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THE PHYSICAL AND MECHANICAL PROPERTIES OF INTERMETALLIC CATALYSTS FOR THE NEUTRALIZATION OF CARBON-CONTAINING COMPONENTS OF EMISSION GASES*

Karina Belokon, Yevheniia Manidina,
Aleksandr Fedchenok, Andrii Banakh, Larysa Mosiyevych**

Zaporizhzhia National University, Zaporizhzhia, Ukraine

Abstract

The analysis of the study results of the physical and mechanical properties of intermetallic catalysts showed that they differ depending on their composition and processing method. The difference in the physical and mechanical properties of the catalysts is explained by differences in their structure, phase composition, porosity and pore size. When manganese is added, the porosity of the catalyst increases as a result of an increase in the volume of large pores while the structure of small capillaries does not change due to the localization of manganese oxide in the catalyst's pores. Yet, the mechanical strength decreases and can be increased if the copper alloy is added in the Ni-Co-Mn catalyst. A major benefit of thermal self-ignition is that the catalyst's strength is 50% higher than that of sintered materials with the same porosity. High temperatures of the process and low impurity content at the grain boundaries (due to self-cleaning) lead to the formation of strong bonds between grains in the crystallite. The average specific surface area for all investigated catalyst samples is 112 m²/g.

Keywords: intermetallic catalyst, phase composition, porosity, strength, specific surface area, thermal stability

1. Introduction

The man-made sources of air pollution with carbon monoxide (CO) and hydrocarbons (C_mH_n) are thermal power stations, internal combustion engines, chemical, petrochemical and metallurgical industries. Large amounts, chemical and biological properties of CO and

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** Corresponding author: e-mail: kv.belokon@gmail.com

C_mH_n in gas emissions cause increased environmental hazards.

One of the most effective methods of protecting air from pollution with carbon monoxide and hydrocarbons is the introduction of advanced waste-free resource and energy-saving technological processes that prevent or reduce emissions of these substances. However, it is not always technologically possible and economically feasible. Therefore, the problems of reducing emissions containing CO and C_mH_n must be solved by both improving conventional methods and by using new alternative, environmentally and cost-effective methods. One of the effective processes of neutralisation of CO and C_mH_n is catalytic oxidation. Strengthening of environmental standards and sanitary regulations prompts to search for new effective and economically viable methods for mitigating gas emissions.

A new generation of modern catalysts requires materials with high catalytic activity and improved mechanical properties. Intermetallic catalysts based on nickel aluminides are of great interest (Borshch et al., 2008). To obtain nickel aluminides, casting and powder metallurgy methods are used with thermal self-ignition techniques gaining more popularity recently (Borshch et al., 2017). Naturally, the method of obtaining a material can largely determine its structure and properties; therefore, it becomes necessary to study these characteristics more thoroughly.

The objective of this paper was to identify patterns in the relationship between porosity and strength of intermetallic catalysts based on the method of their obtaining and alloying degree.

2. Materials and methods

The catalysts studied for the oxidation of carbon monoxide and hydrocarbons were Ni-Al intermetallic systems of stoichiometric composition $NiAl_3$ synthesised by sintering and thermal self-ignition (Belokon et al., 2017; Cheilytko, 2015).

To increase its catalytic activity, the intermetallic $NiAl_3$ was modified by various amounts of transition metals. Thus, the $NiAl_3$ catalysts with additions of Mn, Co and Cu in amounts of up to wt 15% were obtained (Belokon et al., 2020).

Pure powders of nickel, aluminium, cobalt, copper, and manganese oxide were used as the initial components. The dispersion of powders varied from 100 μm to 150 μm . The process of mixture preparation included dosing, mixing, mould filling, pressing, heat treatment, and leaching. The pressing force differed from 2.5 to 5 tons. The mixture was initiated using a tungsten coil. The process was carried out at a pressure of 1 atm.

