Case Studies in Chemical and Environmental Engineering 11 (2025) 101033

Contents lists available at ScienceDirect

Case Studies in Chemical and Environmental Engineering

journal homepage: www.sciencedirect.com/journal/case-studies-in-chemical-and-environmental-engineering

Case Report

Determination of the effect of impurity inclusions in the form of oxy-nitride phases in $NiAl_2O_4$ ceramics on resistance to high-temperature degradation during hydrogen saturation of near-surface layers

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ARTICLE INFO

Keywords:
$NiAl_2O_4$– spinel
Doping
Hydrogenation
High temperature aging
Gas swelling
Structural degradation

ABSTRACT

The degradation resistance growth of anode ceramic materials with the possibility of maintaining the stability of electrochemical and thermal conductivity properties under conditions of long-term high-temperature operation is one of the key directions in the development of solid oxide fuel cells. This article examines the possibility of modification of $NiAl_2O_4$ ceramics by adding aluminum nitride to them during the synthesis process, which leads to the formation of inclusions in the form of oxy-nitride grains. The interest in this class of ceramics is due to their structural features, which allows to consider them as one of the promising types of ceramics in the field of anode materials for solid oxide fuel cells. During assessment of the influence of impurity inclusions in the form of the oxy-nitride $Al_7O_3N_5$ phase in the composition of $NiAl_2O_4$ ceramics on the deformation-induced swelling of the crystal structure of the damaged layer under high-dose irradiation, it was established that an elevation in the impurity phase concentration from 2.5 to 7.0 wt % results in swelling resistance growth by more than 4 times compared to $NiAl_2O_4$ ceramics without impurity inclusions. It was also determined that the presence of impurity inclusions in the composition of $NiAl_2O_4$ ceramics leads to a decrease in the coefficient of thermal volumetric expansion, a reduction of which indicates increased stability of the crystalline structure of ceramics to external temperature influences.

1. Introduction

Today, one of the promising classes of materials considered as anode materials for solid oxide fuel cells are metal aluminates (MAl_2O_4) with a spinel structure [1,2]. Interest in these types of materials is due to the ease of obtaining such structures using solid-phase synthesis methods, alongside the possibility of the phase composition variation by addition of various components as stabilizing dopants [3,4] that increase resistance to external influences and degradation processes associated with operating conditions [5]. During operation at high temperatures (about 600–800 °C, which is the operating temperature of solid oxide fuel cells), anode materials undergo degradation processes, which are associated both with oxidation associated with the formation of oxide and hydroxide phases, and with structural deformation caused by thermal effects that occur when the amplitude of thermal vibrations changes [6,7]. In the case of refractory oxides, which are considered as one of the promising classes of anode materials, thermal expansion is a key factor determining the rate of degradation of materials during operation. In this context, the thermal expansion of the volume of the crystal lattice is due to both the processes of deformation stretching resulting from the migration of introduced hydrogen or oxygen vacancies arising as a result of the structural features of ceramics, as well as oxidation processes accompanying operation at high temperatures [6,7]. At the same time, the reduction of the operating temperature at present does not allow to achieve the desired performance in operation, resulting in a great emphasis on developments related to enhanced resistance of anode materials to degradation in operation [8].

In this case, the hypothesis associated with an efficiency growth and an enhancement of degradation resistance of anode materials is based on the assumption that when stabilizing dopants are added, the formation of impurity inclusions in the structure of ceramics can be initiated. This will lead to the creation of interphase boundaries, the presence of which determines the effect of dislocation hardening associated with dimensional factors and grain boundaries [9–12]. In this case, as a rule, nitride

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https://doi.org/10.1016/j.cscee.2024.101033
Received 18 July 2024; Received in revised form 8 November 2024; Accepted 25 November 2024
Available online 26 November 2024
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compounds are considered as dopants, which have higher thermal conductivity, as well as resistance to external influences, and under certain conditions can be integrated into the structure of ceramics, thereby reducing its porosity, which is one of the criteria that negatively affects the degradation resistance of anode materials.

The main goal of this study is to determine the influence of impurity phases in the form of $Al_7O_3N_5$, which occurs when aluminum nitride is added to the $NiAl_2O_4$ composition, on maintaining the stability of the strength (hardness and resistance to softening), thermophysical and electrochemical parameters of ceramics when assessing the prospects for their use as anode materials of solid oxide fuel cells. Interest in this research topic is due to the need to solve the problem of swelling of ceramic anode materials during their operation, which leads to destabilization of operation, as well as the need for frequent replacement, which increases the cost of energy production. Enhancement of anode materials' stability to high-temperature degradation will not only increase the service life by reducing swelling and destructive embrittlement during thermal cycling, but also reduce production costs.

One of the ways to elevate the resistance of ceramic materials to degradation processes is the method of modification associated with the introduction of impurity inclusions into the composition of ceramics, which in turn act as buffer inclusions preventing the propagation of microcracks under external influences, as well as the migration of defects in the structure. A number of works [13–15] have shown the potential of using this method to enhance the destruction resistance of ceramic materials to external influences. Another method of elevation of resistance to external influences is the method of dislocation hardening by the grain size reduction, which prevents the ion agglomeration processes in the near-surface layer, which makes it possible to restrain the destruction processes [16,17].

The choice of $NiAl_2O_4$ ceramics with the addition of aluminum nitride as the samples under study is due to the great prospects for using these ceramics as anode materials due to the high values of electrical conductivity [18], as well as fairly good stability indicators against prolonged thermal exposure due to the structural features of this type of ceramics, as well as good corrosion resistance indicators. At the same time, stability was determined not only for the initial samples of $NiAl_2O_4$ ceramics, but also those subjected to hydrogenation with different irradiation doses (ranging from 1 to 50 dpa), which made it possible to evaluate the influence of impurity inclusions on the efficiency of increasing the resistance to gas destruction, characteristic of long-term operating conditions of anode materials.

