The Effect of the Addition of Aluminum Nitride to the Composition of NiAl2O4 Ceramics on Hydrogenation Processes and the Increase in Resistance to Swelling and Degradation

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Abstract: This work examines the effects of the formation of impurity inclusions in the structure of NiAl2O4 ceramics when aluminum nitride is added to them and the occurrence of a reinforcement effect that prevents hydrogenation processes and the subsequent destruction of conductive and thermophysical characteristics. The appeal of ceramics possessing a spinel crystal structure lies in their potential use as ceramic fuel cells for both hydrogen generation and storage. Simultaneously, addressing the challenges related to ceramic degradation during hydrogenation, a critical aspect of hydrogen production, can enhance the efficiency of these ceramics while lowering electricity production costs. The selection of aluminum nitride as an additive for ceramic modification is based on its remarkable resistance to structural damage accumulation, its potential to enhance resistance to high-temperature degradation, and its ability to bolster strength properties. Moreover, an examination of the alterations in the strength characteristics of the examined samples subjected to hydrogenation reveals that the stability of two-phase ceramics is enhanced by more than three to five times compared to the initial ceramics (those without the addition of AlN). Additionally, it was noted that the most significant alterations in both structure and strength become apparent at irradiation fluences exceeding 10^{14} proton/cm^2, where atomic displacements in the damaged ceramic layer reach over 5 dpa. During the evaluation of thermophysical properties, it was discerned that ceramics featuring an impurity phase in their composition exhibit the highest stability. These ceramics demonstrated a reduction in the thermal conductivity coefficient of less than 1% at the peak irradiation fluence.

Keywords: oxide ceramics; NiAl2O4 spinel; radiation swelling; hydrogenation; deformation distortion; aluminum nitride

1. Introduction

Present-day ceramic fuel cells (CFCs) designed for hydrogen production and subsequent storage operate at relatively elevated temperatures, ranging from 500 °C to 800 °C. This necessitates that CFC materials exhibit stable performance over extended periods, ensuring their practicality and economic viability [1,2]. Furthermore, in the majority of instances, the generation of hydrogen coincides with the degradation of the ceramic fuel cell (CFC), resulting in a reduction in its efficacy in producing hydrogen [3–5]. In recent years, particular emphasis has been placed on researching processes linked to hydrogenation and gas-induced embrittlement in the composition of ceramic fuel cells (CFC). This includes the examination of their development over time and their influence on the CFC’s overall performance. While there is a substantial volume of scientific research dedicated to the study of hydrogenation processes in ceramic fuel cells (CFCs), numerous unanswered questions persist concerning the mechanisms of defect formation and their subsequent evolution [6–9]. Furthermore, in contrast to the majority of known materials, oxide and nitride compounds can experience anisotropic distortions and deformations as a result of their structural and phase characteristics during damage accumulation. The repercussions of these phenomena...
can have severe consequences for the functionality of the CFC [10,11]. Similarly, understanding the impact of hydrogen accumulation within the structure of ceramic fuel cells (CFCs) holds great significance, addressing both fundamental and practical considerations. This knowledge is crucial for assessing the CFC’s durability and its ability to withstand hydrogenation, gas expansion, and embrittlement elements [12,13]. One of the ways to assess the resistance of ceramics to hydrogenation processes is to simulate these processes by irradiation with protons with a high irradiation fluence (10^{14}–10^{15} proton/cm^2), which can lead to the formation of structural distortions and deformations characteristic of the accumulation of hydrogen in ceramics and the subsequent influence on the properties of materials. The hydrogenation processes themselves are accompanied by the accumulation of deformation distortions and atomic displacements, which leads to disordering of the crystalline structure of ceramics as well as a deterioration in its thermophysical and strength properties [14–16]. At the same time, the use of proton irradiation with specified conditions (proton energy, irradiation fluence) can make it possible to simulate hydrogenation processes at a certain depth of ceramics and to evaluate the dynamics of changes in structural and strength values, the deterioration of which will adversely affect the performance characteristics of ceramics. Additionally, a method for enhancing the resistance of ceramics against hydrogen-induced swelling and degradation involves incorporating oxide or nitride components known for their heightened resistance to degradation. The inclusion of these components in the ceramic composition can result in the creation of additional interphase boundaries that serve as safeguards against structural degradation during hydrogenation [17–20].

