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OPTIMAL COMPOSITION OF INTERMETALLIC CATALYST FOR NEUTRALIZATION OF CARBON CONTAINING COMPONENTS OF GAS EMISSIONS *

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Abstract

The paper presents the results of the optimization of intermetallic compounds used for catalytic neutralization of carbon-containing exhaust gases. The statistical method of designing active experiments was used to analyze the effect of cobalt, manganese and copper on the catalytic, physical and chemical properties of the catalyst. The catalytic activity, specific surface area, and porosity of the catalyst were taken as the response function. The experimental data were mathematically processed using regression analysis. The work used a symmetric composition second-order design. As a result of mathematical programming, regression equations were obtained that describe the effect of the cobalt, manganese and copper content on the catalytic properties and porosity of the catalyst, and the response surfaces. The optimal combination of catalytic, physical and mechanical properties ensures that the compound contains 30% of nickel, 10% of cobalt, 11% of manganese and 2% of copper. When using such intermetallic compound, the conversion of carbon monoxide is 100%, and that of propane is 95 %, the specific surface area of the obtained catalyst is 110 m^2/g, and the porosity is 64 %. The error of the regression equations did not exceed 2%.

Keywords: carbon monoxide, catalyst, hydrocarbons, optimization, porosity, regression analysis

1. Introduction

Managing industrial air emissions is one of the most complicated and urgent environmental issues. Carbon monoxide (CO) and hydrocarbons (C_mH_n) are the most

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widespread industrial air pollutants. CO and C_mH_n come from burning refractories, electrode graphitization, sinter and coke production.

Catalysis is one of the high-potential methods for CO and C_mH_n neutralization. Currently, such noble metals as Pt, Rh, and Pd are used for catalytic processes. As a rule, these metals are applied to Al_2O_3 substrates by various methods, most of which are environmentally harmful and hazardous (Kolesnikov, 2004). However, it is possible to use cheaper materials and methods of their obtaining for many catalytic reactions. These include catalysts based on intermetallic compounds of the Ni-Al system with Raney structure (Raney nickel is formed as a result of leaching reaction when Al is dissolved out of the intermetallic compound with only porous Ni remaining) (Merzhanov and Grigoryan, 1998).

Skeletal nickel catalysts are widely used in various industries, including energy and transport sectors, for effective treatment of exhaust gases as well as flameless combustion processes. The optimization of the characteristics of the active metal is achieved by changing the nature and concentration of the removed component of the initial alloy, by changing the methods of obtaining catalysts, the mode of their heat treatment, and leaching conditions. Modifying the binary Ni-Al alloy by adding transition and non-transition metals is the most common way of increasing the catalytic activity. However, the selection of optimal catalysts is still largely empirical. There is no clarity in the relationship between the phase composition of the initial alloys, the structure and physical and chemical properties of the catalysts obtained from them. It is a fact that in the process of modification the additives affect a whole range of micro and macro factors. Thus, all conclusions about the mechanism of promotion, as well as the selection of optimal catalysts, should be based on the results of a comprehensive study, which makes it possible to investigate the role of individual factors and define their contribution to the characteristics of catalysts.

The objective of this paper was to develop a compound with optimal catalytic, physical and mechanical properties for CO and C_mH_n neutralization.

The task of the mathematical experiment planning was to investigate the effect of the compound composition on the catalytic properties, specific surface area and porosity of the intermetallic catalyst aimed at selecting its optimal composition. Intermetallic compounds in the Ni-Al system with stoichiometric composition $NiAl_3$ were the catalysts under research for the oxidation of carbon monoxide and hydrocarbons. The intermetallic $NiAl_3$ was modified by different amounts of transition metals to increase its catalytic activity. In particular, $NiAl_3$ catalysts were obtained with additions of manganese, cobalt and copper in amounts of up to wt 15 % (Sereda et al., 2009a).

2. Materials and methods

The statistical method of designing active experiments was used to analyze the effect of cobalt, manganese and copper on the catalytic, physical and chemical properties of the catalyst. The catalytic activity, specific surface area, and porosity of the catalyst were taken as the response function. The methods (Novik and Arsov, 1980) using regression analysis were used for the experimental data processing aimed at building a mathematical model of the effect of the chemical composition on the properties. Assuming nonlinear response functions and to reduce the number of experiments we used the symmetric composition second-order design (Adler et al., 1976; Palamar et al., 2014).