2. Materials and methods

Ceramics obtained using the solid-phase synthesis method by mixing nickel (NiO) and aluminum (Al_2O_3) oxides in stoichiometric ratios of 1–3 were chosen as the objects under study. After grinding, the resulting powders were annealed in a muffle furnace at a temperature of 1500 °C for 10 hours, at a heating rate of 20 °C/min. Upon reaching the annealing time, the heating in the furnace was turned off and the samples subsequently cooled naturally until they reached room temperature. According to previously conducted studies [18], it was established that using the solid-phase synthesis method, by mixing the initial components, the most optimal component ratio for obtaining a structurally ordered phase of $NiAl_2O_4$ is the ratio of NiO and Al_2O_3 equal to 1 to 3, as a result of which, during thermal sintering, a $NiAl_2O_4$ cubic phase is formed, which has fairly high resistance to degradation under mechanical influences, alongside hydrogenation processes. In this case, weight ratios of components are used to obtain ceramics. The use of other stoichiometric ratios leads to the formation of ceramics with impurity inclusions in the form of NiO grains, the presence of which has an adverse effect on the stability of the ceramics.

The samples were annealed in a PM-1700 muffle furnace (Rusuniverstal, Chelyabinsk, Russia). The addition of a stabilizing dopant in the form of aluminum nitride (AlN) powder in order to form inclusions in the ceramics in the form of an oxy-nitride phase ($Al_7O_3N_5$) was carried out at the stage of mixing nickel and aluminum oxides by partially replacing them with AlN concentrations equal to 0.1 and 0.15 M. This allowed the formation of impurity inclusions in the form of $Al_7O_3N_5$ grains in the composition of $NiAl_2O_4$ ceramics during thermal annealing of the samples. The phase content itself with a change in stoichiometry was 2.5 and 7 wt %, respectively (see X-ray phase analysis data presented in Fig. 1). At the same time, analyzing the data on the positions of diffraction reflections for the ceramics under study in comparison with each other, one can notice a tendency for the reflections to shift to the region of large values of 2θ angles, which are characterized by smaller values of interplanar distances. The latter indicates an alteration in the structural ordering of doped ceramics and their compaction due to a reduction in the crystal lattice volume of the main cubic $NiAl_2O_4$ phase. X-ray diffraction patterns were obtained on a D8 ADVANCE ECO diffractometer (Bruker, Karlsruhe, Germany), using the Bragg – Brentano shooting mode, in the angular range of $2\theta = 20–80°$.

Simulation of the hydrogenation processes of ceramic samples with different phase compositions was carried out by irradiating them with protons with an energy of about 1.5 MeV and fluences of 10^{14}, 10^{15}, 2×10^{15} and 5×10^{15} proton/cm^2, which corresponds to about 1, 10, 20 and 50 dpa, considering recalculation according to the method proposed in the work [19]. The use of the SRIM Pro 2013 program code made it possible to determine that the maximum proton path length in the damaged layer is about 10–11 μm, which indicates that the main accumulation of implanted hydrogen occurs in the near-surface layer, which is most susceptible to external influences and destruction during operation. Simulation of hydrogenation processes was carried out on the UKP-2.1 accelerator (Almaty, Kazakhstan), irradiation was carried out in vacuum, at room temperature.

Determination of the stability of the electrochemical parameters of the studied ceramics as anode materials depending on the conditions of external influences (accumulated radiation dose and temperature of long-term thermal exposure) was assessed by measuring the electrical conductivity of the ceramics. The measurements were carried out using the four-point probe method, where platinum contacts were used as contacts, and platinum paste was used for better connection and to provide voltage control. A VersaSTAT 3 potentiostat (Ametek-AMT, USA) was used for measurements. The measurements were carried out at constant current (2.5 A/cm^2). Temporary stability measurements were carried out by heating samples to temperatures of 600–800 °C, which made it possible to evaluate the resistance of ceramics to degradation caused by migration processes of implanted hydrogen. The main objective of these tests was to evaluate the influence of temperature effects associated with hydrogen migration in the structure of ceramics, leading to agglomeration and subsequent swelling of the surface layers. Moreover, due to the low solubility of hydrogen, its agglomeration in the near-surface layers can result in destabilization of strength properties due to the formation of microcracks, and an elevation in deformation distortions due to the formation of gas-filled inclusions. The selection of test temperatures was chosen considering the potential for using these materials as a basis for solid oxide fuel cells operating in extreme conditions associated with high temperatures.

Determination of the influence of thermal effects associated with the volumetric thermal expansion of the crystal lattice was carried out by measuring data on the crystal lattice volume of the main cubic phase of $NiAl_2O_4$ with varying exposure temperatures, as well as time typical for simulation of operating processes in the mode of anode materials.

Thermal conductivity measurements were carried out using a universal thermal conductivity meter KIT – 800, the basic operating principle of which is based on measuring the thermal conductivity coefficient at a stationary heat flow. For the measurement, a thermocouple and a heater of equal diameter (10 mm) were used. A ceramic sample was placed between them and alterations in the thermal conductivity coefficient of the samples were recorded. The effect of thermal expansion of the crystal structure was determined using the method of