The purpose of this work is to study the processes of hydrogenation in NiAl\_2\textsubscript{2}O\_4 ceramics and to increase ceramics’ resistance to structural and strength degradation through the addition of aluminum nitride [21–23], which causes high resistance to degradation due to the accumulation of protons in the structure of the damaged layer [24,25]. Meanwhile, the simulation of hydrogenation processes involved subjecting the investigated ceramics to proton irradiation with an energy level of 1.5 MeV. This irradiation resulted in the creation of a layer exceeding 10 \( \mu \)m in thickness, with hydrogen exposure and accumulation occurring within this layer. The selection of irradiation fluences in the range of \( 10^{11}–5 \times 10^{15} \) proton/cm\(^2\) was deliberate, as it allowed for the replication of radiation damage levels within the range of 20 to 50 displacements per atom (dpa) at the highest irradiation fluences. Additionally, it enabled the evaluation of the radiation damage accumulation kinetics within the ceramic structure. The choice of NiAl\_2\textsubscript{2}O\_4 ceramics as objects of research was due to their great potential for use as materials for ceramic fuel cells capable of operating in aggressive environments as well as high temperatures, as reported in several scientific papers [26–28]. Simultaneously, a range of studies [29–31] emphasized the necessity of modifying these ceramics to enhance their resistance against external factors related to operational processes, such as hydrogenation or mechanical stresses at elevated temperatures.

2. Materials and Methods
2.1. Synthesis of Ceramic Samples

NiO, Al\_2O\_3, and AlN powders purchased from Sigma Aldrich (St. Louis, MO, USA) were used as initial components for the production of ceramics. The sizes of the powders in the initial state were about 10 microns, and the chemical purity was 99.95%. Nickel oxide (NiO) and aluminum oxide (Al\_2O\_3) powders in a stoichiometric ratio of 1:3 M were chosen as the starting components for the synthesis of ceramics with a spinel structure of the NiAl\_2\textsubscript{2}O\_4 type. During mechanochemical synthesis and subsequent thermal sintering, according to previous studies, it was established [32] that the use of a molar ratio of components NiO:Al\_2O\_3 \rightarrow 1:1 results in the formation of a low content of impurity inclusions in the form of nickel oxide, which makes it impossible to obtain a highly ordered spinel structure. The use of this stoichiometric ratio made it possible to obtain highly ordered ceramics with a spinel-type crystal structure of the NiAl\_2\textsubscript{2}O\_4 type. The addition of aluminum nitride
(AlN) was conducted by mechanochemical mixing and subsequent thermal sintering of powders ground to a homogeneous (uniform in composition) state in a muffle furnace at a temperature of 1500 °C for 10 h, during which the formation of a NiAl$_2$O$_4$ phase with a high degree of structural ordering occurs. The concentration of AlN was adjusted within the range of 0 to 0.15 M. The decision to use AlN was driven by its potential to reinforce the ceramic’s crystalline structure and enhance its resistance to external factors, including increased resistance against gas swelling induced by hydrogenation.

The process of mechanochemical mixing, aimed at achieving a uniform powder composition, was executed using a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany). The mixing procedure was conducted at a grinding speed of 400 rpm for a duration of 5 h. Subsequently, thermal annealing was performed within a Nabertherm LHT 04/18 muffle furnace (Nabertherm GmbH, Lilienthal, Germany) in an oxygen-containing atmosphere. Annealing of the samples was carried out on samples pressed into tablets with a thickness of about 15 microns and a diameter of 10 mm. The samples were pressed into a special mold under a pressure of 300 MPa. The samples were placed in corundum crucibles, which were placed in the muffle furnace chamber, after which the samples were heated to a temperature of 1500 °C at a heating rate of 20 °C/min until the set annealing temperature was reached, after which the temperature in the chamber was stabilized and maintained for 10 h. After 10 h, the samples were cooled together with the chamber for 24 h until they reached room temperature.

Cooling of the samples to room temperature was carried out together with the oven for 24 h, the main purpose of which was to avoid the occurrence of oxidation effects when hot samples interact with the atmosphere when removed from the oven.

2.2. Characterization of the Ceramic Samples under Study

The morphological features of the synthesized ceramics, changes in which are caused by the addition of AlN to the composition, were studied using scanning electron microscopy. Images were taken on a Hitachi TM3030 microscope (Hitachi, Tokyo, Japan).