The microstructure of the obtained catalysts was investigated using a light microscope Neophot-21 and a scanning electron microscope; the phase composition was analysed using an X-ray diffractometer DRON-3. The microhardness of the catalysts was defined using a tester PMT-3. The thermal analysis was carried out using Derivatograph Q 1050 with the sample heated at a rate of 10 degrees per minute. The mechanical strength of the coated samples was determined using a UG-20 machine. Compression and bending tests were carried out according to the state standard 25.503-97. The compression test samples had a diameter of 20mm and a height of 20mm. The specific surface area of the samples was defined using an analyser SORBI-M (Sereda et al., 2015).

The porosity of the samples, which characterises the density of the mixture, strongly affects the combustion process, namely, the maximum temperature of synthesis and burn rate. The porosity was calculated by the formula:

$$\eta = \frac{d_c - d_p}{d_c} \cdot 100\% , \quad (1)$$

where: η is the initial porosity of the sample, %;

d_c is the density of the compact material, g/cm³;

d_p is the density of the pressed sample, g/cm³.

The density of the compact material was calculated by the formula:

$$d_c = d_A \cdot d_B \cdot 100\% (M_A \cdot d_A + M_B \cdot d_B), \quad (2)$$

where: the indices A and B denote the initial components;

M_A and M_B is the weight of components in the composition, %;

d_A and d_B is the density of the corresponding components, g/cm³.

The density of the pressed samples was calculated by the formula:

$$d_p = \frac{m}{V} \quad (3)$$

where: m is the mass of the sample, g;

V is the volume of the sample, cm³.

The pycnometric density was defined by the generally accepted method with measuring vessels known as pycnometers and calculated by the formula:

$$\rho_{pyc} = \frac{M_1 - M}{V_{pyc} - V_1}, \quad (4)$$

where M_1 is the mass of a dry pycnometer with the sample, g;

M – is the mass of a dry pycnometer, g;

V_{pyc} is the volume of the pycnometer, cm³;

V_1 is the volume of liquid in the pycnometer, cm³.

The porosity of the catalyst was calculated by the equation:

$$\Pi = 1 - \frac{\rho_{pyc}}{\rho_{theor}}, \quad (5)$$

where ρ_{pyc} is the pycnometric density, g/cm³;

ρ_{theor} is a theoretical density of the studied material.

3. Results and discussion

The optimal pore structure can be determined for each catalytic process based on the kinetic characteristics of the reaction, the conditions of its conducting and the specific catalytic activity of the catalyst.

The pore structure of the catalyst is controlled by pressing the reaction mixture after thermal self-ignition in the process of heat treatment. The activity of the catalyst often depends on the compaction pressure. When regulating the pore structure of the catalyst focus should be kept on both activity and mechanical strength which can differ significantly as the porosity changes. When preparing the Ni-Co catalysts, the pore structure can be controlled in two ways- by changing the compaction pressure of the reaction mixture and by adding manganese (which forms a metal-oxide structure on the catalyst surface) into the initial mixture before tableting. Table 1 demonstrates the effect of compaction pressure of the reaction mixture on the pore structure and mechanical strength of the prepared catalyst (Belokon et al., 2017).

Table 1. Characteristics of the pore structure and mechanical strength of the catalyst specimens tabletted at different pressures

Compaction pressure, kg/cm ²	Bulk weight, g/cm ³	Porosity, %			SSA, m ² /g	Compressive strength, MPa
		Overall	Pores with $d > 1.8 \times 10^{-5}$ cm	Pores with $d < 1.8 \times 10^{-5}$ cm		
600	1.04	61.8	12.6	49.2	110	14.3
700	1.05	61.4	11.1	50.3	112	14.5
1000	1.11	58.8	2.2	56.6	114	16.9

As Table 1 shows, the overall porosity of the catalyst decreases with a tabletting pressure increase, which is caused by a decrease in the volume of large pores. Yet, the volume of small pores slightly increases. The change of the compaction pressure does not change the radius of the maximum pore volume of the catalyst samples, which equals to about 450Å. The specific surface area of the catalyst per unit of weight remains constant, and the mechanical strength of the products increases with a compaction pressure increase.

