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Original Research Article

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STUDY OF THE INFLUENCE OF THE ACCUMULATED DOSE OF DAMAGE IN THE NEAR-SURFACE LAYER ON RESISTANCE TO EXTERNAL INFLUENCES ASSOCIATED WITH CORROSION PROCESSES DURING HIGH-TEMPERATURE ANNEALING

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Abstract. Investigating the challenges associated with the structural and strength degradation of ceramic fuel cells, which hold significant potential for hydrogen production through electrolysis methods, is a current focus of research. Understanding the degradation processes and their occurrence rate is crucial in the assessment of the efficacy of these ceramics for applications in alternative energy production, specifically in the realm of hydrogen energy. The aim of this study is to ascertain the impact of doping ceramics with aluminum nitride $NiAl_2O_4$, irradiated with protons with a dose of approximately 50 dpa, on resistance to high-temperature degradation, and associated corrosive processes of oxidation and swelling, as well as migration processes of implanted hydrogen. Three types of ceramics were selected as objects for study: $NiAl_2O_4$ ceramics, $NiAl_2O_4$ ceramics stabilized with 0.05 M AlN, $NiAl_2O_4$ ceramics stabilized with 0.15 M AlN, that are distinguished by the formation of impurity phases in $Al_7O_3N_8$, with an orthorhombic type of crystal lattice. As a result of high-temperature tests, it was observed that $NiAl_2O_4$ ceramics, when stabilized, exhibit reduced susceptibility to destructive alterations in strength characteristics, primarily attributed to the deformation distortion of the crystal structure caused by its swelling. These processes are associated with an augmentation in the thermal expansion of the crystal structure, manifested in the deformation swelling of the crystal lattice volume.

Keywords: ceramic fuel cells, radiation embrittlement, high-temperature aging, degradation, swelling, reduction in strength parameters.

1. Introduction

Addressing challenges in energy production is a crucial criterion for the sustainable development of any country's economy. Exploring alternative energy sources, such as nuclear or hydrogen energy, stands as a cornerstone in the development of the energy sector. The growing interest in alternative energy sources and the diversification of production methods primarily stem from the necessity to diminish the energy sector's reliance on fossil resources, including hydrocarbons [1-3]. The use of new sources of energy, including alternative sources, will in the short term reduce the amount of natural resources consumed for energy production, as well as the pressure on the environment, by reducing harmful emissions from the burning of fossil energy resources for energy production. In this connection, considerable emphasis in research is directed towards hydrogen energy, particularly focusing on methodologies for hydrogen production through electrolysis or steam reforming [4,5].

The growing interest in ceramic fuel cells within the realm of hydrogen energy primarily stems from the potential to broaden sustainable approaches for hydrogen production and reduce its production costs. This reduction in cost is pivotal for the advancement of green technologies, serving as an alternative means to diminish hydrocarbon dependence within the energy sector [6,7]. Concurrently, study of degradation processes in fuel cells, linked to their operational procedures such as oxidation at elevated temperatures, represents a crucial research area. This exploration not only evaluates the suitability of ceramics in fuel cells but also contributes fundamental insights into the degradation mechanisms. Simulation of operational conditions, especially the elevated temperatures typical of fuel cells, enables an assessment of the degradation mechanisms in ceramic fuel cells. In scenarios involving gas-filled bubbles containing accumulated hydrogen, this simulation aids in understanding the kinetics of their migration and gauging their influence on changes in strength properties [8,9]. It is acknowledged that the high mobility and ability of hydrogen to aggregate within voids and pores can accelerate degradation processes when exposed to external factors, such as high-temperature heating. The high-temperature corrosion processes are instigated not only by the accelerated mobility of accumulated hydrogen in the near-surface layer of ceramic fuel cells, but also the processes of oxygen penetration through pores and microcracks [10-13]. Which results in destruction because of the accumulation of deformation distortions and stresses in cavities filled with hydrogen, as well as the crystalline structure into which oxygen is introduced. Moreover, an elevation in deformation distortions and stresses occurs both due to the expansion of the crystal lattice during the introduction of oxygen into nodes and interstices, and an elevation in gas-filled bubbles due to their merging or a growth in volume during the accelerated migration of hydrogen near these cavities [14,15].