The core of the chosen design is a half-replicate 2^{3-1} with the defining contrast $1 = x_1x_2x_3$. For this reason, the model's estimated coefficients b_1, b_2, b_3, b_{12}, b_{13}, b_{23} were correlated among themselves. The chosen replicate made it possible to independently estimate the linear effects and all paired interaction effects. The coefficients b_0 and b_{ii} also correlate among themselves. The statistically insignificant coefficients b_i and b_{ij} were excluded from the model without recalculating the remaining coefficients.

As a result of experimental data processing using regression analysis, the following equations were obtained:

$$Y = b_0 + \sum_{1 \le i \le k} b_i x_i + \sum_{1 \le i < j \le k} b_{ij} x_i x_j + \sum_{1 \le i \le k} b_{ii} x_i^2 \cdot \quad (1)$$

The model (1) coefficients were calculated by the formula:

$$b_i = \frac{\sum_{u=1}^{N} x_{i_u} y_u}{N}, \quad i = 0, 1, 2, ..., k. \quad (2)$$

The significance of the regression coefficient was defined using Student's t-test, based on the ratio:

$$|b_i| \ge b_{rc} = t(0{,}05; f_y) \frac{S_y}{\sqrt{n}}, \quad (3)$$

where $t(0{,}05; f_y)$ is the p-value of 5% with $f_y = n - 1$ degrees of freedom;

n is the number of cases.

The adequacy of the model was defined from the ratio:

$$F = \frac{S_{ad}^2}{S_y^2} \le F(0{,}05; f_{ad}; f_y), \quad (4)$$

$$S_{ad} = \frac{\sum_{N=1}^{N} (\overline{y} - y)^2}{N - k - 1}, \quad (5)$$

where:

y is the calculated value (calculated response) in the experiment;

$\overline{y}$ is the actual value (response value) in the experiment;

S_y is the standard error variance;

f_{ad} is the number of degrees of freedom (residual);

k is the number of statistically significant regression coefficients.

To define the optimal composition of elements, the extremum method was used to check the obtained equations. The extremum were found by solving a system of partial differential equations of the corresponding response functions of the form:

$$\begin{cases} \frac{d_y}{d_{x_1}} = 0 \\ ... \\ \frac{d_y}{d_{x_i}} = 0 \end{cases} . \quad (6)$$

To analyse the dependencies, the method of least squares was used. The obtained equations were estimated by the value of the correlation coefficient *r*, calculated by the formula:

$$r = \sqrt{1 - \frac{\sum \left(\overline{y} - y\right)^2}{\sum \left(y - y_{average}\right)^2}}, \quad (7)$$

where:

y is the calculated value of the function;

$\overline{y}$ is the actual value of the function;

$y_{average}$ is the average value of the function.

MatLab software package was used for the mathematical processing of the research results.

3. Results and discussion

The tests for the catalytic activity were carried out at the temperature of 200°C. The composition of the gas mixture at the outlet of the reactor was determined by the chromatographic method using argon or air as the carrier gas.

Optimization parameters:

- Y_1 is the specific surface area of the catalyst (SSA), m^2/g;
- Y_2 is the total catalyst porosity (*P*), %;
- Y_3 is the catalytic activity of carbon monoxide at 200°C (α_{CO}), %;
- Y_4 is the catalytic activity of propane at 200°C (α_{C3H8}), %.

The content of cobalt in the mixture (X_1), the content of manganese in the mixture (X_2), and the content of copper in the mixture (X_3) were selected as independent variables. High-purity nickel, aluminum, cobalt, manganese oxide, and copper powders were used as initial components. The powder particle size varied from 100 μm to 150 μm. The process of mixture preparation included dosing, mixing, mould filling, pressing, heat treatment, and leaching (Belokon and Belokon, 2018).

The calculated levels of variability intervals, the nature of their changes and codes are presented in Table 1. The main level and variability intervals were chosen based on the fact that the phase $NiAl_3$ contains all nickel, according to the reaction Ni + 3Al = $NiAl_3$. Consequently, its minimum concentration is at least wt 25%. When nickel concentration is increased to 30%, Ni_2Al_3 is formed. The specific activity of Ni_2Al_3 phase is 1.8-3.4 times lower than that of $NiAl_3$. Ni_2Al_3 has a low catalytic activity because of a low degree of leaching of the named aluminide (Sereda et al., 2009b).