Table 2 presents the results of the study of the pore structure of the Ni-Co catalysts doped with manganese. As Table 2 shows, when manganese is added, the porosity of the catalyst increases as a result of an increase in the volume of large pores while the structure of small capillaries does not change due to the localisation of manganese oxide in the catalyst's pores. When the additive amount is increased, the maximum of the pore volume distribution in terms of their radii shifts towards large pores. Table 2 also shows that the porosity of the studied catalyst samples is mainly determined by the volume of large pores, and the size of the inner surface is determined by the development of small capillaries.

When manganese is added, the mechanical strength of the specimen dramatically decreases. However, the catalyst strength can increase if the Ni-Co-Mn catalyst is additionally doped with copper. Copper shifts the equilibrium in the Ni-AL system towards nickel, forming a solid solution based on Ni₂Al₃, double and ternary intermetallics, which contributes to an increase in the mechanical strength of the samples. Thus, when 2% of copper was added during replicate testing of catalysts with 10% and 15% of manganese content, the mechanical strength of the samples changed: from 12.2 to 15.8MPa for the former sample, and from 12.1 to 14.5MPa for the latter one (Table 3) (Sereda et al., 2019a). The pore structure of the catalyst depends also on the method of its obtaining. The catalysts synthesized under thermal self-ignition have a number of advantages over the same catalysts obtained using conventional powder metallurgy methods. Ultimately, they have very high final porosity (from 5% to 10% higher). There are a few reasons for that: first, a negative volume effect of the combustion reaction since the molecular volume of the products of combustion is usually less than that of reagents; second, the emission of impurity gases in the process of transforming the mixture into the final product. There is no such effect with conventional sintering of catalysts.

Table 2. Characteristics of the pore structure and mechanical strength of the Ni-Co catalyst doped with manganese

Catalyst properties	Manganese content, wt %			
	5	10	15	20
Apparent density, g/cm ³	1.83	1.80	1.72	1.56
Overall porosity, %	61.4	62.0	63.5	67.1
Overall specific surface, m ² /g	112	117	116	107
Pores with $d > 1.8 \times 10^{-5}$ cm	44.4	45.2	46.8	50.0
Pores with $d < 1.8 \times 10^{-5}$ cm	17.0	16.8	17.1	17.1
Compressive strength, MPa	14.5	12.2	12.1	10.95

Table 3. Investigation of the compressive strength for the Ni-Co catalysts doped with manganese and copper

<i>Content of alloying elements in the Ni-Co catalyst, wt %</i>	<i>Compressive strength, MPa</i>
Ni-Co-Mn 80-10-10	12.2
Ni-Co-Mn 75-10-15	12.1
Ni-Co-Mn-Cu 68-10-15-2	14.5
Ni-Co-Mn-Cu 73-10-10-2	15.8

Another major benefit of thermal self-ignition is that the catalyst's strength is 1.5 times higher than that of sintered materials with the same porosity. High temperatures of the process and low impurity content at the grain boundaries (due to self-cleaning) lead to the formation of strong bonds between grains in the crystallite. It is similar to "fusion" of the grains with the formation of a frame which is another reason of high strength. Fig. 1 shows the dependence of the catalyst's strength on porosity for the Ni-Co-Mn-Cu alloy obtained in the process of thermal self-ignition and conventional sintering.

The size of the inner surface of a unit of weight of the catalyst almost does not change with a change in the compaction pressure. The average specific surface area for all investigated catalyst samples is 112 m²/g.

