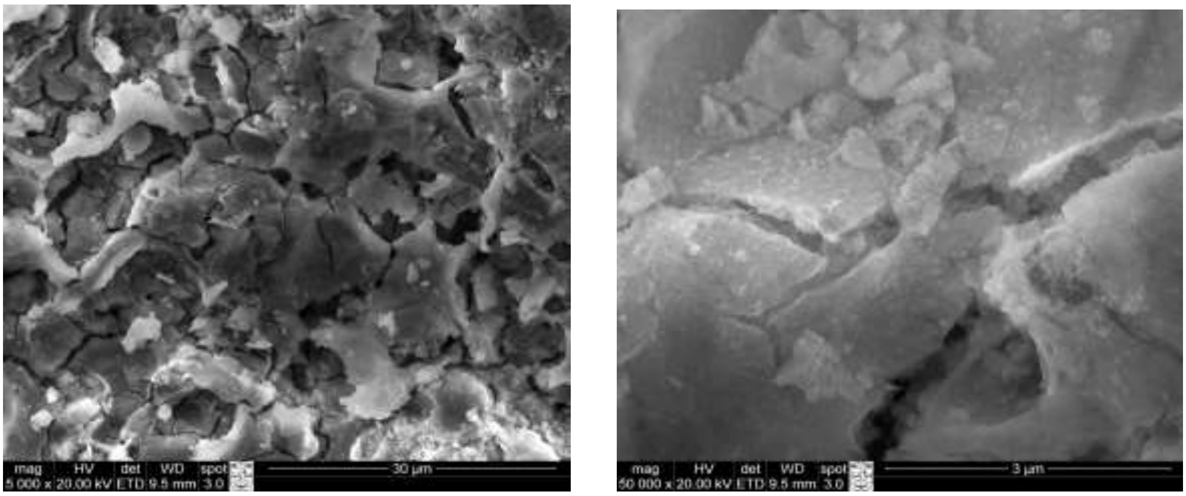
Analysis of common chemical elements spectrum (EDS) on the surface area of 10 mm^2 has been reported to be predominant in Ni content in all three cases (Fig. 14). The highest content of Ni (63.2%) was observed in the first case (Th method) while the lowest content was 51.5% in the Ht-Th method.



a

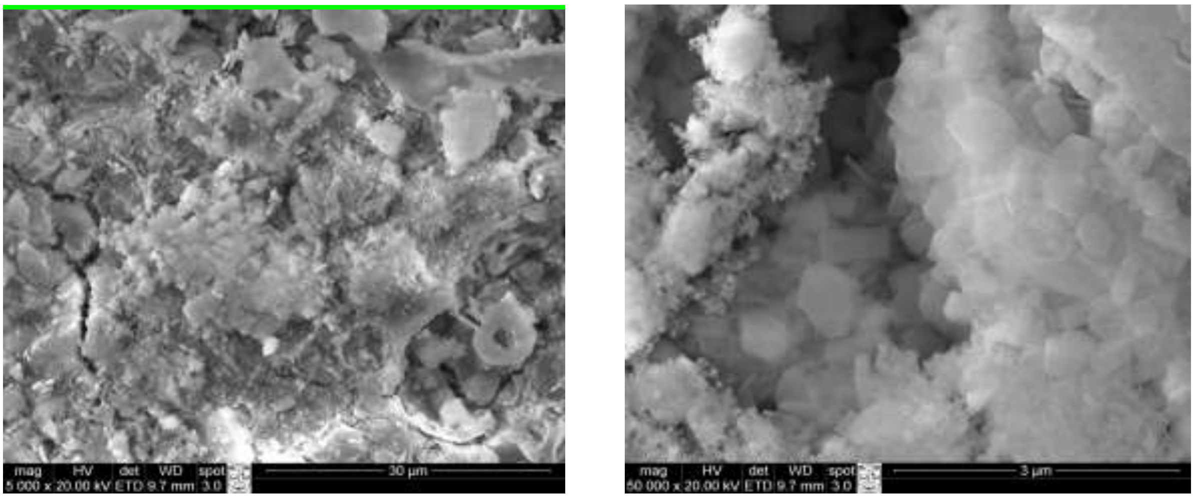
b

Fig. 10 Morphology of a Ni-Al-O coating on a Sandvik 0C-404 strip steel after thermal treatment 900°C (Th method)



a b

Fig. 11 Morphology of a Ni-Al-O coating on a Sandvik 0C-404 strip steel after hydrothermal treatment (Ht method)



a b

Fig. 12 Morphology of a Ni-Al-O coating on a Sandvik 0C-404 strip steel after hydrothermal treatment and heat treatment at 900 °C (Ht-Th method)