The structural characteristics and phase composition of the ceramics, which vary with the concentration of AlN added, were ascertained through the analysis of X-ray diffraction patterns obtained from the ceramic samples under investigation. These diffraction patterns were obtained via a D8 Advance ECO X-ray diffractometer (Bruker, Berlin, Germany). The diffraction patterns were recorded in the Bragg–Brentano geometry within the angular range of 2θ = 15–100°, with this range selection made while considering the potential presence of inclusions in the small-angle region. The diffraction patterns were analyzed with the assistance of the DiffracEVA v.4.2 software code. The refinement of crystal lattice parameters and volume involved approximating diffraction reflections and identifying the positions of their peaks, considering deformation distortions resulting from mechanochemical grinding or the accumulation of radiation-induced damage. The evaluation of impurity inclusions and their impact was achieved by assessing the weight contributions of diffraction reflections for both the main phase and impurities.

To calculate the structure factor of ordering, the data on changes in the crystal lattice parameters of the samples obtained by varying the ratio of the components as well as data on the reference values of the crystal lattice parameters taken from the PDF-00-010-0339 database were used. In the case of a spinel crystal lattice type, the parameters were refined using parameter a (for a cubic crystal lattice type). Data from card values PDF# 00-010-0339, a = 8.048 Å, were taken as reference parameters from the PDF-2 NiAl$_2$O$_4$ database.

2.3. Simulation of the Ceramics’ Hydrogenation Processes by Irradiation

To prepare for irradiation, tablets were formed from the obtained powders with a diameter of 10 mm and a thickness of approximately 15 µm. These tablets underwent annealing at a temperature of 700 °C for a duration of 20 h to eliminate deformation distortions stemming from the pressing process. The choice of ceramic thicknesses was made considering prior knowledge about the maximum proton penetration depth in
ceramics, ensuring that the irradiated layer constituted more than 80–90% of the total thickness. Additionally, in determining the ceramic thickness, consideration was given to the diffusion of structural damage, which extends beyond the maximum depth of proton penetration associated with high-dose irradiation.

The simulation of hydrogenation processes was achieved through proton irradiation, with a proton energy level of 1.5 MeV and fluences ranging from $10^{11}$ to $5 \times 10^{15}$ proton/cm$^2$. The irradiation temperature was 700 °C, which made it possible to bring the conditions for hydrogen accumulation in the damaged layer as close as possible to the actual operating conditions of the ceramics. The selected irradiation conditions allowed for the simulation of radiation damage accumulation in a near-surface layer exceeding 10 µm in thickness. This range corresponded to atomic displacement values spanning from 0.0001 dpa to 46 dpa, achieved at the maximum irradiation fluence. The simulation results of proton ionization losses along their path as they interact with the ceramic’s crystal structure were acquired through the SRIM Pro 2013 software code. These calculations are illustrated in Figure 1, depicting the resulting trends in ionization loss variations and the evaluation of atomic displacements based on the irradiation fluence.

![Graph of the change in the value of ionization losses of incident protons along the trajectory of motion in the near-surface layer; (b) dependence of plotting the value of atomic displacements along the trajectory of proton motion in the near-surface layer of ceramics.](image)

Based on the calculated data, it was determined that the maximum penetration depth exceeds 10 µm. At this depth, the primary factor contributing to structural alterations in ceramics arises from the interactions between incident protons and the electronic subsystem. Given the dielectric characteristics of ceramics, these interactions can induce anisotropic modifications in electron distribution, leading to disruptive changes in the crystal lattice. This disruption results from the accumulation of residual mechanical stresses within the ceramic composition. At the same time, the effect of atomic displacements linked to the interaction of protons with the nuclear subsystem is most likely at a travel depth of 10–12 µm, in the region where the contribution of ionization losses during interaction with electrons is minimal, and the dominant role in structural distortions is played by the interactions of incident particles with nuclei.

2.4. Determination of Strength and Thermophysical Parameters of Ceramics before and after Hydrogenation

The impact of the additive on alterations in strength properties was evaluated through indentation and single-compression testing of the specimens. Indentation tests were conducted using a LE CO LM700 microhardness tester (LECO, Tokyo, Japan), using a Vickers diamond pyramid as the indenter and applying a load of 100 N to the indenter. A single-compression examination aimed at assessing resistance to cracking and crack formation was performed using a testing apparatus (Walter + Bai AG, Löhningen, Switzerland), which
applied a constant loading speed of 0.1 mm/min to the specimens. The determination of hardening and crack resistance values, along with their variations under external influences (such as hydrogenation), involved conducting a comparative analysis of the provided hardness values and the maximum pressure that the ceramics could endure during the compression of irradiated samples, considering their initial characteristics.