Based on the above, the key aim of this article is to investigate the processes of high-temperature degradation of $NiAl_2O_4$-based ceramics stabilized with aluminum nitride, alongside to determine the influence of accumulated structural damage linked to the accumulation of hydrogen in the surface layer of ceramics on the degradation rate of the strength properties of ceramics.

2. Materials and methods

The objects of investigation were ceramic samples exhibiting a $NiAl_2O_4$ spinel structure, synthesized through mechanochemical solid-phase methods using NiO and Al_2O_3 compounds in a stoichiometric ratio of 1:3 M, followed by annealing at a temperature of 1500°C. Doping of $NiAl_2O_4$ ceramics in order to increase their resistance to external influences was carried out with aluminum nitride (AlN) with different molar ratios of 0.05 and 0.15 M, which were also annealed at a temperature of 1500°C. The specimens underwent grinding using a Pulverisette 6 planetary mill (Fritsch, Berlin, Germany), followed by thermal annealing conducted in a Nabertherm LHT 04/18 muffle furnace. (Nabertherm GnbH, Lilienthal, Germany). The choice of AlN dopant concentrations was determined by the possibility of obtaining ceramics exhibiting a significant structural ordering degree (exceeding 95% at a dopant concentration of 0.05 M) and ceramics containing impurity inclusions in the form of $Al_7O_3N_8$ impurity phases, characterized by an orthorhombic crystal lattice. A detailed study of the structural features of $NiAl_2O_4$ ceramics depending on the AlN stabilizing additive concentration was presented in the work [16]. The samples were irradiated at the UKP-2.1 accelerator (Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan, Almaty, Kazakhstan) with protons with an energy of 1.5 MeV and a fluence of 5×10^{15} ion/cm^2 (which, according to SRIM Pro 2013 calculations, corresponds to a displacement value of about 50 dpa).

To determine the degradation mechanisms characteristic of high-temperature corrosion processes of ceramic fuel cells exposed to proton irradiation with accumulated structural distortions caused by high-dose irradiation (about 50 dpa), the following experiments were carried out. The studied ceramic samples after irradiation were subjected to thermal heating in a muffle furnace for 500 hours at temperatures of 500, 600 and 700°C. The choice of the annealing temperature range (500 – 700°C) is due to the possibility of modeling the main operating modes of ceramic fuel cells during hydrogen production under conditions as close as possible to real ones. The choice of research objects subjected to irradiation is based on the ability to ascertain operational conditions and the accompanying structural deformations that manifest in samples with high concentrations of deformation distortions attributed to hydrogen accumulation.

Determination of the resistance of ceramics to high-temperature heating and corrosion processes was assessed by measuring hardness before and after testing. At the same time, measurements were performed

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both on initial samples that were not exposed to irradiation, and after high-dose irradiation with protons with a dose of about 50 dpa. Determined values of changes in hardness and resistance to single compression made it possible to estimate the rate of degradation of ceramics as a result of high-temperature exposure, as well as to estimate the contribution of accumulated radiation damage to the degree of disorder of the surface layer. The hardness measurement was carried out using the indentation method, which was implemented using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey). A Vickers pyramid was used for indentation; the load on the indenter was about 100 N. At the same time, the measurements were carried out taking into account the possible propagation of cracks at the indentation sites, which could affect the following results, in order to avoid such an influence, each subsequent measurement was performed at a distance of at least 20 μm from the previous indentation. Determination of resistance to single compression was carried out on a testing machine LFM-L 10kH (Walter + Bai AG, Löningen, Switzerland) by compressing samples in special holders at a constant speed of 0.1 mm/min. Determination of crack resistance was carried out by comparing alterations in the maximum pressure that ceramics can withstand during compression before and after external influences (proton irradiation and high-temperature aging).