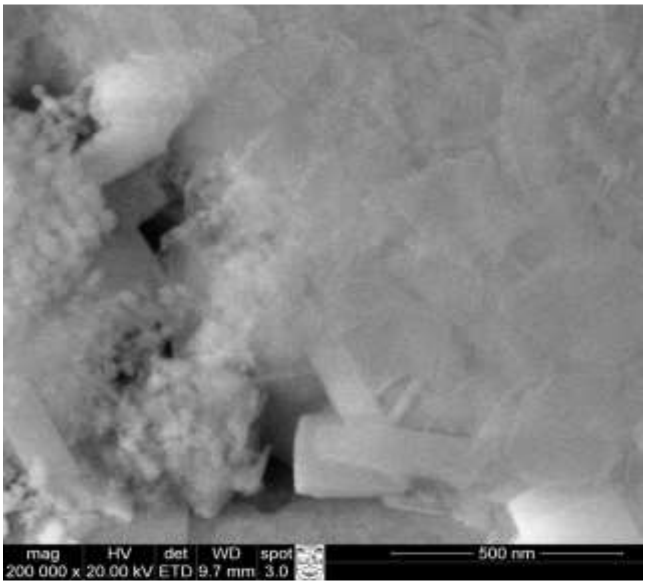


Fig. 13 Morphology of a Ni-Al-O coating on a Sandvik 0C-404 strip steel plate after hydrothermal treatment and heat treatment at 900°C (Ht-Th method). Magnification 200000×

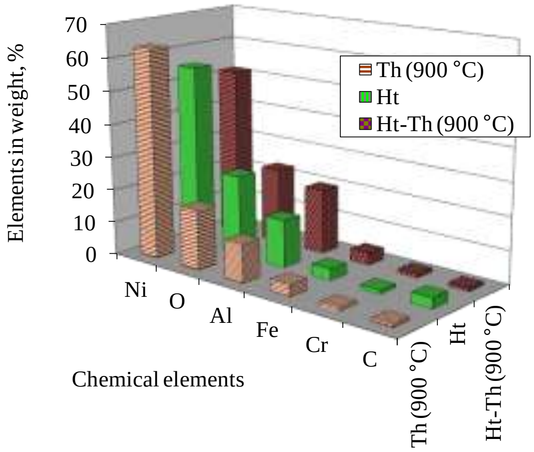
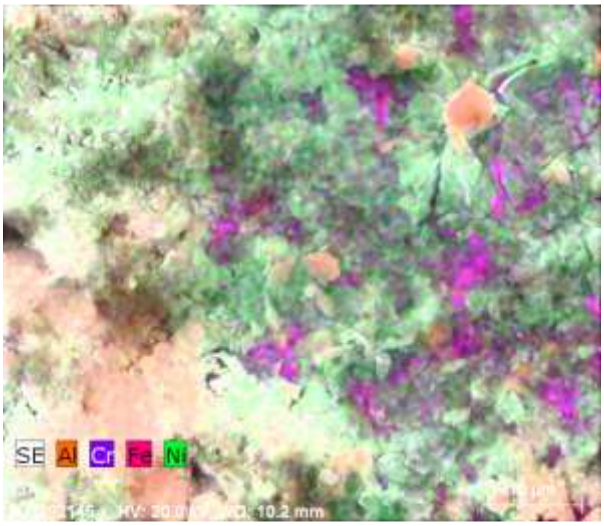


Fig. 14 Elemental chemical composition in the surface area of 10 mm^2 (from EDS spectra), %