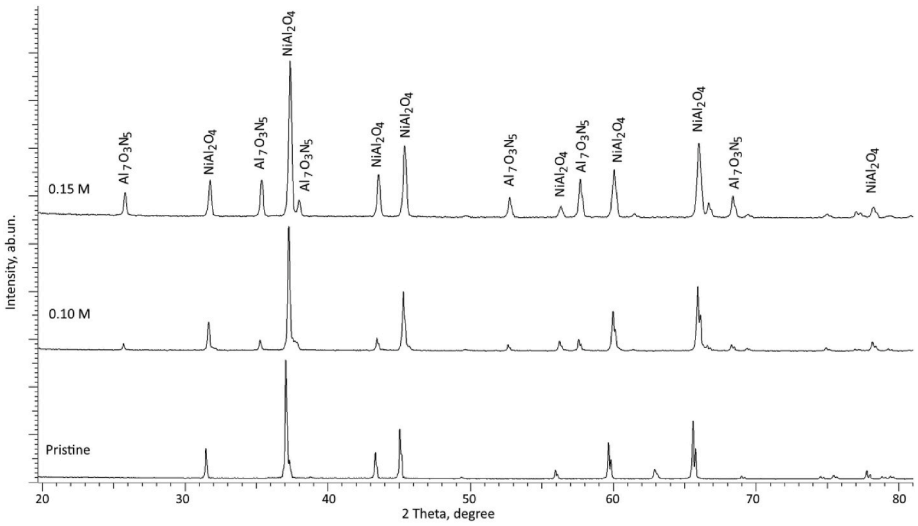


Fig. 1. Results of X-ray phase analysis of the studied $NiAl_2O_4$ ceramics in the initial state and with the addition of aluminum nitride containing 0.1 and 0.15 M.

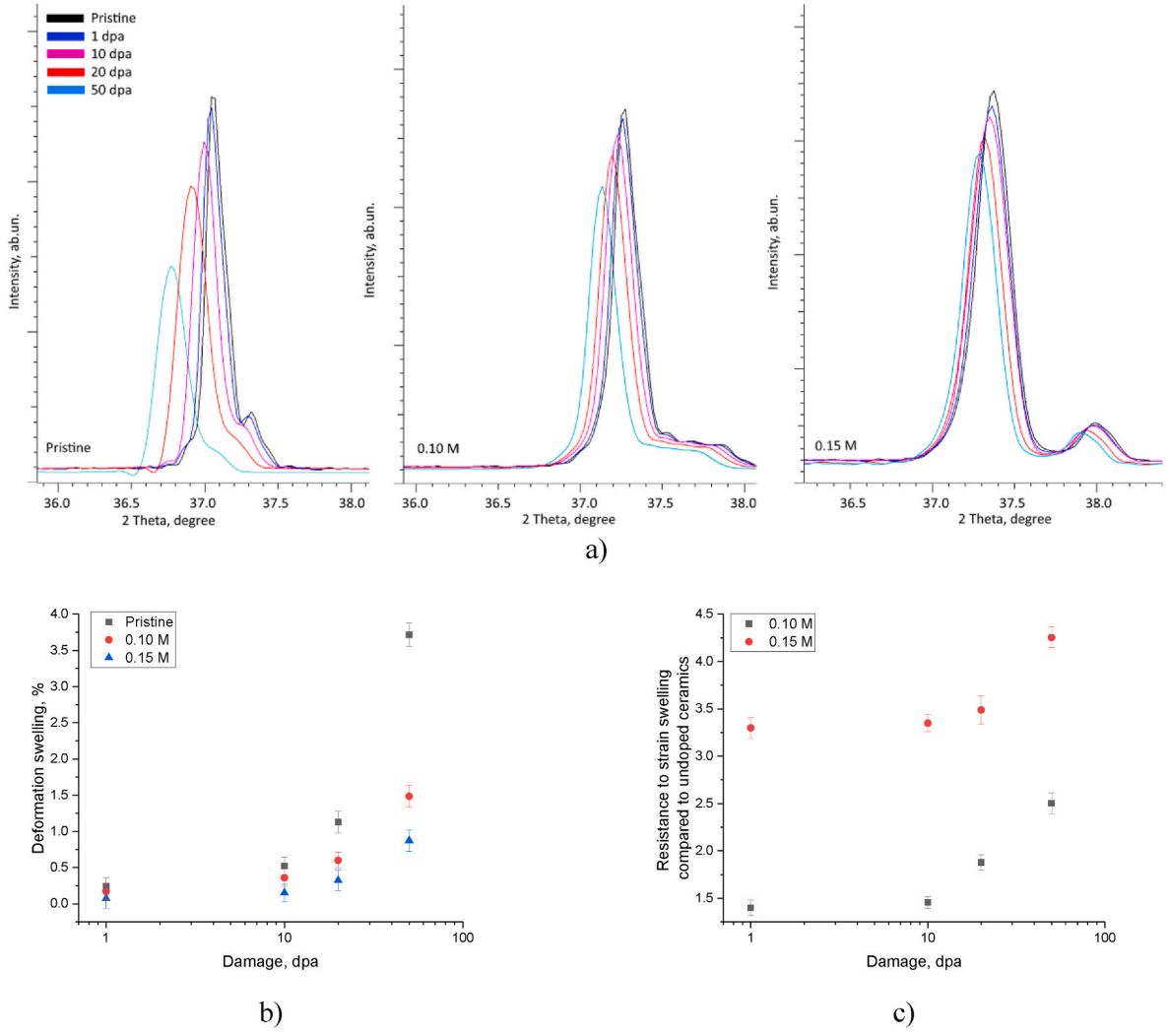


Fig. 2. a) Results of deformation distortion of the structure as a result of simulation of hydrogenation processes; b) Assessment results of deformation swelling of the crystal structure depending on the values of atomic displacement; c) Assessment results of the influence of elevation of alloying impurity concentration on the resistance to deformation swelling of a damaged ceramic layer.

analyzing the structural data of samples subjected to long-term thermal exposure, which were obtained by recording X-ray diffraction patterns at all test intervals.