3. Results and discussion

Figure 1 reveals data on variations in the hardness and cracking resistance of ceramic specimens before and after irradiation. The data were acquired through sequential testing of samples to assess the consistency of the properties of the synthesized ceramics and their resistance to external influences, with the aim of eliminating any artifactual effects stemming from irradiation. As indicated by the presented data, the inclusion of a stabilizing additive like aluminum nitride results in an increase in hardness and resistance to cracking under single compression. Additionally, similar to irradiated samples, it contributes to enhanced resistance to softening linked with the accumulation of structural distortions and deformations in the surface layer. The growth in resistance to radiation-induced softening for stabilized ceramics can be explained by the effects associated with the formation of inclusions in the form of impurity phases (for an additive concentration of 0.15 M), and in the case of lower concentrations of the stabilizing additive by a higher structural ordering degree of the ceramics' crystal structure. Moreover, analysis of variations in hardness and resistance to single compression indicates an almost identical trend of enhancing stability of the ceramics' strength properties as concentration of the stabilizing additive grows. The maximum reduction in strength characteristics is observed for unstabilized $NiAl_2O_4$ ceramics, for which high-dose irradiation results in a decline in strength characteristics by more than 15 – 16 %, while the addition of a stabilizing additive at concentrations of 0.05 and 0.15 M results in a more than twofold and fivefold increase in the stability of the strength characteristics of ceramics. The significant improvement in the resistance to strength property destruction observed in stabilized ceramics with a dopant concentration of 0.15 M is primarily linked to the emergence of inclusions in the shape of an impurity phase, $Al_7O_3N_8$. As demonstrated in work [16], these inclusions fill the intergranular space in the form of a fine fraction, thereby enhancing degradation resistance.

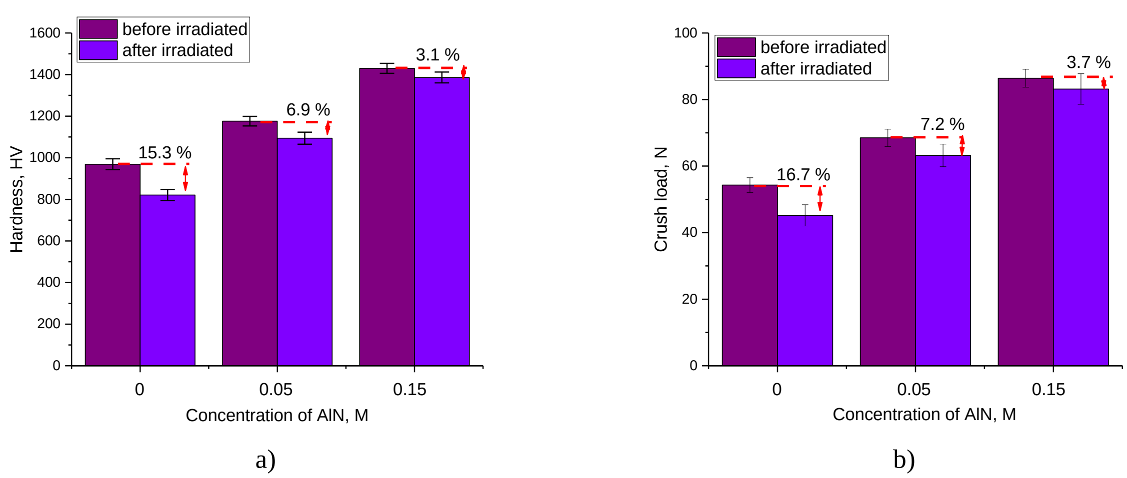


Fig.1. Irradiation effect on variations in strength parameters: a) variation in hardness; b) variation in the compressive force that the ceramic can withstand during a single impact

The observed softening for irradiated samples stems from the accumulation of deformation distortions of the crystal structure, alongside the formation of gas-filled inclusions in the pores, a growth in the concentration of which, alongside their combination into larger agglomerates, results in deformation of the near-surface damaged layer, as a consequence of a rise in internal pressure in the gas-filled cavities. The alteration in the deformation values of the crystal structure as a result of irradiation can be assessed by calculating the volumetric swelling of the crystal lattice, the value of which characterizes the deformation distortion of the damaged layer structure, alongside the effects related to the accumulation of distorting factors and residual tensile stresses. The assessment results are demonstrated in Figure 2 as a diagram reflecting percentage of the crystal lattice' volumetric alteration (swelling) in comparison with the initial values of the crystal lattice volume of ceramic samples.