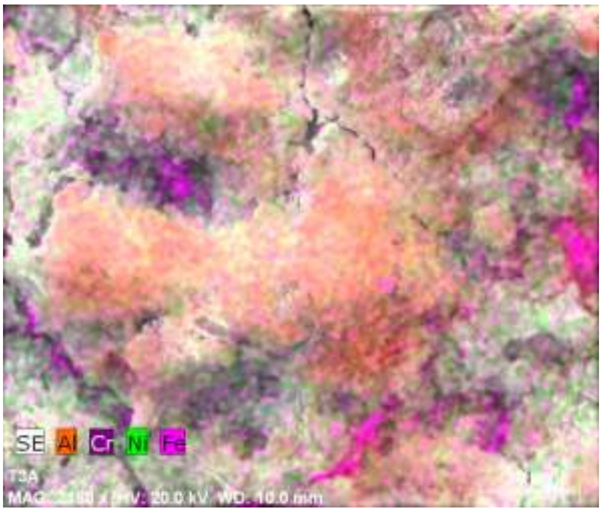
Al content was the lowest at Th method (11.5%) and highest (19.7%) in Ht-Th method.

This trend suggests that under the hydrothermal treatment, chemical elements in the vapour phase were transported and redistributed on the surface towards content distribution equilibrium. Next, heat treatment was performed. When setting the temperature to 400°C, crystal water was removed and a further temperature increase to 700-900°C lead to surface microstructure formation. Increased carbon (3.2%) and oxygen (24.5%) amount in Ht method technology represents hydrotalcite structure presence in the coating.

Morphological characteristics of distribution of chemical elements in surface coating Ht (Fig. 15, a) and Ht-Th (Fig. 15, b) processes are identified by colour coating mapping in Fig. 15.



a



b

Fig. 15 Morphology (mapping) of a Ni-Al-O coating on a Sandvik 0C-404 strip steel after a) hydrothermal treatment (Ht method), b) hydrothermal - thermal treatment at 900°C (Ht-Th method)

Special attention must be given to the change in Ni concentration when Ni moves inside coating (Fig. 15, b). NiO dispersedly mixed with γ-Al_2O_3 and thus increased catalyst conversion and selectivity. Furthermore, it reduced catalyst volume used for the same technological process.

The distribution of chemical elements was investigated for each of morphologically different coating surface layers. This was done for Th, Ht and Ht-Th methods using 5 EDS spectra for a small surface area. When determining the chemical elements after heat treatment at 900°C (Th method), the obvious imbalance in the distribution was observed with respect to all 5 spectra (Table 2). The spectra indicate Ni as dominant chemical element, but the amounts are very different in various locations on the surface.

Table 2

Elemental chemical composition at different locations of the coating surface (Th method) after thermal treatment at 900°C (from EDS spectra)

Th method	Element, surface concentration, %					
Spectrum	Ni	O	Al	Fe	Cr	C
Spectrum 1	78.92	14.18	1.4	3.6	1.15	1.35
Spectrum 2	65.34	13.77	16.24	2.93	1.08	0.63
Spectrum 3	66.47	2.12	11.42	15.44	4.4	0.15
Spectrum 4	39.21	37.79	18.17	2.46	1.28	1.09
Spectrum 5	11.2	54.02	31.26	1.47	0.55	1.49

When determining the chemical elements after hydrothermal treatment (Ht method) the spectra from a small increment surface area show a relatively low nickel content. At the same time, an increase in carbon and, in particular, oxygen was observed which in some cases was up to 62% (Table 3). This is related to carbon and crystalline water hydrotalcite presence in the coating structure.

Table 3

Elemental chemical composition at different locations of the coating surface (Ht method) after hydrothermal treatment (from EDS spectra)

Ht method	Element, surface concentration, %					
Spectrum	Ni	O	Al	Fe	Cr	C
Spectrum 1	9.45	58.63	28.78	1.17	0.53	0.86
Spectrum 2	54.3	23.97	5.32	3.68	1.86	2.57
Spectrum 3	6.77	62.65	25.37	1.1	0.57	1.56
Spectrum 4	52.01	23.71	13.04	3.24	1.12	1.11
Spectrum 5	56.75	19.31	8.39	10.16	3.36	0.89

Examination of the chemical elements of the hydrothermal-heat treatment at 900°C (Ht-Th method) under a spectrum increment in small surface areas shows homogenization of chemical elements. Results of chemical decomposition at different locations on coating surface are presented in Table 4.