3. Results and discussion

Fig. 2a demonstrates the assessment results of the shift of the main diffraction reflection characteristic of the $NiAl_2O_4$ phase at $2\theta = 37.0–37.3^\circ$, the change in intensity and position of which characterizes the deformation distortion of the structure as a result of an increase in the irradiation dose, as well as the reflecting influence of the formation of impurity inclusions in the composition of ceramics on the resistance to deformation distortion of the structure. The general appearance of deformation shifts in the position of the maxima to the region of small angles (displacement relative to the position of the maximum), as well as changes in the intensity and width of the line, indicate the accumulation of tensile stresses in the structure, the contribution of which rises with the atomic displacement value (irradiation fluence) growth. According to the data presented on Fig. 2a, in the case of $NiAl_2O_4$ ceramics obtained without the addition of aluminum nitride, the main (pronounced) changes in the position of the diffraction reflection at $2\theta = 37.0–37.3^\circ$ are observed at displacements above 10 dpa. The observed reduction of the intensity and expansion of the reflex, as well as its asymmetry, indicate partial disordering of the crystal structure. At the same time, the observed shift to the region of small angles characterizes the accumulation of deformation tensile stresses in the structure, leading to swelling of the damaged volume. Moreover, the cubic shape of the crystal structure in this case allows to conclude that the deformation swelling is isotropic. In the case of addition of aluminum nitride to the composition of $NiAl_2O_4$ ceramics in concentrations of 0.1 M and 0.15 M, which leads to the formation of inclusions in the form of $Al_7O_3N_5$, the shifts in the diffraction reflection at $2\theta = 37.0–37.3^\circ$ are less pronounced, which indicates a greater resistance of ceramics to radiation-induced swelling associated with the accumulation of implanted hydrogen in the damaged layer, as well as processes characteristic of gas swelling during hydrogen agglomeration by filling existing pores in the damaged layer with it. An analysis of the calculations of the deformation swelling of the near-surface layer depending on the value of atomic displacements, presented in Fig. 2b, quite clearly reflects the influence of impurity phases on the resistance to swelling under high-dose irradiation. In the case of unmodified $NiAl_2O_4$ ceramics, the effects of volumetric swelling of the crystal structure are observed at atomic displacement values above 10 dpa. The established growth in the deformation swelling value is from 1.3 to 3.9 % for 20 and 50 dpa values, respectively.

The volumetric deformation swelling of the crystalline structure during irradiation can be explained by several factors, one of which is the accumulation of implanted hydrogen in the near-surface damaged layer and its subsequent agglomeration in voids, which is most pronounced during high-dose irradiation.

Calculation of the effectiveness of the influence of variations in dopant concentration on resistance to deformation swelling in comparison with the results of deformation swelling of $NiAl_2O_4$ ceramics without the addition of AlN is presented in Fig. 2c. According to the analysis, it was found that the addition of aluminum nitride, which during thermal sintering of ceramics results in the formation of inclusions in the form of $Al_7O_3N_5$, causes an elevation in resistance to destruction. At the same time, a more pronounced resistance (increase in stability) is observed for samples irradiated with fluences, which are characterized by the achievement of atomic displacement values of more than 10 dpa. Such a strong difference in the stability parameters of modified ceramics ($NiAl_2O_4$ + AlN) compared to $NiAl_2O_4$ ceramics without the addition of AlN under high-dose irradiation indicates the inhibition of degradation processes due to the presence of impurity inclusions. In this case, the observed effects of deformation swelling resistance growth are due to the presence of interphase boundaries, the density of which becomes greater with increasing weight contribution of the impurity phase. According to the data obtained, a rise in the weight contribution of $Al_7O_3N_5$ from 2.5 to 7 % under high-dose irradiation (about 50 dpa) results in deformation swelling resistance growth by 2.5 and 4.3 times compared to the value of deformation swelling of ceramic samples that do not contain impurity inclusions.

Fig. 3 demonstrates the results of a study of changes in the electrical conductivity values of the ceramics under study during long-term life tests at different heating temperatures of the samples for 500 hours. Fig. 4 reveals the results of changes in the electrical conductivity value (decrease in electrical conductivity) after measurements taken for 500 hours in different temperature regimes for the ceramic samples under study. The data were obtained by comparing the electrical conductivity value in the initial state (initial state at the start of measurements) and after 500 hours of testing at temperature heating. The presented results reflect changes in electrochemical characteristics over long heating times at different temperatures associated with the migration processes of implanted hydrogen in the damaged contact layer, as well as the degradation of ceramics caused by oxidation and structural degradation processes. As can be seen from the data presented, a change in the phase composition of the ceramics under study results in a change in the electrical conductivity from 322 S/cm to 340 and 380 S/cm, respectively. Moreover, such alterations are due to structural changes associated with the fact that when aluminum nitride is added, the observed decrease in the crystal lattice parameters (as evidenced by the shift of diffraction reflections presented in Fig. 1) results in compaction of the ceramics, thereby reducing porosity, and the formation of impurity inclusions creates additional opportunities for charge transport. At the same time, analysis of the time and temperature dependences of the change in electrical conductivity for initial samples not subjected to irradiation indicates the high stability of ceramics when used as anode materials. In the case of irradiated samples, for $NiAl_2O_4$ ceramics without the addition of AlN, a change in the electrical conductivity value is observed for samples irradiated with doses, with a characteristic value of atomic displacements of more than 10 dpa. Moreover, an elevation in the structural damage degree in the samples leads to a reduction not only in the electrical conductivity initial value, indicating the negative impact of accumulated structural damage associated with implanted hydrogen, but also in a destructive change characteristic of hydrogen migration processes. This results in heightened destruction of the anode material, which manifests itself during prolonged thermal exposure. It should also be noted that the degradation processes occurring in anode materials, as can be seen from the data presented, have not only a direct dependence on the accumulated dose of structural damage associated with the concentration of implanted hydrogen, but also on thermal effects, which is expressed in more accelerated degradation of the material at high temperatures (700–800 °C), manifested in the form of electrical conductivity reduction at an earlier test time interval than at a temperature of 600 °C. The observed trends of electrical conductivity reduction during long-term thermal exposure, which are most pronounced with the exposure temperature growth, indicate diffusion processes of implanted hydrogen in the damaged layer, manifesting themselves under high-dose irradiation. For samples of $NiAl_2O_4$ ceramics irradiated with doses of 20–50 dpa at a temperature of 800 °C, the observed decrease in electrical conductivity after 200–300 hours of testing indicates an acceleration of the near-surface layer destruction processes. The latter is caused by the agglomeration of hydrogen in voids due to the acceleration of diffusion at high temperatures, which leads to a rise in deformation distortion of the structure and partial amorphization.