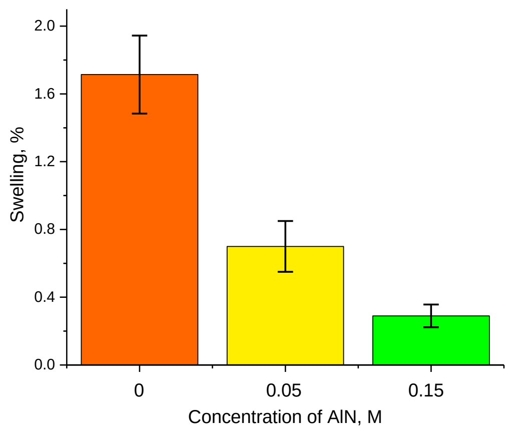
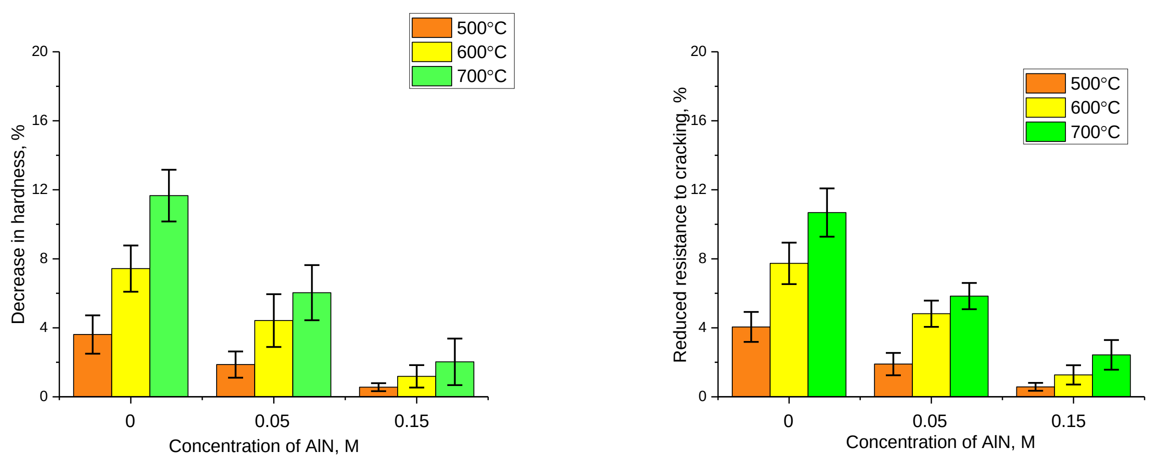


Fig.2. Results of volumetric swelling of the crystal lattice of $NiAl_2O_4$ ceramics subjected to irradiation

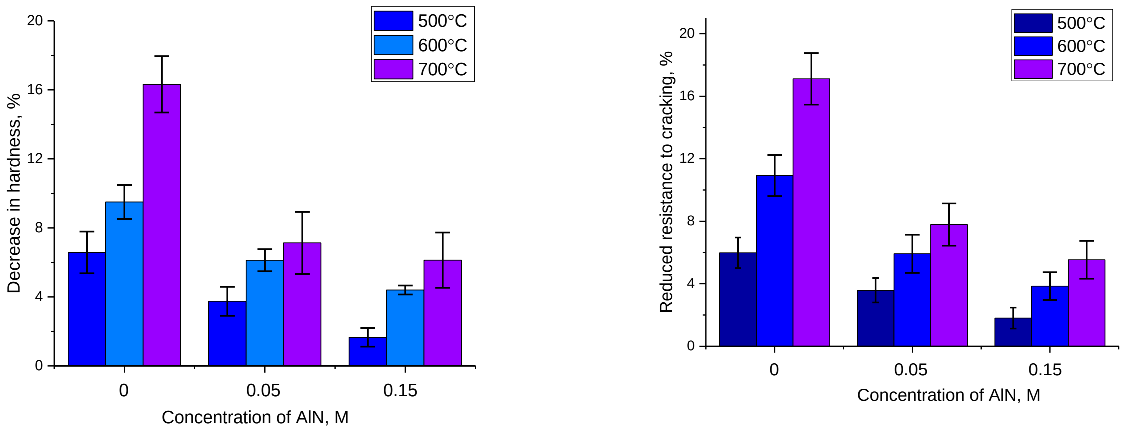
In accordance with the data acquired, presented in Figure 2, the incorporation of a stabilizing additive results in an elevation in the swelling resistance of ceramics, which, as a consequence, leads to a rise in resistance to destruction of strength characteristics. Moreover, more pronounced changes in elevated swelling resistance were observed for $NiAl_2O_4$ ceramics stabilized with 0.15 M AlN, for which the emergence of inclusions as $Al_7O_3N_8$ grains was observed. The enhanced swelling resistance is explained by the presence of interphase boundaries, alongside a higher dislocation density, the alteration in which is associated with the appearance of impurity inclusions. Figures 3 and 4 reveals the results of a comparative analysis of changes in strength properties (reduction in hardness and change in resistance to cracking under single compression) of ceramics under varying conditions of high-temperature exposure (temperature change).