Thermophysical parameters were measured, and their decline due to the accumulation of crystal lattice deformation was determined using the technique of measuring longitudinal heat flow in ceramic specimens, followed by the calculation of the thermal conductivity coefficient. These measurements were conducted utilizing a KIT-800 device (Teplofon, Moscow, Russia), and the thermal conductivity coefficient was assessed across a temperature range spanning from 25 to 800 °C.

3. Results and Discussion
3.1. Characterization of Initial Samples by Varying the Addition of Aluminum Nitride with Different Concentrations

Figure 2 demonstrates the results of X-ray phase analysis of the ceramics under study depending on the concentration of the AIN component, reflecting alterations in the phase composition of the ceramics associated with the formation of impurity inclusions, the occurrence of which is due to an increase in the AIN concentration. The overall impression of the provided diffraction patterns highlights a significant level of structural order in the acquired samples. This is evident in the substantial disparity between the intensities of diffraction reflections and background radiation. Additionally, the analysis of the position and relative intensities of diffraction reflections in the examined samples is consistent with the cubic crystal structure characteristic of NiAl2O4, specifically belonging to the Fd-3m(227) spatial system (PDF-00-010-0339). Furthermore, with regard to the initial ceramic samples (without the addition of AIN), the diffraction patterns do not reveal any low-intensity reflections that would typically signify the presence of impurity inclusions in the form of unreacted initial component oxides. Conversely, the altered shape of diffraction reflections suggests the existence of factors within the structure that introduce distortions. These distortions manifest as reduced structural order and deviations in crystal lattice parameters from their reference values.

Figure 2. The results of X-ray diffraction of the studied ceramic samples depending on the variation in AIN concentration upon its addition (red dotted lines indicate the formation of inclusions in the form of the Al2O3N8 orthorhombic phase).
When incorporating AlN at concentrations ranging from 0.01 to 0.05 M, there was no evidence of the emergence of new diffraction reflections indicative of impurity inclusions in the resulting diffraction patterns. This observation can be attributed to the influence of the relatively low concentrations of AlN utilized during synthesis, which do not result in the formation of any impurities within the ceramic composition. It is important to note that an elevation in AlN concentration leads to the alignment of diffraction reflections, signifying an enhancement in their structural order and the mitigation of deformation distortions.

According to the obtained X-ray phase analysis data, at AlN concentrations of 0.10–0.15 M, the formation of the oxide-nitride phase Al\(_7\)O\(_3\)N\(_8\) (PDF-00-048-1580) occurs in the ceramic structure, the appearance of which is due to the processes of phase transformations between aluminum oxide and nitride at high temperatures. In this case, a variation in AlN concentration from 0.10 to 0.15 M results in an elevation in the contribution of this phase from 2.1 to 6.4 wt.%. The existence of this phase within concentrations of 0.10 to 0.15 M can be attributed to the heightened presence of aluminum nitride. When aluminum nitride interacts with aluminum and nickel oxides, it gives rise to a complex orthorhombic phase. The emergence of this phase can exert a notable influence on the alterations in the strength properties of the ceramics.

Using the acquired diffraction patterns, an evaluation of the structural parameters was conducted, along with an assessment of the degree of structural order. Changes in this factor indicate a reduction in deformation distortions within the crystal structure, which can be attributed to mechanochemical grinding processes and subsequent phase transformations during thermal sintering. Table 1 provides data on the crystal lattice parameters and volume, showcasing how they change in response to variations in the AlN concentration within the ceramic composition.

Table 1. Data on the structural parameters of the ceramics under study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration of AlN, M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Phase—NiAl(_2)O(_4)—Spinel, Cubic Fd-3m(227)</td>
</tr>
<tr>
<td>Lattice parameter, Å</td>
<td>8.0521</td>
</tr>
<tr>
<td>Volume crystal lattice, Å(^3)</td>
<td>522.1</td>
</tr>
<tr>
<td>Factor of structural ordering *</td>
<td>1.92</td>
</tr>
<tr>
<td>Density **, g/cm(^3)</td>
<td>4.494</td>
</tr>
</tbody>
</table>

* The structural ordering factor was calculated based on a comparative analysis of alterations in the structural parameters of the NiAl\(_2\)O\(_4\) phase with the data on the card values PDF-00-010-0339 for this phase from the PDF-2 database. A decrease in the structural ordering factor indicates an improvement in structural parameters and a decrease in their differences from the reference values. ** The density of the ceramic was estimated by calculating these changes in crystal parameters (lattice volume (V)) using the formula \(p = \frac{16602 \times Z \times A}{V}\), \(A\)—molar weight, \(Z\)—8.