Summarizing the observed conductivity alterations, it can be concluded that, in reality, the annealing temperature growth has little effect on the conductivity value at the initial stages of measurements, however, temperature effects for hydrogenated samples manifest themselves as an earlier conductivity reduction in experiments at higher temperatures. It is important to highlight that the main changes in the conductivity value are due to the destructive hydrogen accumulation in

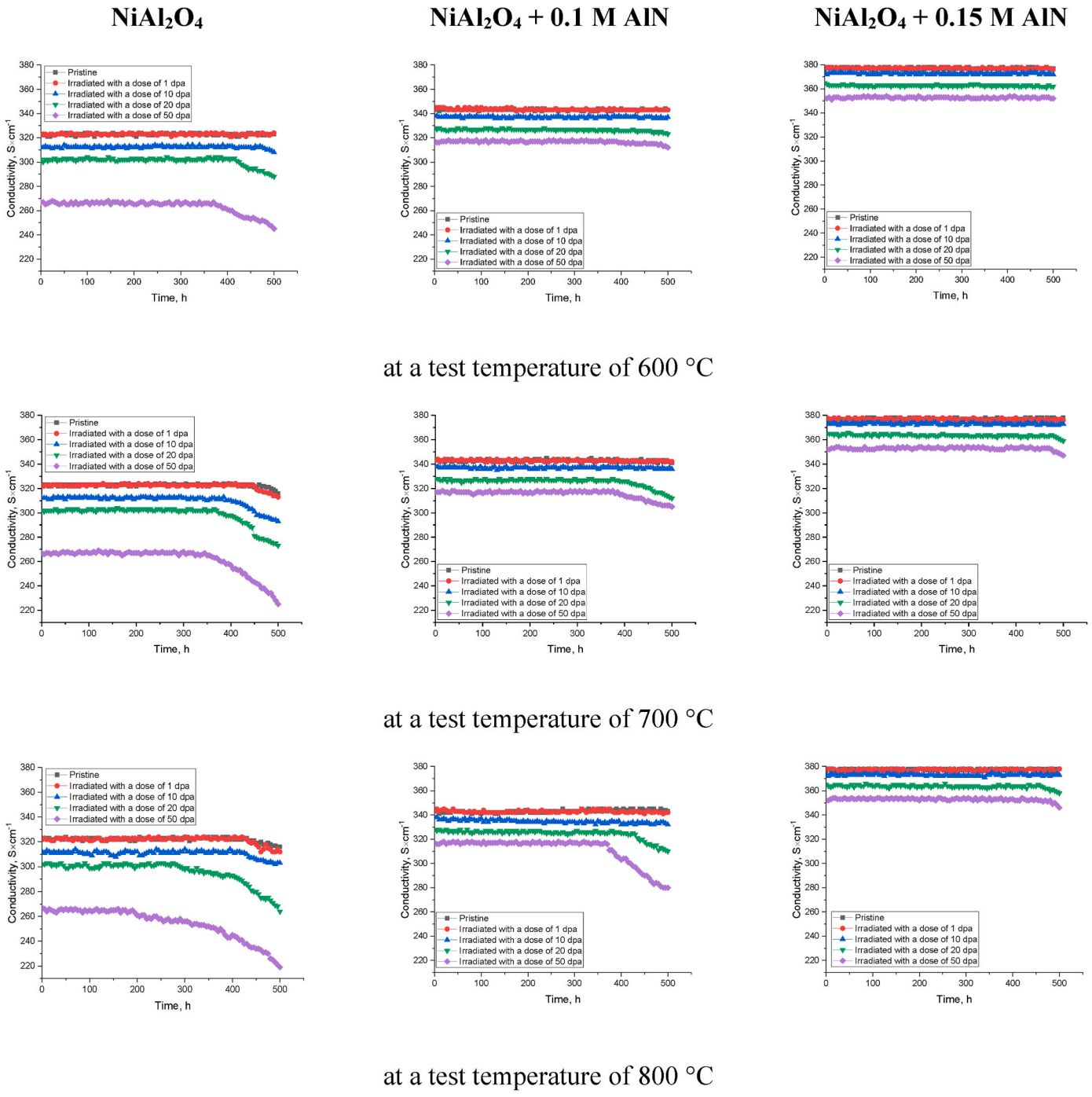


Fig. 3. Assessment results of changes in electrical conductivity depending on test time at different temperatures.

ceramics, since an elevation in the radiation dose, resulting in its concentration growth, negatively affects the degradation resistance of ceramics. However, the formation of inclusions in the composition of ceramics, as is evident from the data presented, results in growth in stability to conductivity degradation, as well as its preservation during long-term thermal exposure.

The addition of aluminum nitride to the composition of $NiAl_2O_4$ ceramics, as can be seen from the data presented, leads not only to an increase in the electrical conductivity values of the studied samples, but also to maintenance of the stability of the electrical conductivity values in the case of irradiated samples, the decreasing trend of which is presented in Fig. 4. At the same time, degradation resistance of electrical conductivity has a direct dependence on the dopant concentration, and, as a consequence, on the concentration of inclusions formed in the structure of the ceramics.

According to the data presented in Fig. 3, the most resistant to a decrease in electrical conductivity with variations in thermal exposure temperature, even in samples irradiated with doses of about 20–50 dpa, are $NiAl_2O_4$ ceramics, in which the content of $Al_7O_3N_5$ inclusions is about 7.5 wt %. As can be seen in Fig. 3 shows the data from temperature tests at 800 °C, for $NiAl_2O_4$ + 0.15 M AlN samples, a decrease in electrical conductivity is observed only for samples irradiated with doses of 20–50 dpa after 440–450 hours of testing, and the decrease itself is no more than 2–3 % of the initial values (see data in Fig. 4 shows the data for $NiAl_2O_4$ ceramics with the addition of 0.15 M AlN).