When studying the changes in the pore structure of the Ni-Co-Mn-Cu catalyst, the samples were prepared by pressing of sifted powder. Obviously, this is the reason why the catalyst specimens are an agglomeration of fine particles penetrated by numerous tiny capillaries. The study results of the pore structure prove that with a change in the compaction pressure, it is possible to more or less bring these particles closer or apart without affecting their pore structure. Taking into account the fact that the specific surface area per unit of weight of the samples remains constant, and the change in the overall porosity is mainly determined by the change in the volume of large pores, it is possible to conclude that the Ni-Co-Mn-Cu catalyst samples have an inhomogeneous pore structure consisting of large pores and short thin capillaries (Sereda et al., 2015).

Thermal stability is another important characteristic of the catalyst. To identify the ways of the practical application of the catalyst in a particular contact process, it is necessary to have data on its stability under operating conditions. The information on its thermal stability is also necessary for laboratory tests. Obviously, kinetic studies carried out under conditions of possible catalyst sintering can result in false conclusions.

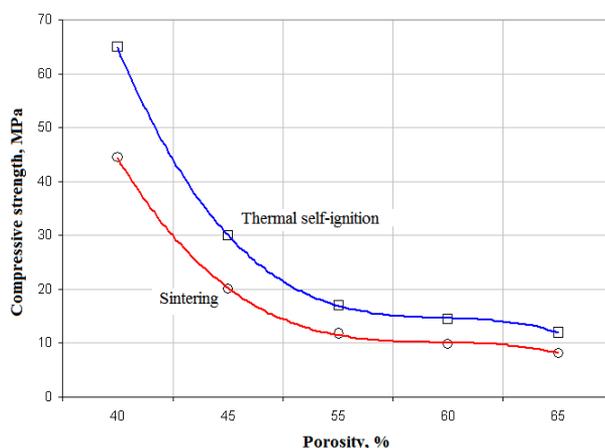


Fig. 1. Strength of the porous Ni-Co-Mn-Cu catalyst

Sintering causes the catalyst recrystallisation and is accompanied by an increase in the size of its particles, resulting in a decrease of the specific surface area. The decrease in the activity of multicomponent catalysts during sintering is caused by a decrease in the surface of the active component. During sintering, the part of the surface taken by the active component can change which results in the change of the specific catalytic activity per unit of total surface area. An increase in the specific catalytic activity which is sometimes observed during sintering can be caused also by sintering of small pores which are inaccessible to reactants. The catalyst's thermal stability can change depending on the gaseous phase. Considering that the Ni-Co catalyst is mainly used in the oxidation of carbon monoxide and hydrocarbons, the data on its thermal stability in carbon-containing gases are important for characterising this catalyst (Sereda et al., 2015).

Derivatographic studies were carried out in order to investigate the burnout of compaction products and, consequently, the possibility of regenerating catalysts based on the NiAl_3 system doped with cobalt, manganese and copper (Fig. 2).

The analysis of the derivatogram of the initial Ni-Co-Mn-Cu sample recorded an increase in the mass by wt 2% in the temperature range from 200°C to 300 °C. The increase in mass can be explained by the formation of nickel oxide (NiO), especially since the TGA curves show a diffusion peak at a temperature of 310°C (Fig. 2, *a*) (Sereda et al., 2015).

After the catalytic tests during the oxidation of carbon monoxide, the catalysts were subjected to coking. The derivatogram (Fig. 2, *b*) demonstrates the regularities of the burnout of the formed compaction products. The maximum exoeffect in the system is observed at a temperature of 495°C. In this case, the weight loss is up to wt 6%. Thus, there is a regular decrease in the mass of the catalyst, which corresponds to the burnout of the compaction products to a temperature of about 790°C (at which the NiO sublimation is likely to occur). Then, there is an increase in mass associated with the oxidation of nickel, which is confirmed by X-ray diffraction data (Sereda et al., 2015).