When the water and gas phase interact, they form different and statistically heterogeneous coating surface energy fields.

Table 4

Elemental chemical composition at different locations of the coating surface (Ht-Th method) after hydrothermal-thermal treatment at 900°C (from EDS spectra)

Ht-Th method	Element, surface concentration, %					
Spectrum	Ni	O	Al	Fe	Cr	C
Spectrum 1	31.17	40.55	23.1	2.14	0.81	1.16
Spectrum 2	48.92	36.86	7.5	3.88	1.27	0.68
Spectrum 3	20.97	49.31	25.86	1.69	0.57	0.93
Spectrum 4	33.76	38.01	21.95	2.73	1.09	1.3
Spectrum 5	35.28	30.58	29.04	2.29	0.77	0.8

After analysis of all three methods, the elemental redistribution appeared dispersedly, creating a lot of phase variation in the coating micro area.

4. Conclusions

1. Repetitive properties of Ni-Al-O coatings for gasification and steam reforming catalytic technological processes were formed on a 40 µm thick Sandvik 0C-404 strip steel. The formation was achieved by the use of the activated thermal-chemical condensate deposition method. The coating thickness obtained was 30 µm on each side of the strip. Three technological treatments after coating formation were analyzed: thermal, hydrothermal and thermal-hydrothermal.

2. The coating adhesion strength increased by raising the temperature and was 34 N at the temperature 900°C. The chemical resistance of system was tested by short-term experiments on 20% HCl and HNO_3 acid (ratio 3:1) solution. As a result, the chemical resistance exceeded the 70 hour limit.

3. All surface phases were obtained in nanocrystalline size. When a hydrothermal treatment was applied to the coating, it had a new hydrotalcite-takovite and plohmite phases with crystallite sizes of 4.4 nm and 28.3 nm respectively. After the hydrothermal-thermal treatment these phases transformed into oxide and spinel phases. Due to a dispersed chemical elements distribution, a relative decrease in the size of all system “coating-support” crystallites was observed.

4. According to the technological process sequence, redistribution of the coating’s chemical elements took place with respect to homogenization direction.

5. A technical solution for the catalytic block gas channels formation was presented. The system “Ni-Al-O coating – Sandvik 0C-404 strip steel” can be used as a commercial catalyst for gasification and steam reforming processes.

6. The system “Ni-Al-O coating - Sandvik 0C-404 strip steel” application would reduce the industrial catalytic converters’ volume, process temperature and energy consumption.