Fig. 5a illustrates the assessment results of the change in the thermal

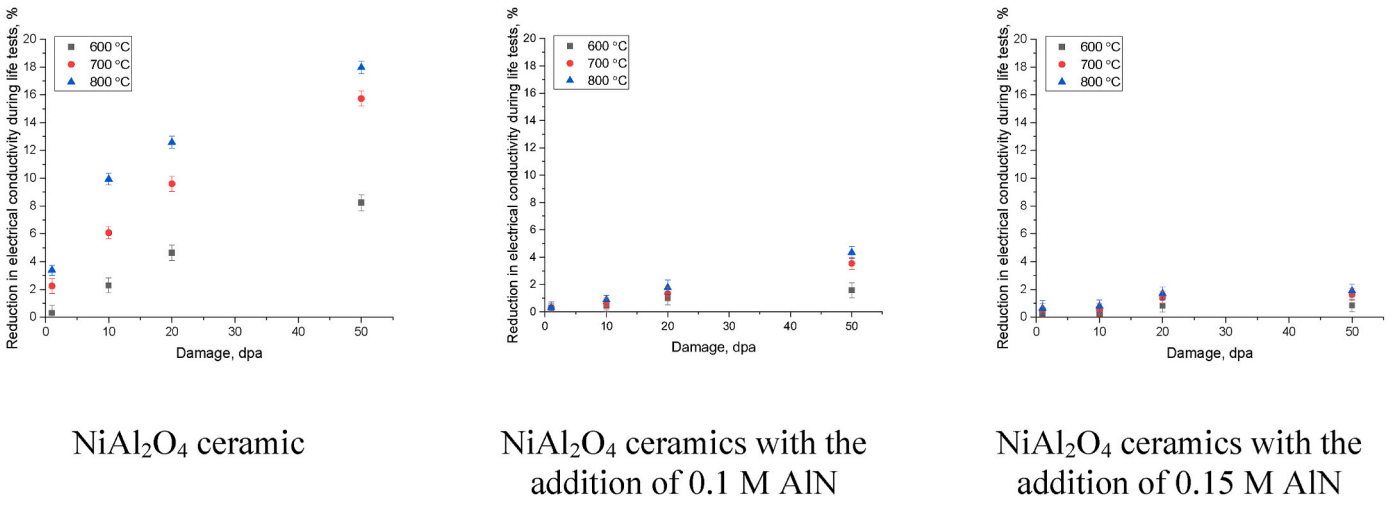


Fig. 4. Changes in electrical conductivity after 500 hours of testing at different temperatures for the studied ceramic samples.

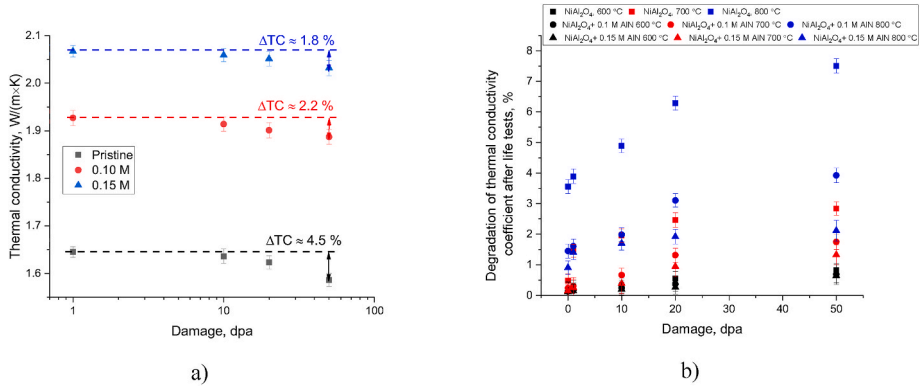


Fig. 5. Assessment results of the thermophysical parameters of ceramics contingent upon the conditions of external influences: a) change in the thermal conductivity coefficient depending on the dose of damage in ceramics; b) comparison of changes in the thermal conductivity coefficient of ceramic samples after life tests at different temperatures.

conductivity coefficient of the ceramics under study depending on the value of atomic displacements, which reflect the kinetics of thermal conductivity degradation, alongside the influence of the presence of phase inclusions in the composition of the ceramics on determining the resistance to degradation of the thermal conductivity of the samples. According to the data presented, the presence of impurity inclusions in the composition of ceramics leads to a rise in the thermal conductivity coefficient from 1.66 W/(m × K) to 1.93 and 2.07 W/(m × K). Such changes are caused not only by the influence of the presence of impurity inclusions filling the inter-boundary space, but also by an elevation in the structural ordering degree associated with compaction of the crystal lattice, caused by the effect of structural ordering during thermal sintering. In this case, filling the interboundary space with grains of the impurity phase results in the pore space alteration, which leads to the acceleration of phonon heat transfer processes, causing an increase in heat transfer.

The overall appearance of the presented dependences of the change in the thermal conductivity coefficient on atomic displacements indicates that the most significant changes are observed at atomic displacements above 10 dpa. Moreover, the most pronounced alterations causing deterioration in thermal conductivity are observed for ceramic samples that do not contain impurity inclusions. In the case of ceramic samples, an increase in the concentration of the impurity phase leads to a decrease in the decreasing trend in the thermal conductivity coefficient, and the maximum change in the ΔTC value is 1.8 % and 2.2 % for AlN concentrations equal to 0.1 and 0.15 M, respectively, while for undoped ceramics the change in ΔTC is about 4.5 % at a maximum value of atomic displacements of 50 dpa. This difference in the value of the change in ΔTC of the samples under study indicates the positive influence of the impurity phase on stability maintenance of the ceramics' thermophysical parameters.