As is evident from the information presented in Table 1, the introduction of AlN into NiAl\(_2\)O\(_4\) ceramics results in a reduction in the crystal lattice parameters and its volume. The reduction in the crystal lattice parameters of the NiAl\(_2\)O\(_4\) phase with the growing concentration of the AlN dopant is due to the effects of structural ordering associated with the ordering of the crystal lattice and its compaction. A decline in the crystal lattice parameters results in a decrease in its volume, which in turn directly affects the number of porous inclusions (density changes). At the same time, a rise in the structural ordering degree (a decrease in the parameters of the crystal lattice, as well as its volume) is due to a decrease in deformation distortions caused by the processes of mechanochemical grinding of samples. This reduction signifies an enhancement in the structural order of the ceramics and a decrease in deformation-related irregularities within the structure. Simultaneously, a substantial decline of more than four to six times in the structural ordering factor in samples where the presence of an Al\(_7\)O\(_3\)N\(_8\) impurity phase was identified suggests that
these ceramics exhibit minimal deformation distortions. This, in turn, contributes to their reinforcement and densification, leading to a reduction in the volume of the crystal lattice.

Figure 3 displays scanning electron microscopy (SEM) images depicting the morphology of ceramics. These images illustrate alterations in grain structure and their packing density as the composition varies.

Figure 3. The results of morphological features of synthesized ceramics depending on alterations in AlN concentration in the composition: (a) pristine; (b) 0.01 M; (c) 0.03 M; (d) 0.05 M; (e) 0.10 M; (f) 0.15 M.
Upon analyzing the obtained SEM images of ceramics with varying AlN content, the observed changes can be categorized into two distinctive stages. The initial stage is noticeable when AlN concentrations range from 0.01 to 0.03 M. In this range, an increase in AlN content leads to the development of a densely packed structure consisting of grains of irregular cubic or pentagonal shape. As the AlN concentration increases, the sizes of these grains diminish. In the second stage, not only do grain sizes decrease but there is also the emergence of inclusions possessing a distinct structure. The variation in color gradation within the images indicates that these new inclusions possess a different phase composition. Simultaneously, the concentration of these inclusions rises proportionally with the increase in AlN content in the ceramic composition. It is noteworthy that these inclusions are situated at grain boundaries, thereby generating additional interphase boundary effects. The presence of these boundaries can contribute to the strengthening of ceramics. When comparing the findings from morphological studies concerning the formation of new inclusions at higher concentrations with the data from X-ray phase analysis, we can deduce the following conclusion. The emergence of these inclusions can likely be attributed to the formation of the Al$_7$O$_3$N$_8$ phase, which was detected in X-ray diffraction patterns of samples featuring an AlN concentration ranging from 0.10 to 0.15 M. It is noteworthy that the escalation in the contribution of this phase aligns well with the data estimating the quantity of these inclusions in the provided SEM images (the concentration of inclusions clearly rises according to the data in Figure 3e,f). However, the absence of reflections indicative of the Al$_7$O$_3$N$_8$ phase in the X-ray diffraction patterns (as shown in Figure 2), despite the observation of these inclusions in the morphological images (as seen in Figure 3d), can be rationalized by the low concentration of these inclusions, which falls below the detection threshold of the X-ray method (detection limit less than 0.1 wt.%).

Thus, summing up the characterization of the ceramic samples under study with variations in the AlN component, the following conclusions can be drawn. Firstly, increasing the concentration from 0.01 to 0.05 M results in heightened structural order and densification of the ceramics, consequently leading to a reduction in grain size. Secondly, at concentrations of the AlN component above 0.05 M, according to X-ray diffraction data, the formation of an Al$_7$O$_3$N$_8$ impurity phase is observed, the presence of which results in the formation of fine-grained ceramics with close-packed grains, at the boundaries of which impurity phase grains are formed. This phenomenon gives rise to the presence of interphase boundaries. Simultaneously, the reduction in grain size results in an elevated dislocation density and intergrain boundaries. These factors collectively contribute to enhanced resistance against external influences, including mechanical and radiation-related factors.