a) b)

Fig.3. Assessment results of variations in strength characteristics of initial ceramics after 500 hours of high temperature exposure: a) change in hardness; b) change in crack resistance

The tests were executed during 500 hours of annealing in a muffle furnace at various temperatures. The samples were subjected to strength properties measurements afterwards. The overall trend in the changes to the strength properties of ceramics suggests the detrimental impact of high-temperature corrosion on the stability of these characteristics, particularly evident at elevated temperatures (600 – 700°C). However, the data obtained indicates that the addition of the stabilizing additive AlN to the ceramic composition leads to an enhanced resistance to high-temperature degradation, manifested in a reduction of more than 2-3 times in the value of changes in strength characteristics. Additionally, it is noteworthy that a comparable pattern is evident not solely in the initial ceramics, where the decline in strength characteristics is primarily attributable to corrosion processes and alterations in the amplitude of thermal vibrations of atoms at the nodes of the crystal lattice, resulting in its destruction. The corrosion processes, in the case of prolonged high-temperature degradation, are prompted by the penetration of oxygen into the ceramics, thereby amplifying the deformation distortion of the structure and generating distorted areas that contribute to the destabilization of strength properties.



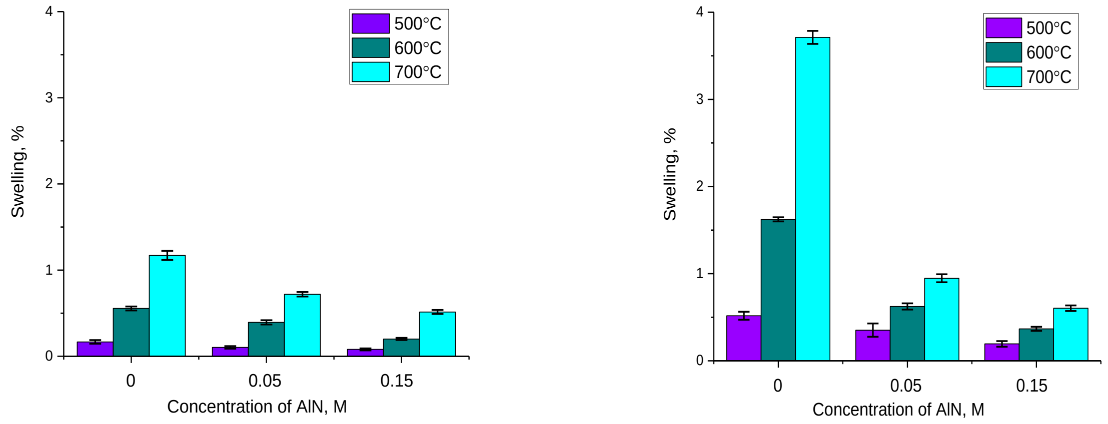
a) b)

Fig.4. Assessment results of variations in strength characteristics of irradiated ceramics after 500 hours of high temperature exposure: a) change in hardness; b) change in crack resistance