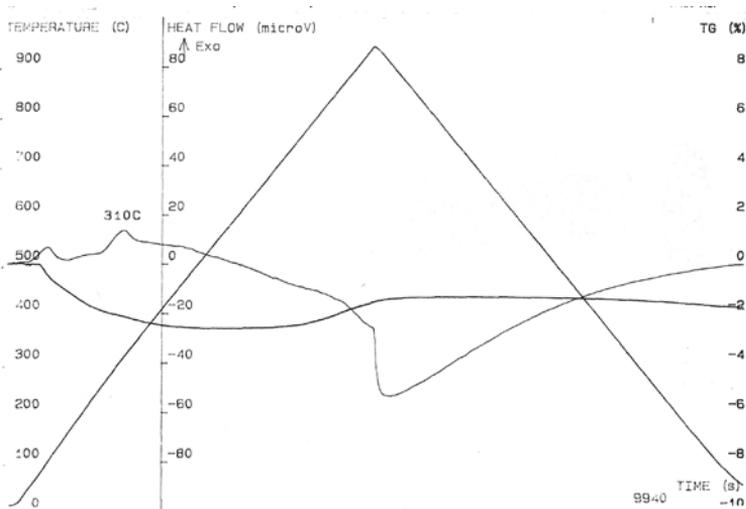
To restore the catalytic activity, the catalyst is intermittently regenerated directly in the reactors by thermal or steam treatment (Kachan and Yerofieieva, 2018).

To determine the optimal heat treatment time, two sets of experiments were performed. In the first set, the catalyst granules were treated for 60 min at 400, 500, and 600°C. Then the surface as well as its inner structure were studied using the light-microscopic method, which allowed to determine the optimal temperature and grain diameter for the regeneration process. In the second set of experiments, the granules were preliminarily ground and fractions of different sizes were subjected to heat treatment at 580°C.

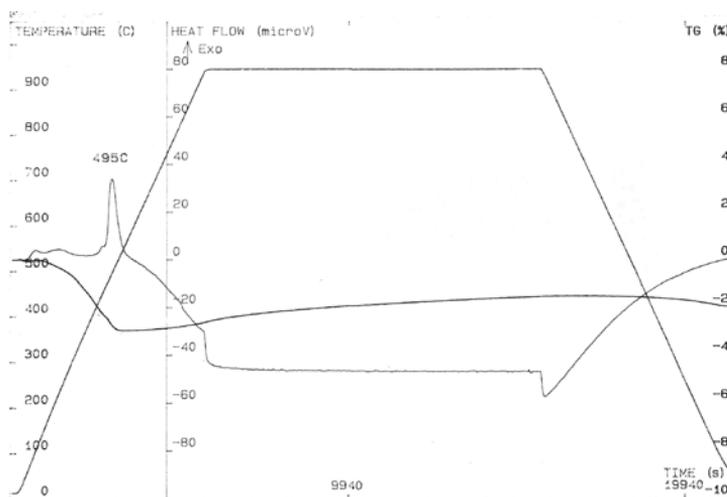
To define the optimum degree of the catalyst grinding, the granules were fired during 30 and 60 min at a temperature of 400, 500, and 600°C.

The study results showed that an increase in temperature from 400 to 600°C with a firing time of 30 min leads to an increase in the thickness of the layer that has changed its phase composition. An increase in the firing time to 60 min at 600°C makes it possible to practically remove carbon compounds from the granules, which demonstrates that, with a particle size of up to 500 μm , the firing of the catalyst is almost complete.

To get the quantitative parameters of firing, the fractions of the catalyst <0.25, 0.25-0.5 mm were studied. The study results show that at a temperature of 580°C 60 min is enough for fractions 0.25-0.5 mm and <0.25 mm to remove carbon from the catalyst. Moreover, the weight loss of these fractions is almost the same, which allows concluding that it is possible to reduce firing temperatures up to 580°C when the size of the catalyst grain is about 500 μm . Without grinding the catalyst, firing at this temperature is not complete even after 2 hours.



a



b

Fig. 2. Thermogravimetric analysis of the Ni-Co-Mn-Cu catalyst
a – before the catalytic studies, *b* – after the catalytic studies.