Adding more than 15% of cobalt into the mixture reduces the specific surface area of the catalyst, its porosity, the average radius and the proportion of mesopores while adding less than 5% is not sufficient to increase the catalytic activity. Adding wt 1% to 5% of copper slightly increases the catalyst activity. Further increase in copper concentration decreases the catalyst activity. With more than 5% of copper added, the equilibrium shifts towards nickel as a result of which the Ni_2Al_3 phase is formed. Adding up to 15% of manganese allows increasing the catalytic activity due to the formation of a thick layer of nanoparticles 80-90 nm thick, which are oxide formations on the sites of the catalyst enriched in manganese (Belokon et al., 2017). Increasing manganese concentration above 15% does not lead to a significant increase in the specific surface area of the catalyst, due to a relatively small number of such sites. To obtain 100% powder mixture, aluminum was added.

Table 1. Studied factors

Item	***Factors***		
	Co, wt %	***Mn, wt %***	***Cu, wt %***
Code	X_1	X_2	X_3
Basic level	10	10	3
Variability interval	5	5	2
Low level	5	5	1
Upper level	15	15	5

Table 2. Checking the results of regression analysis for significance and adequacy

Parameter	***Response function***			
	Y₁	***Y₂***	***Y₃***	***Y₄***
Δb	0.54	0.21	0.58	0.58
t-test	2.78	2.78	2.78	2.78
F-test	6.09>4.39	6.26>5.61	6.16>4.88	6.26>4.79

The numerical values of the regression coefficients and their significance defined with due regard to the dispersion difference for each response function, as well as the significance check based on Student's t-test and the model adequacy check based on Fisher's exact test are presented in Table 2.

As a result of the regression analysis, several equations were obtained, showing the dependence of the catalytic properties, specific surface area and porosity of the catalyst on the content of alloying elements.

As a result of calculations, the following equations were obtained:

$$Y_1 = 80.98 + 13.3\,X_1 + 16.5\,X_2 + 3.2\,X_3 - 1.72\,X_1^2 - 0.72\,X_2^2 - 1.22\,X_3^3 + 7.75\,X_1X_2 + 0.5\,X_1X_3 + 0.5\,X_2X_3 \quad (8)$$

$$Y2 = 58.8 + 4.2\,X_1 + 6.7\,X_2 + 0.4\,X_3 - 0.52\,X_1^2 - 2.1\,X_2^2 - 0.97\,X_3^3 + 0.34\,X_1X_2 - 0.45\,X_1X_3 + 0.4\,X_2X_3 \quad (9)$$

$$Y3 = 86.8 + 10.9\,X_1 + 6.7\,X_2 + 2.8\,X_3 - 3.28\,X_1^2 - 2.3\,X_2^2 - 0.78\,X_3^3 + 1.5\,X_1X_2 - 0.25\,X_1X_3 - 1.75\,X_2X_3 \quad (10)$$

$$Y4 = 83.9 + 12\,X_1 + 8.2\,X_2 + 1.3\,X_3 - 4.1\,X_1^2 - 3.1\,X_2^2 - 1.6\,X_3^3 - 0.75\,X_1X_2 + 2\,X_1X_3 + 0.75\,X_2X_3 \quad (11)$$

The coefficients the absolute value of which is equal to or greater than the confidence interval Δb should be considered statistically significant. Statistically insignificant coefficients (in this case b_8, b_9 – equations (8), b_8 – (10)) can be excluded from the models.

The model adequacy check demonstrates that they can be used to predict the values of the response functions for any factor scores between the upper and lower levels. For this reason, it is advisable to switch to natural variables using conversion formulas presented in the following form (Adler et al., 1976):

$$X_{ij}^{k} = \frac{X_{ij}^{n} - X_{ij}^{o}}{\Delta_i} \quad (12)$$

where:

X_{ij}^{k} is the coded value of the studied *i*-th factor in the *j*-th equation;

X_{ij}^{n} is the natural value of the studied *i*-th factor in the *j*-th equation;

X_{ij}^{o} is the value of the studied *i*-th factor in the *j*-th equation at the basic level;

Δ_i is the value of the variability interval of the studied *i*-th factor.

By replacing the variables X_i in equations (8-11) by the right side of equation (12) and then collecting like terms, we obtain natural equations describing the effect of the content of alloying elements on the catalytic activity, specific surface area and porosity of the catalyst:

$$SSA=38.1+ 0.79Co + 0.63Mn + 2.4Cu – 0.0688Co2 – \\ – 0.0288Mn2 –0.305Cu2 + 0.31CoMn \quad (13)$$

$$P=24.4+1.26Co + 2.76Mn + 1.71Cu – 0.0208Co2 – 0.084Mn2 – \\ – 0.243Cu2 + 0.0136CoMn – 0.045CoCu + 0.04MnCu \quad (14)$$

$$\alpha_{CO,\%} =23.1+4.3Co + 3.1Mn + 4.57Cu – 0.132Co2 – 0.092Mn2 – \\ – 0.195Cu2 + 0.06CoMn – 0.175MnCu \quad (15)$$

$$\alpha_{C_3H_8,\%} =14.4 +5.4Co + 4.2Mn + 0.3Cu – 0.164Co2 – 0.124Mn2 – \\ – 0.4Cu2 – 0.03CoMn + 0.2CoCu + 0.075MnCu \quad (16)$$