3.2. Evaluation of the Efficiency of Enhancing the Resistance to Structural Disorder and Swelling of NiAl$_2$O$_4$ Ceramics by Adding AlN to the Composition

One approach for assessing the resistance of ceramics to radiation-induced damage, linked to the accumulation of deformation distortions in the structure, involves monitoring the dynamic of alterations in structural parameters. This method entails ascertaining the structural characteristics (such as crystal lattice parameters or volume) for irradiated samples, contingent upon the irradiation fluence or the degree of accumulated atomic displacements, and subsequently comparing these values with those of the original samples. The outcomes of this comparative analysis enable the determination of the nature of structural changes connected to the accrual of radiation damage. Furthermore, it aids in gauging a material’s resistance to external influences, including the accumulation of structural distortions in cases where modifications have been made. Structural parameters for samples subjected to hydrogenation (irradiation with protons with different fluences) were determined based on the obtained X-ray diffraction patterns. The results of a comparative analysis of changes in structural parameters (changes in the crystal lattice volume and the factor of structural ordering) are presented in Figure 4.
The swelling value was determined using the following calculation method. The swelling value was determined by calculating changes in the crystal lattice volumes of the studied samples in the initial state (depending on the concentration of the AlN dopant) and their changes as a result of hydrogenation processes under high-dose irradiation.

The structural disorder value was calculated based on changes in the structural order values (calculated for the initial values of the crystal lattice parameters) as a result of external influences (in this case, hydrogenation processes under high-dose irradiation).

It is worth noting that the data obtained are presented depending on the magnitude of atomic displacements, calculated on the basis of data from the simulation of the interaction of incident protons with the crystal structure of ceramics. The choice of such a representation is due to the possibility of a comparative analysis of the observed structural changes, if necessary, with other types of radiation effects.

The general trend of changes in structural parameters indicates the formation of deformation distortions and residual tensile mechanical stresses in the structure of ceramics, since the change parameters are characteristic of a rise in the crystal lattice volume and the structural ordering factor grows with the accumulation of atomic displacements. In this case, the observed changes in structural parameters can be divided into two types: (1) small changes characteristic of atomic displacements of less than 1 dpa; and (2) a sharp deformation distortion of the crystal lattice at large values of atomic displacements. At the same time, the formation of the Al₃O₅N₈ impurity phase in the structure of ceramics results in a reduction of more than fivefold to sixfold in structural disorder compared to ceramic samples that do not contain AlN. The heightened resistance to structural deterioration in two-phase ceramics could be attributed to the presence of interphase boundaries. These boundaries serve to inhibit the degradation of the crystal structure arising from the accumulation of structural distortions associated with ionization effects [33,34]. It is important to highlight that the most significant structural alterations occur at irradiation fluences where substantial atomic displacements become the prevailing factor. This phenomenon signifies the impact of hydrogenation on the damaged layer, leading to its structural degradation due to deformations and residual mechanical stresses resulting from the interaction of incident particles with the crystalline structure. This interaction also involves the conversion of transferred kinetic energy into thermal energy within the crystalline structure [35,36].
Figure 5 illustrates the outcomes of a comparative assessment of the extents of structural alterations recorded at maximum irradiation fluences, contingent upon the AlN concentration within the ceramic composition. These patterns exemplify the enhancement in ceramics’ stability in response to the inclusion of AlN when subjected to radiation-induced damage and hydrogenation processes that transpire during high-dose irradiation.

As evident from the depicted trends in structural parameter changes following irradiation, ceramics devoid of AlN exhibited the highest susceptibility to structural degradation. In these ceramics, the decline in the structural ordering factor exceeded 1.5 times in comparison to the initial value, and the expansion of the crystal lattice at the maximum fluence reached nearly 2%. In contrast, similar metrics for two-phase ceramics samples (where the presence of an Al7O3N8 impurity phase was confirmed) remain below 0.5% (crystal lattice swelling) and less than 1% (deterioration of the structural ordering factor). Furthermore, for samples featuring AlN concentrations ranging from 0.01 to 0.10 M, a noticeable reduction in the degradation of structural parameters is observed. This reduction indicates an enhanced resistance to the destruction of the crystal lattice and a decrease in the effect of disorder arising from the accumulation of deformation distortions and residual tensile mechanical stresses (arising during the deformation of the crystal lattice).