The results of changes in the thermal conductivity coefficient of the studied ceramics after life tests are presented in Fig. 5b in the form of a dependence calculated on the basis of the data obtained in the initial value of the thermal conductivity coefficient and its decrease after thermal exposure for 500 hours at different temperatures. The presented percentage changes reflect the degradation of the thermal conductivity of the ceramics under study, caused by degradation processes associated with operating processes with temperature changes. According to the presented data, the greatest change in the thermal conductivity coefficient during life tests is observed for samples of $NiAl_2O_4$ ceramics without the addition of AlN, the maximum reduction in thermal conductivity for which at a dose above 10 dpa is about 3–8 % depending on the temperature of thermal exposure. The formation of inclusions in the form of $Al_7O_3N_5$ in $NiAl_2O_4$ ceramics not only leads to an increase in the stability of the thermophysical properties of ceramics when the irradiation dose changes, but also reduces the effect of thermal conductivity degradation associated with prolonged temperature exposure during life tests. A direct explanation for the observed changes in resistance to a decrease in the thermal conductivity of ceramics during life tests is the increased resistance to destructive disordering of near-surface layers caused by migration and diffusion processes.

One of the key factors associated with the degradation of thermal conductivity and electrical conductivity is a change in the coefficient of thermal expansion of the crystalline structure of ceramics, a change in which causes volumetric broadening of the crystal lattice due to changes in the amplitude of thermal vibrations, as well as the migration of implanted hydrogen and vacancy defects in the structure that can be introduced into internodes. The calculation of the volumetric coefficient of thermal expansion was carried out by assessing the change in the parameters and volume of the crystal lattice of the studied samples under various conditions: depending on the variation in the concentration of the AlN dopant, which reflects the influence of impurity inclusions on the amplitude of thermal vibrations of the main cubic phase and its broadening; depending on the radiation dose and the accumulated value of atomic displacements, reflecting the degradation of the surface during the accumulation of implanted hydrogen and associated structural changes in the form of deformation distortions; depending on the conditions of long-term temperature heating, reflecting the relationship between long-term heating and the associated structural changes that determine the processes of destruction and oxidation of ceramics. The estimation results of the thermal volumetric expansion coefficient values are presented in Fig. 6a–c.

In the case of initial ceramic samples not subjected to hydrogenation processes and prolonged thermal exposure, the variation in heating temperature reflects the influence of the phase composition, in particular, the presence of $Al_7O_3N_5$ impurity inclusions on the thermal expansion of the crystal structure. In the case of $NiAl_2O_4$ ceramics without the addition of AlN, an elevation in heating temperature from 600 to 800 °C leads to a more than 4-fold increase in the coefficient of thermal volumetric expansion, which indicates the negative effect of high temperatures on the resistance of the crystal lattice to expansion due to thermal effects. The addition of the AlN dopant to the ceramics leads to stabilization of the crystal structure, which is expressed in less pronounced thermal broadening under heating temperature variations (see data in Fig. 6a).

Fig. 6b and c reflect the dependences of the change in the coefficient of thermal volumetric expansion of the studied samples exposed to irradiation with different fluences (data are given depending on the magnitude of atomic displacements) after 5 hours of heating and 500 hours of life tests at various temperatures corresponding to the testing modes of the samples as anode materials. The overall view of the observed alterations indicates that the most significant changes in the coefficient of thermal volumetric expansion are observed for samples of $NiAl_2O_4$ ceramics without the addition of AlN at a temperature of 800 °C, especially for samples irradiated with high fluences. In the case of doped ceramic samples, irradiation with low doses (less than 20 dpa) and subsequent long-term thermal exposure (for 500 hours) has an insignificant effect (in comparison with undoped samples) on the thermal volumetric broadening of the crystal lattice. Moreover, in the case of high-dose irradiation (at atomic displacement values above 20 dpa), ceramics' destruction acceleration effect due to a growth in the crystal lattice volume, which is most pronounced at a temperature of 800 °C, is observed.

Fig. 6d illustrates the results of a comparative analysis of alterations in the thermal volumetric expansion coefficients of the studied samples in the initial and irradiated states up to a dose of 50 dpa at a test temperature of 800 °C, at which, according to measurements of electrochemical and thermal conductivity properties, maximum degradation was observed. As is evident from the data presented, in the case of $NiAl_2O_4$ ceramics without the addition of AlN, irradiation and subsequent tests lead to a 3-fold increase in volumetric expansion in the case of irradiation and heating to 800 °C and holding for 5 hours, and with prolonged heating, the growth in the thermal volumetric expansion coefficient in comparison with the initial value is more than 8 times, which indicates the weak resistance of undoped $NiAl_2O_4$ ceramics to operating processes in the presence of implanted hydrogen in the near-surface layer. The addition of aluminum nitride to the composition, as