References

1. **Sakai, T.; Kawshima, A.; Koshikawa, T.** 2009. Economic assessment of bath biodiesel production processes using homogeneous and heterogeneous alkali catalysts, Bioresource Technology 100: 3268-3276. http://dx.doi.org/10.1016/j.biortech.2009.02.010.
2. **Brigwather, A.V.; Toft, A.V.; Brammer, J.G.** 2002. A techno- economic comparison of power production by biomass fast pyrolysis with gasification and combustion, Renewable and Sustainable Energy Reviews 6: 181-248. http://dx.doi.org/10.1016/S1364-0321(01)00010-7.
3. **Rapagna, S.; Provendier, H.; Petit, O.; Kiennemann, U.; Foscollo, P. U.** 2002. Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification, Biomass and Bioenergy 22: 377-388. http://dx.doi.org/10.1016/S0961-9534(02)00011-9.
4. **Corella, J.; Toledo, J. M.; Padilla, R.** 2004. Catalytic hot gas cleaning with monoliths in biomass gasification in fluidized beds. 1. Their effectiveness for tar elimination, Industrial and Engineering Chemistry Research 43: 2433-2455. http://dx.doi.org/10.1021/ie0307683.
5. **Kolbitsch, P.; Pfeifer, C.; Hofbauer, H.** 2008. Catalytic steam reforming of model biogas, Fuel 87: 701-706. http://dx.doi.org/10.1016/j.fuel.2007.06.002.
6. **Jarosh, K.; El Solh, T.; De Lasa, H. I.** 2002. Modeling the catalytic steam reforming of methane: discrimination between kinetic expressions using sequentially designed experiments, Chemical Engineering Science 57: 3439-3451. http://dx.doi.org/10.1016/S0009-2509(02)00214-2.
7. **Levent, M.; Gunn, D. J.; Ali el – Bousiffi, M.** 2003. Production of hydrogen - rich gases from steam reforming of methane in an automatic catalytic microreactor, International Journal of Hydrogen Energy 28: 645-959. http://dx.doi.org/10.1016/S0360-3199(02)00195-7.
8. **Van Beurden, P.** On the catalytic aspects of steam – reforming. A literature survey, ECN - I04 - 003: 5-26.
9. **Rudzinski, W.; Borowiecki, T.; Panczyk, T.; Dominko, A.; Gac, W.** 2002. Thermosorption studies of energetic properties of nickel and nickel- molybdenum catalysts based on the statistic rate of interfacial transport, Applied Catalysis A: General 224: 299-310. http://dx.doi.org/10.1016/S0926-860X(01)00848-1.
10. **Williford, R.E.; Chick, L.A.** 2003. Surface diffusion and concentration polarization on oxide - supported metal electrocatalyst particles. Surface Science 547: 421-437. http://dx.doi.org/10.1016/j.susc.2003.10.026.
11. **Eguchi, K.; Kojo, H.; Takeguchi, T.; Kikuchi, R.; Sasaki, K.** 2002. Fuel flexibility in power generation by solid oxide fuel cells, Solid State Ionics 152-153: 414-416. http://dx.doi.org/10.1016/S0167-2738(02)00351-X.
12. **Krumdieck, S.; Page, S.; Round, S.** 2004. Solid oxide fuel cell architecture and system design for secure power on an unstable grid, Journal of Power Sources 125: 189-198. http://dx.doi.org/10.1016/j.jpowsour.2003.07.011.
13. **Sutton, D.; Kelleher, B.; Ross, J.R.** 2001. Review of literature on catalysts for biomass gasification, Fuel Processing Technology 73: 155-173. http://dx.doi.org/10.1016/S0378-3820(01)00208-9.
14. **Gorshkov, V.S.; Saveljev, V.G.; Fiodorov, N.F.** 1988. Physical Chemistry of Silicates and Other Refractory Combinations. Moscow: Vishaja shola, 400p.
15. **Hou, Z.; Yokota, O.; Tanoka, T.; Yashima, T.** 2003. Investigation of CH_4 reforming with CO_2 on mesoporous Al_2O_3- supported Ni catalyst, Catalysis Letters 89(1- 2): 121-127.
16. **Meille, V.** 2006. Review of methods to deposit catalysts on structured surfaces, Applied Catalysis A: General. 315: 1-17. http://dx.doi.org/10.1016/j.apcata.2006.08.031.
17. **Kish, E.; Marinkovic - Neducin, R.; Lomic, G.; Boskovic, G.; Obadovic, D.Z.; Kiurski, J.; Putanov, P.** 1998. Structural and textural properties of the NiO - Al_2O_3 catalyst, Polyhedron l(1): 27-34. http://dx.doi.org/10.1016/S0277-5387(97)00263-5.
18. **Itianu, M.; Itianu, A.; Zaharescu, M.; Crisan, D.; Marchidan, R.** 2000. IR structural evidence of hydrotalcites derived oxidic forms, Vibration Spectroscopy 22: 75-86. http://dx.doi.org/10.1016/S0924-2031(99)00067-3.