To assess the adequacy of the equations, we used the obtained regression equations to calculate the basic level of thermal self-ignition. The calculation results were compared with the experimental studies. Table 3 shows that the error between the calculated and experimental values of the response function does not exceed 2%.

To determine the composition that ensures the optimal catalytic properties and porosity of the catalyst, 3D dependency graphs were drawn (Fig. 1).

First of all, one should note that all considerations about the direction and effect of the studied factors on the catalytic properties, specific surface area, and porosity of the catalyst can be expressed only for the variability intervals selected in the work. In these intervals, the effect of copper content, as well as all double effects containing copper, turned out to be noticeably weak. Overall, taking into account all the studied factors, the copper content is considered to have the least effect. The diagrams (Fig. 1) show other effects.

Table 3. Comparison of the calculated and experimental data

Indicator	***Calculated value***	***Experimental value***	***Error, %***
SSA	80.96	80	1.2
P	58.273	58	0.5
$\alpha_{CO,\%}$	86.6	85	1.8
$\alpha_{C_3H_8,\%}$	84.15	83	1.4

The analysis of the diagrams shows that the catalytic properties, specific surface area and porosity of the catalyst mostly depend on the content of cobalt and manganese in the mixture. The ratio between the amount of cobalt and manganese has a noticeable effect. The presentation of the experimental results by a second-order polynomial is justified as a considerable part of the nonlinear terms are significantly different from zero. Since the nonlinear regression coefficients (13-16) have the same signs, the response surface is an ellipsoid, and its centre is an extreme, moreover, a maximum, since the regression coefficients are negative.

As we assumed when setting the task, the optimal content of alloy elements of the analyzed composition is in the scope of the experiment, moreover, close to the centre. The optimal cobalt content is wt 10%. The research of porosity showed that with an increase in the manganese content, the pore size and the overall porosity of the catalyst increase. The optimal manganese content is wt 11%. The study of the effect of the amount of copper on the catalytic properties and porosity of the catalyst showed that adding it in the amount of 5% leads to a decrease in the porosity and catalytic activity of the oxidation of carbon monoxide and propane. The optimal content is wt 2% since a smaller amount does not provide the required mechanical strength of the catalyst. It is recommended to have the nickel content at the upper level of wt 30% to compensate for metal losses.

The recommended optimal catalyst composition is: nickel – wt 30 %, cobalt – wt 10 %, manganese – wt 11 %, copper – wt 2 %, aluminum – the rest.

To get the comparative data, tests of the catalyst of the known composition obtained during combustion were carried out in parallel (Belokon et al., 2019). We evaluated the catalytic activity and specific surface area of the obtained catalyst of known composition.