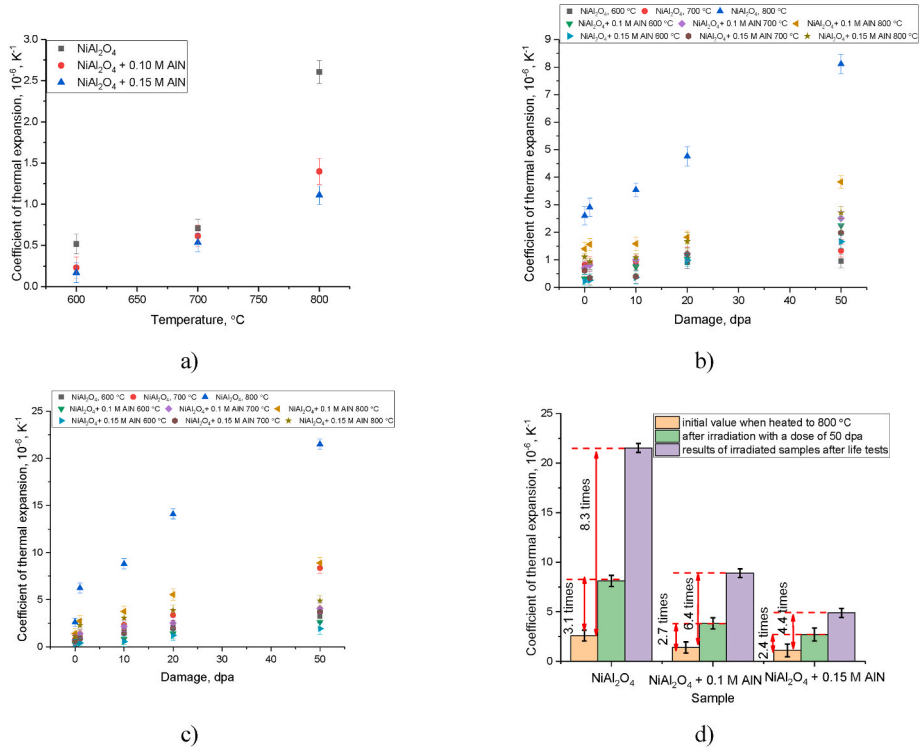


Fig. 6. a) Measurement results of the thermal volumetric expansion coefficient at variation of heating temperatures; b) Measurement results of the thermal volumetric expansion coefficient contingent upon the radiation dose; c) Measurement results of the thermal volumetric expansion coefficient of the studied irradiated samples after 500 hours of resource testing; d) Comparative analysis results of the volumetric expansion coefficient values for samples in the initial state and irradiated with a dose of 50 dpa, heated at a temperature of 800 °C.

can be seen from the presented comparative analysis data, leads to a decrease in the value of the coefficient of thermal volumetric expansion in the initial state (without irradiation and prolonged heating), which indicates the positive effect of the presence of an impurity phase in the composition of ceramics on resistance to thermal effects and associated thermal effects that influence the amplitude of thermal vibrations of atoms. During assessment of the irradiation effect on the change in the thermal volumetric expansion coefficient, it was also found that an increase in the concentration of $Al_7O_3N_5$ impurity inclusions results in smaller changes in the coefficients in comparison with undoped ceramics. In this case, such alterations, especially for irradiated samples under prolonged thermal exposure, indicate the preservation of the stability of the structural properties of ceramics, and may also be due to the fact that the presence of impurity inclusions, according to X-ray diffraction analysis data, results in smaller changes in the crystal lattice parameters due to the deformation processes of stretching and swelling. The presence of $Al_7O_3N_5$ inclusions helps to restrain the migration of implanted hydrogen in the structure, thus, during prolonged thermal exposure, the rate of hydrogen migration, leading to its movement in the near-surface layer, creating additional structural distortions, is significantly reduced and restrained by additional interphase boundaries. Also, the presence of inclusions and interphase boundaries in the case of irradiation and in the case of long-term thermal exposure are sinks of defects near which point and vacancy defects, as well as implanted hydrogen, are concentrated, which makes it possible to restrain its diffusion in the sample, as well as reduce the likelihood of agglomeration in cavities, thereby preventing an increase in the deformation distortion of the near-surface damaged layer. According to the results of a comparative analysis, the presence of $Al_7O_3N_5$ inclusions in the composition of irradiated ceramics under prolonged thermal exposure leads to a decrease in the thermal volumetric swelling coefficient by more than 2.5 and 5 times at a concentration of inclusions in the composition of $NiAl_2O_4$ ceramics equal to 2.5 and 7 wt %, respectively.

4. Conclusion

During experiments carried out to determine the structural disorder associated with volumetric swelling, it was found that the formation of impurity inclusions in the form of $Al_7O_3N_5$ grains in the composition of $NiAl_2O_4$ ceramics results in enhanced resistance to deformation swelling under high-dose irradiation. It was determined that an elevation in the contribution of the $Al_7O_3N_5$ phase leads to a more than 2-fold increase in resistance, expressed in a smaller value of deformation volumetric swelling, which is most pronounced at atomic displacement values above 20 dpa.

During determination of the kinetics of changes in the electrical conductivity of the ceramics under study during their testing as anode materials, it was established that the formation of inclusions in $Al_7O_3N_5$ ceramics results in electrical conductivity growth by 8–20 % depending on the concentration of inclusions, as well as an increase in resistance to destructive changes in electrical conductivity during high-temperature long-term heating of irradiated samples, in which, under the influence of temperature, diffusion processes are initiated, leading to the damaged layer destruction.

In the course of determination of changes in the structural features of the ceramics under study under prolonged thermal exposure, it was found that the presence of impurity inclusions in the composition in the form of grains of the oxy-nitride phase leads to a decrease in the coefficient of thermal volumetric expansion by more than 2.5–5 times. At the same time, an important role in this case is played by the concentration of inclusions, the change in which determines not only the stability of the crystal structure to volumetric expansion and swelling, but also the preservation of the stability of capacitive parameters over a long test period, even in the case of high temperature conditions.

Thus, it can be concluded that the addition of aluminum nitride to the composition of ceramics allows not only to enhance its thermal conductivity and capacitive characteristics as an anode material, but also to increase the stability of maintenance of structural parameters for long-term high-temperature life tests due to the low value of the thermal volumetric expansion coefficient.

Based on the obtained results, it can be concluded that the use of AlN as a stabilizing dopant for the purpose of modification of $NiAl_2O_4$ ceramics to enhance their degradation resistance during hydrogenation, alongside thermal effects, is a very effective modification method. The obtained results indicate not only an elevation in the stability of the crystalline structure of ceramics to degradation processes, but also the possibility of increasing the conductive characteristics of ceramics, which can also be used in the design of solid oxide fuel cells. Further plans in this area of research will include testing the obtained samples for resistance to external environments, as well as processes associated with mechanical effects comparable to operating conditions.

CRediT authorship contribution statement

Gulnaz Zh Moldabayeva: Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Artem L. Kozlovskiy:** Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Funding

The work was performed under financial support of the State Institution “Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan” within the framework of the Scientific-Technical Program BR20280986.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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