3.3. Assessment of the Irradiation Effect on Softening and Reduction of Strength and Thermophysical Parameters of NiAl2O4 Ceramics

Figure 6 displays the outcomes pertaining to alterations in hardness and resistance to cracking (maximum pressure threshold ceramics can endure during a single compression). These results reflect the degradation of ceramics’ strength properties in relation to the accumulation of atomic displacements (as fluence increases). Prior to examining the correlation between changes in the strength characteristics of irradiated samples, it is important to acknowledge the impact of the ceramics’ strengthening (manifested as an increase in hardness and maximum pressure) in response to variations in AlN concentration. Such a change in the strength characteristics of the ceramic samples under study depending on the change in the composition of the AlN concentration may be due to several factors. Firstly, the incorporation of AlN into the ceramic composition, as indicated by the X-ray diffraction analysis in Figure 2 and the information in Table 1, results in heightened structural order.
This enhancement is accompanied by the densification of ceramics, subsequently leading to a reduction in residual deformation and structural distortions that originated during the synthesis and phase formation of the ceramics. This kind of structural ordering can result not only in strengthening but also in an elevated crack resistance when subjected to external pressure. This effect is clearly demonstrated in the obtained data, as presented in Figure 6b. Secondly, as illustrated in Figure 3 (providing information on the morphological characteristics of the studied ceramics), an increase in the concentration of the AlN additive in the ceramic composition results in a reduction in grain size. Additionally, it prompts the formation of a structure in which the intergranular space is occupied by grains of the Al$_7$O$_3$N$_8$ impurity phase (occurring at concentrations of 0.05–0.15 M). A reduction in grain size, coupled with the creation of these structures, gives rise to what is known as the dislocation strengthening effect. This effect involves an increase in dislocation density and the quantity of grain boundaries, and it is prominently evident in the alterations observed in the strength characteristics of the examined ceramics.

![Graph](image.png)

**Figure 6.** The results of changes in strength characteristics: (a) change in hardness depending on irradiation fluence (value of atomic displacements); (b) change in the maximum pressure that ceramics can withstand during a single compression.

General trends in changes in strength characteristics depending on the magnitude of atomic displacements can be divided into two clearly defined zones. The first zone is characterized by the absence of significant changes in strength parameters and is typical for fluences of $10^{11}$–$10^{14}$ proton/cm$^2$, characteristic of atomic displacement values of less than 1 dpa. The absence of visible changes in this case is due to the high resistance of ceramics to mechanical influences, due to both high strength characteristics and small structural changes caused by the accumulation of deformation distortions during irradiation. The second zone is typical for atomic displacement values greater than 1 dpa, which is characterized by a decrease in strength characteristics; however, the trends of changes depending on the concentration of AlN in the composition of ceramics are different. These differences consist of a decrease in the change in these values of hardness and maximum pressure for the samples depending on the increase in AlN concentration. In this case, such changes can be explained both by the effect of dislocation strengthening (most pronounced for samples containing impurity inclusions in the form of Al$_7$O$_3$N$_8$) and by the initial values of structural ordering.

The outcomes demonstrating alterations in the strength properties, which signify a weakening and reduced resistance to cracking, of the studied ceramics based on accumu-
lated radiation damage are depicted in Figure 7. The overall presentation of the acquired data suggests a two-stage pattern in the evolution of ceramics’ resistance to external factors, encompassing the accumulation of structural distortions and deformation inclusions within the damaged layer. The variations in the concentration of these factors directly influence the deterioration of the strength parameters.

Figure 7. The results of changes in strength characteristics: (a) decrease in hardness (softening); (b) reduction in crack resistance.

As can be seen from the presented data, the most pronounced changes in strength parameters associated with hardness degradation and a decrease in crack resistance are observed in samples of NiAl2O4 ceramics that do not contain AlN. At the same time, the maximum value of degradation of strength properties was more than 15% at the maximum irradiation fluence. Meanwhile, the reduction in strength parameters for samples in which the formation of an Al7O3N8 impurity phase was observed amounted to less than 3–4% at the maximum irradiation fluence. This is notably more than three to five times lower than the corresponding values for ceramics that lack impurity inclusions (i.e., those without the addition of AlN to the composition). The findings concerning alterations in strength characteristics highlight a favorable impact stemming from the presence of impurity inclusions in the form of the Al7O3N8 phase within the ceramic composition. This effect extends beyond strengthening and also encompasses an increase in resistance to the degradation of strength properties resulting from the accumulation of radiation damage and hydrogenation processes.

A crucial consideration in assessing the viability of ceramics for use in fuel cells is their thermophysical properties and their capacity to maintain stability in the face of external factors, including processes of degradation and hydrogenation during operation. A decrease in thermal conductivity characteristics can potentially result in detrimental outcomes, including effects linked to the inhibition of phonon heat transfer, given the dielectric nature of ceramics. An elevation in the inhibition of phonons involved in heat transfer, as a consequence of increased collisions with deformation inclusions, can lead to the development of localized areas of overheating. This, in turn, can bring about a destructive reduction in heat transfer efficiency, which would have an adverse impact on the ceramics’ operational performance.