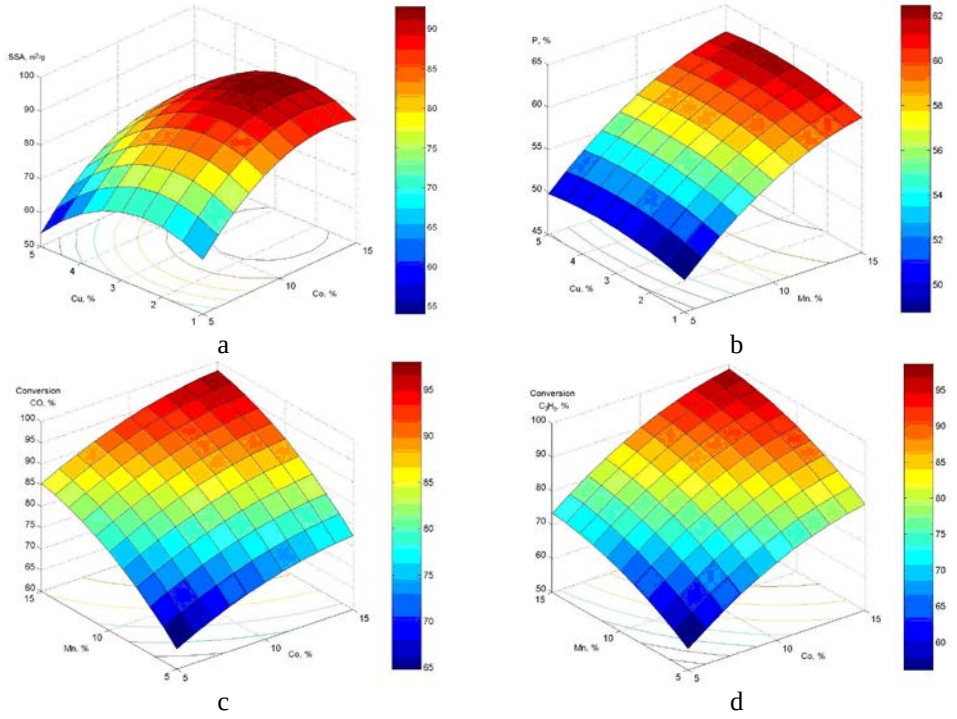

Fig. 1. Optimization of the catalyst composition by its performance: *a* - specific service area; *b* - overall porosity; *c* - the activity of carbon monoxide oxidation; *d* - the activity of propane oxidation

The obtained catalysts were used in the processes of neutralization of carbon monoxide and hydrocarbons (Belokon et al., 2019).

The catalyst was loaded into the unit with a catalytic reactor. Then gas of the following composition: 1.0 % C_3H_8; 1.5 % CO; 5.8 % O_2; 91.7 % N_2; with a space velocity of 120000 hr^{-1} at a temperature from 100 to 400-500°C with an interval of 50-100°C was then injected. When using the obtained catalyst, the conversion of CO is 100 %, and conversion of C_3H_8 is 95 %. When using the known catalyst, the conversion of CO is 85 %, and conversion of C_3H_8 is 75 %. The specific surface area of the obtained catalyst is 110 m^2/g, while that of the known catalyst is 65 m^2/g (Belokon et al., 2019).

4. Conclusions

As a result of mathematical programming, regression equations were obtained which describe the effect of the cobalt, manganese and copper content on the catalytic properties and porosity of the catalyst, and the response surface. The optimal combination of catalytic, physical and mechanical properties ensures that the compound contains 30% of nickel, 10% of cobalt, 11% of manganese and 2% of copper. When using the obtained intermetallic catalyst, the conversion of CO is 100 %, conversion of C_3H_8 is 95 %, specific surface area of the obtained catalyst is 110 m^2/g, porosity is 64 %. The error of the regression equations did not exceed 2%.

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References

Adler Yu.P., Markova E.V., Granovsky Yu.V., (1976), *The design of experiments in search of optimal conditions*, (in Russian), Nauka, Moscow, Russia.

Belokon K.V., Belokon Yu.A., (2018), The study of catalysts based on intermetallic Ni-Al alloys, In *Ceramic Transactions Series*, Ohji T., Matyas J., Colorado H., Kanakala R. (Eds.), John Wiley & Sons, Inc., Hoboken, NJ, USA, 219-225.

Belokon K.V., Manidina Y., Fedchenok A., Matukhno E., (2019), Development of a method for catalytic purification of carbon-containing components of gas emissions from industrial enterprises, *Procedia Environmental Science, Engineering and Management*, **6**, 545-552.

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.

Kolesnikov M.I., (2004), *Catalysis and catalyst production*, (in Russian), Tekhnika, Moscow, Russia.

Merzhanov A.G., Grigoryan E.A., (1998), The XXI century catalysts, (in Russian), *Science for Industry*, **3**, 30-41.

Novik F.S., Arsov Ya.B., (1980), *Optimisation of metal technology processes by methods of experimental design*, (in Russian), Mashinostroyeniye, Moscow, Russia.

Palamar M., Marek A., Pohrebennyk P., (2014), Synthesis and Optimization of Neural Network Parameters for Control of Non-linear Objects, *Przeglad Elektrotechniczny*, (05/2014), 207-210.

Sereda B.P., Kozhemyakin G.B., Ryzhkov V.G., Savela K.V., Belokon Yu.A., (2009a), Effect of the composition of a nickel-aluminum alloy with Co, Mn and Cu additives on the structure and specific activity of the catalyst based on them, (in Russian), *Construction, materials science, mechanical engineering*, **48**, 101-104.

Sereda B.P., Kozhemyakin G.B., Savela K.V., Belokon Yu.A., Ryzhkov V.G., (2009b), Studying the effect of the phase composition of the Ni-Al alloys on the physical and chemical properties of skeletal nickel catalysts, (in Russian), *Metallurgiya*, **20**, 112-117.