19. **Chmielarz, L.; Kustrovski, P.; Rafalska - Lasocha, A.; Majda, D.; Dziembaj, R.** 2002. Catalytic activity of Co-Mg-Al, Cu-Mg-Al and Cu-Co-Mg-Al mixed oxides derived from hydrotalcites in SCR of NO with ammonia, Applied Catalysis. B: Environmental 35: 195-210. http://dx.doi.org/10.1016/S0926-3373(01)00254-5.
20. **Marchi, J.; Apasteguia, C.R.** 1998. Impregnation - induced memory effect of thermally layered double hydroxides, Applied Clay Science 13: 35-48. http://dx.doi.org/10.1016/S0169-1317(98)00011-8
21. **Reijers, H.Th.J.; Valster - Schiermeier, S.E.A.; Cobden, P.D.; Van den Brink, R.W.** Hydrotalcite as CO_2 sorbent for sorption- enhanced steam reforming of methane, ECN – RX – 05 – 122: 2-28.
22. **Zahao, Y.; Czyzniewska, J.; Prins, R.** 2003. Mechanism of the direct hydrodenitrogenation of naphthylamine on sulfidedNiMo/ Al_2O_3, Catalysis Letters 88(3-4), June 2003: 155-162. http://dx.doi.org/10.1023/A:1024061706148
23. **Babilius, K.; Babilius, A.** 2006. Research of coatings obtained in the activated thermo-chemical condensate deposition method, Al-O system, Materials Science (Medžiagotyra) 2(8): 114-119.
24. **Babilius, K.; Babilius, A.** 2008. Cu-Al-O system: Catalytic coatings obtained by the activated thermo-chemical condensate deposition method, Materials Science (Medžiagotyra) 1(14): 23-28.
25. http://www.matweb.com/search/datasheettext.aspx?matguid=a6393c6cb14144f2ac1d6b26262a1950 [2014.01.30].
26. **Babilius, K.; Babilius, A.** 2010. Mechanical, structural and catalytic properties of the Co-Al-O coatings, Materials Science (Medžiagotyra) 1(16): 40-46.
27. JSPDS Cards – International Center for Diffraction Data. 12 Campus Boulevard Newtown Square, PA 19073-3273, USA.
28. **Cheary, R.W.; Coelho, A.A.** Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England, (http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm).

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Ni-Al-O SISTEMOS KATALIZINIŲ DANGŲ, SUKURTŲ GAZIFIKACIJOS IR REFORMINGO GARU PROCESAMS, TYRIMAS

Reziumė

Straipsnyje tyrinėjama aktyvuotu terminiu- cheminiu kondensato nusodinimo metodu gauta katalizinė sistema „Ni-Al-O danga- juostinis feritinės klasės Sandvik 0C-404 plienas.

Po atlikto terminio, hidroterminio ir hidroterminio- terminio apdorojimo, nustatyti adhezijos, atsparumo agresyvioje aplinkoje, cheminės ir fazinės sudėties, kristalitų dydžio ir kiti parametrai. Visos dangos fazės visais trimis atvejais buvo gautos nanokristalinės eilės. Hidroterminio apdorojimo pasėkoje, dangoje buvo gauta dalinai hidrotalcitinė struktūra. Sukurti katalizatoriai yra patvarūs, turi gerą technologinį atsikartojamumą

Pagal gautus rezultatus galima spręsti, kad sistema „Ni-Al-O danga- Sandvik 0C-404" plienas" gali būti naudojama kaip efektyvus ir pigus, komercinės paskirties nikelio katalizatorius, skirtas gazifikacijos ir reformingo garu procesams atlikti. Tai leistų sumažinti: pramoninių katalizinių konverterių tūrį, technologinio proceso temperatūrą ir energetines sąnaudas.

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RESEARCH OF Ni-Al-O SYSTEM CATALYTIC COATINGS DEVELOPED FOR GASIFICATION AND STEAM REFORMING PROCESS

Summary

This paper explores the catalytic system "Ni-Al-O coating - Sandvik 0C-404 strip steel" obtained by the activated thermo-chemical condensate deposition method.

After the thermal, hydrothermal and hydrothermal-thermal treatment, adhesion, resistance to aggressive environments, chemical and phase composition, crystallite size and other parameters were determined. All coating surface phases for all three methods were obtained in the nanocrystalline range. As a result of hydrothermal processing, the coating had a partly hydrotalcitic structure.

The developed catalysts have excellent adhesion, are chemically stable; in addition, they are technologically repetitive. The system "Ni-Al-O coating - Sandvik 0C-404 strip steel" can be used as a commercial catalyst for gasification and steam reforming processes. Application of such system would reduce the catalytic converters' volume, process temperature and energy demand.

Keywords: coatings, catalysts, steam reforming, gasification, technological treatments, nanostructure, XRD, SEM, EDS, properties.

Received June 19, 2013
Accepted May 09, 2014