Later, it is possible to recycle the spent catalyst in two ways: recovering nickel from the catalyst with the help of various solvents, or using the spent catalyst for re-preparation of new carriers and contacts (Sereda et al., 2019b).

4. Conclusions

The analysis of the study results of the physical and mechanical properties of intermetallic catalysts showed that they differ depending on their composition and processing method. The difference in the physical and mechanical properties of the catalysts is explained by differences in their structure, phase composition, porosity and pore size.

It was concluded that adding manganese to the catalysts obtained under thermal self-ignition makes it possible to increase the porosity of the material by 5-10% by volume, as a result of increasing of the volume of large pores by 1.2-1.3 times, without changing the structure of small capillaries. The porosity of the catalyst was 60-65%. Also, obtaining the catalysts under thermal self-ignition and additional doping of the Ni-Co-Mn catalysts with copper result in the formation of strong bonds between grains in the crystallite, which increases the compressive strength of the catalyst 1.4-1.5 times reaching 14.5-15.8MPa. High temperatures of the process and low impurity content at the grain boundaries (due to self-cleaning) lead to the formation of strong bonds between grains in the crystallite, which is also a reason for high strength.

The study results of thermal stability of intermetallics showed that weight loss did not exceed wt 6%. There is a regular decrease in mass up to a temperature of about 790°C. Then, there is an increase in mass associated with the oxidation of nickel, which is confirmed by X-ray diffraction data.

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References

- Belokon K.V., Manidina Ye.A., Troicka O.O., Ryzhkov V.G., (2020), Study of the nature of ni-al intermetallic compounds catalytic activity in the oxidation of carbon monoxide and hydrocarbons, (in Ukrainian), *Collection of scholarly papers of Dniprovsk State Technical University (Technical Sciences)*, **1**, 129-134.
- Belokon Yu.A., Zherebtsov A., Belokon K.V., Fedchenok A., (2017), The investigation of physical-mechanical properties of intermetallic Ni-Al catalyst with nanostructure, In *2017 IEEE International Young Scientists Forum on Applied Physics and Engineering (YSF)*, IEEE, Lviv, 299-302.
- Borshch V.N., Pugacheva E.V., Zhuk S.Ya., Andreev D.E., Sanin V.N., Yukhvid V.I., (2008), Multicomponent metal catalysts for deep oxidation of carbon monoxide and hydrocarbons, *Doklady Physical Chemistry*, **419**, 77-79.
- Borshch V.N., Pugacheva E.V., Zhuk S.Ya., Sanin V.N., Andreev D.E., Yukhvid V.I., (2017), Deep oxidation catalysts based on SHS-produced complex intermetallics, *International Journal of Self-Propagating High-Temperature Synthesis*, **26**, 124-128.
- Cheilytko A.A., (2015), The influence of synthesis of the initial mixture and blowing agents on the formation of a porous structure, (in Russian), *Eastern-European Journal of Enterprise Technologies*, **5**, 35.
- Kachan Yu.G., Yerofieieva A.A., (2018), The innovative control of the heating up process of the metal in the furnace using spatial electric field, (in Ukrainian), *Radio Electronics, Computer Science, Control*, 193-199.
- Sereda B., Belokon Yu.A., Belokon K.V., Krugljak I., Sereda D., Korobochka A., (2019a), The formation of intermetallic catalysts porous structures, In *MS and T 2019 - Materials Science and Technology 2019*, 1324-1328.
- Sereda B., Belokon Yu.A., Belokon K.V., Kruglyak I., Sereda D., (2019b), Modeling of the processes of obtaining porous materials under SHS conditions, In *MS and T 2019 - Materials Science and Technology 2019*, 1331-1335.
- Sereda B.P., Belokon Yu.A., Belokon K.V., Sereda D.B., (2015), The researching of physical-mechanical properties of intermetallic catalysts obtained in SHS conditions, (in Russian), *Construction, materials science, mechanical engineering*, **80**, 297-301.