More pronounced degradation of the strength characteristics of irradiated ceramics, in addition to deformation distortions associated with corrosion processes, is also due to the presence of gas-filled cavities that distort the crystalline structure (the presence of these inclusions is indirectly explained by the deformation swelling of the crystal lattice, which is caused by high-dose irradiation, as well as the very nature of hydrogen, associated with its poor solubility). Moreover, the addition of stabilizing additives also results in a reduction in destructive alterations in ceramics' strength properties, which in turn indicates the positive effect of incorporation of aluminum nitride to the ceramics' composition, and the very trend of alterations in strength characteristics depending on the stabilizing additive concentration in comparison with similar changes for non-irradiated samples indicates the same mechanisms of destruction of ceramics caused by high temperature exposure. Figure 5 demonstates the alteration results of the structural swelling value of the crystal lattice of ceramics under diverse thermal exposure conditions (variations in annealing temperature).

These variations delineate the processes of structural degradation in ceramics linked to deformation distortions induced by thermal influences (volumetric thermal expansion of the crystal structure). Additionally, they represent degradation processes associated with corrosion and oxygen penetration. In the case of irradiated samples, these processes also involve migration, resulting in the agglomeration of implanted hydrogen due to heightened mobility.

Analyzing the obtained dependences of the crystal lattice swelling value of ceramics in the initial and irradiated states, the subsequent deductions can be made. The exposure temperature growth leads to a rise in the structural deformation of the crystal lattice, which indicates the influence of changes in the amplitude of thermal vibrations and the mobility of vacancy defects in the ceramics' structure (for non-irradiated samples), the combined effects of which lead to deformation swelling of the structure, most pronounced at temperatures of 600 - 700°C.



a) b)

Fig.5. Assessment results of the crystal lattice swelling value of ceramics after 500 hours of high-temperature exposure: a) non-irradiated ceramics; b) irradiated ceramics

In this case, analysis of variations in the crystal lattice swelling value for irradiated unstabilized $NiAl_2O_4$ ceramics implies that irradiation temperature rise from 500 to 700°C leads to a more than a 7-fold crystal lattice volume growth, which indicates the following. For irradiated unstabilized $NiAl_2O_4$ ceramics, in which the concentration of implanted hydrogen can reach the order of several atomic percent (according to estimated calculations of modeling the hydrogen accumulation processes in the damaged layer). Subjected to temperature, implanted hydrogen, given its mobility, can accelerate agglomeration processes, consequently augmenting the volume of gas-filled regions. This phenomenon is widely recognized in metals and alloys during post-irradiation annealing of defects, leading to an elevation in bubbles through their agglomeration. At the same time, for stabilized $NiAl_2O_4$ ceramics, the presence of impurity phases results in the creation of additional barriers to implanted hydrogen in the form of grain boundaries and interphase boundaries, which leads to difficulty in its migration, and as a result, even at high temperatures, little effect on destruction processes.

4. Conclusion

The paper presents the assessment results of the effect of doping $NiAl_2O_4$ ceramics with aluminum nitride on the high-temperature degradation resistance under conditions closely aligned with the actual operating conditions of these ceramics when used as anode materials for solid oxide fuel cells. During determination of the effect of high-dose proton irradiation on variations in the strength properties of $NiAl_2O_4$ ceramics, it was discovered that the stabilizing additive concentration growth results in an enhanced resistance of the near-surface layer of ceramics to softening processes, alongside swelling of the crystal structure due to deformation distortions. During high-temperature tests in the case of varying exposure temperatures, it was found that a rise in the concentration of the stabilizing additive results in a rise in resistance to degradation processes, which are caused by changes in the amplitude of thermal vibrations of atoms, alongside corrosion processes associated with the crystal lattice deformation distortion and swelling. In conclusion, the addition of the stabilizing additive AlN to $NiAl_2O_4$ ceramics is quite effective, which is not only due to a rise in strength characteristics (increased hardness and resistance to single compression) but also enhanced resistance to destructive changes in strength performance as a result of long-term high temperature exposure. Moreover, for irradiated samples, the $NiAl_2O_4$ ceramics without stabilization exhibit the lowest resistance to high-temperature corrosion, with a degradation of strength properties exceeding 15 – 18 %. Testing for resistance to high-temperature corrosion at different exposure temperatures revealed that elevation in the temperature from 500 to 700°C accelerates the degradation processes.

Conflict of interest statement
Author declares that he has no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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