Figure 8 provides an illustration of the evaluation of variations in the thermal conductivity coefficient, which serves as an indicator of heat transfer within ceramics. The changes observed in irradiated samples suggest a degradation in heat transfer processes and the
emergence of supplementary heat losses within the structure of damaged ceramics. An examination of the thermophysical characteristics of the initial ceramic samples in relation to the increment in AlN concentration within the composition reveals a favorable trend toward enhancing thermal conductivity. These alterations in thermal conductivity in the context of dielectric ceramics are inherently linked to the extent of structural ordering. In this context, the enhancement of the crystal structure resulting from increased ordering of the crystal lattice and greater compaction as the AlN concentration rises results in a thermal conductivity increase of over 5–10% for AlN dopant concentrations between 0.01 and 0.05 M. Additionally, the presence of the Al$_2$O$_3$N$_8$ impurity phase within the composition significantly enhances thermal conductivity by more than 15–20% when compared to the undoped samples.

![Figure 8](image_url)

**Figure 8.** The results of changes in the thermal conductivity coefficient of ceramics depending on the value of atomic displacements.

As can be seen from the presented data on alterations in the thermal conductivity coefficient of irradiated samples, the most significant manifestations of deterioration in thermophysical parameters appear in the case when the magnitude of deformation distortions corresponds to atomic displacements of more than 5 dpa (at fluences above $10^{14}$ proton/cm$^2$). In this case, the deterioration of thermal conductivity is due to the accumulation of deformation distortions in the structure and the formation of regions of disorder, the presence of which results in the appearance of additional scattering centers for phonons, which leads to the deterioration of thermal conductivity. It is important to highlight that in the case of ceramics that contain impurity inclusions that prevent severe destruction of the crystal structure (see data on the results of assessing changes in structural parameters), the decline in the thermal conductivity coefficient is less than 1% even in cases of high irradiation doses. Moreover, for ceramics without the addition of AlN in the ceramic composition, the decrease in the thermal conductivity coefficient at maximum irradiation fluence is more than 7%. Furthermore, it is important to emphasize that the structural ordering observed in the samples at low AlN concentrations within the ceramic composition results in heightened stability of the thermophysical parameters. Notably, the reduction in the thermal conductivity coefficient, in comparison to the variations in strength characteristics, is considerably smaller (more than two times). This suggests
that hydrogenation processes exert a more pronounced effect on alterations in strength characteristics compared to their impact on thermophysical parameters.

4. Conclusions

This study aimed to investigate the kinetics of radiation damage linked to the accumulation of hydrogen within the near-surface damaged layer of ceramics. It was determined that the primary deformation processes linked to the expansion of the near-surface ceramic layer stem from the emergence of residual tensile mechanical stresses. The presence of these stresses is a consequence of the destructive alteration of the crystal structure during hydrogenation, which also involves partial amorphization. The connection between alterations in strength properties, specifically hardness and crack resistance in ceramics, was explored in relation to the extent of deformation distortions stemming from the accumulation of implanted hydrogen. It was ascertained that the composition of the ceramics, along with the presence of two distinct phases, engenders structural strengthening attributed to dislocation strengthening and an augmented crack resistance. Moreover, an examination of alterations in the strength characteristics of the examined samples subjected to hydrogenation reveals that the stability of two-phase ceramics is enhanced by more than three to five times compared to the initial ceramics (those without the addition of AlN). Additionally, it was noted that the most significant alterations in both structure and strength become apparent at irradiation fluences exceeding $10^{14}$ proton/cm$^2$, where atomic displacements in the damaged ceramic layer reach over 5 dpa. During the evaluation of thermophysical properties, it was discerned that ceramics featuring an impurity phase in their composition exhibit the highest stability. These ceramics demonstrated a reduction in the thermal conductivity coefficient of less than 1% at the peak irradiation fluence.

Analysis of the data obtained revealed that the formation of two-phase ceramics with the main phase of NiAl$_2$O$_4$ and impurity inclusions in the form of Al$_7$O$_3$N$_8$ grains located along the grain boundaries had increased resistance to hydrogenation while maintaining stability of strength and thermophysical characteristics at high irradiation doses (20–50 dpa), simulating hydrogenation processes.

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