

# Study of ZrN-AlN formation solid-phase reaction in a nitrogen atmosphere during microwave heating

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**Abstract.** This paper is devoted to the discussion of the experimental results on the solid-phase synthesis of the nitride material ZrN-AlN. A mixture of powders of metallic zirconium and aluminum nitride was heated by means of microwave radiation in a nitrogen atmosphere for 90 minutes. Phase composition by sample volume and electron microscopy of the surface were studied to confirm the solid-phase reaction of zirconium with aluminum nitride. Thermodynamic calculations showed that several possible processes happen at once and lead to the formation of the nitride material ZrN-AlN in a nitrogen atmosphere. Experimental results showed a relatively low content of zirconium nitride (32.8 mol.%) and a significant content of metallic zirconium residues (8.8 at.%) in the upper layers of the sample despite contact with the gas phase. While in the sample volume, the conversion of metallic zirconium to nitride was almost complete (the content is 74.9 mol.%). Experimental observations have shown that, due to microwave heating, the formation of characteristic coral-like growths on the surface of particles with the concentration of chemical impurities, due to the purity of the initial reagents, is evident.

## 1. Introduction

The increasingly complex operating conditions of modern technology, the increased requirements for its reliability cause the development and creation of new structural and functional materials. Particular attention is also paid to materials used as coatings and alloying elements. Promising properties in this direction have materials made on the basis of refractory compounds - nitrides. They have valuable properties: heat resistance, refractoriness, heat resistance, resistance in aggressive environments. Nitrides are the raw material for the production of refractories, heat-resistant alloys, heat-resistant and heat-resistant coatings, abrasives, conductive elements of cathodes, instrumental, structural and various purpose ceramics with high performance characteristics [1-3].

Zirconium nitride is of the most interest materials among other transition metal nitrides, since it has such properties as high melting point, hardness, chemical stability, corrosion and oxidation resistance, wear resistance. The creation of promising nitride ceramics and composite materials in the Zr-Al-N system has become widespread in recent years [4-8]. It is assumed that the creation of a composite material ZrN-AlN will provide a highly efficient material with high hardness and sufficient thermal conductivity for use as an abrasive, cutting and heat-resistant material.

The study of the production of ceramics by microwave heating [9, 10] makes it possible to obtain both powdered and cast materials with a significant reduction in energy and time costs. This paper is devoted to the study of the solid-phase interaction of Zr-AlN to obtain ceramics of the composition ZrN-AlN using microwave heating in a nitrogen atmosphere.



## 2. Experiment

### 2.1. Raw materials

Aluminum nitride synthesized by gas-phase technology at the Department of Rare Metals and Nanomaterials of Ural Federal University (99%, 5 microns) [11], metallic zirconium (96.9%, 40 microns, PCRK1 according to TU 48-4-234- 84) and nitrogen (99.9999%) were used as raw materials.

### 2.2. The experiment

The zirconium metal powder stored in water was placed in a drying cabinet, where water was evaporated at a temperature of 95 °C for 4 hours. After that, a portion of aluminum nitride and powdered zirconium (1: 2 by moles) was placed in an alundum crucible, which was loaded into a quartz cell in a microwave oven. The reaction cell was evacuated and filled with nitrogen. Details of the installation have been discussed previously [12]. The mixture was heated by microwave radiation for 90 minutes.

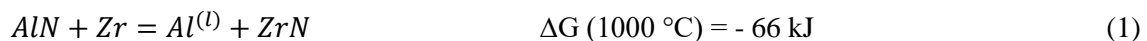
### 2.3. Research methods

The powders obtained as a result of the experiments were investigated using X-ray phase analysis on XpertPROMRD and on SEM Jeol JSM 6490LV.

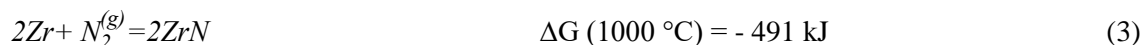
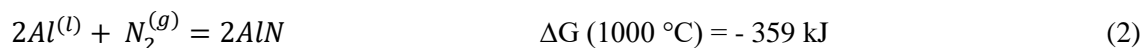
## 3. Results and discussions

The charge was heated due to the effect of microwave radiation on metallic zirconium with the formation of Foucault eddy currents; direct heating of aluminum nitride under the effect of microwave was also observed [10]. Due to the rapid heating by microwave radiation, nonequilibrium processes can be observed, which together with high heating rates favorably distinguishes microwave heating from the traditional one.

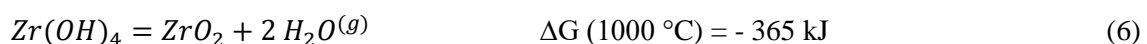
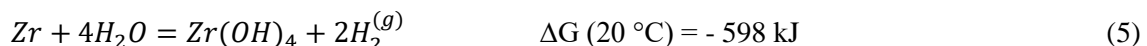
Zirconium metal has a greater affinity for nitrogen than aluminum, which is confirmed by thermodynamic calculations. At 1000 °C, the Gibbs energy of reaction (1) is -65,604 kJ and increases with increasing temperature.



At the same time, the following reactions take place:

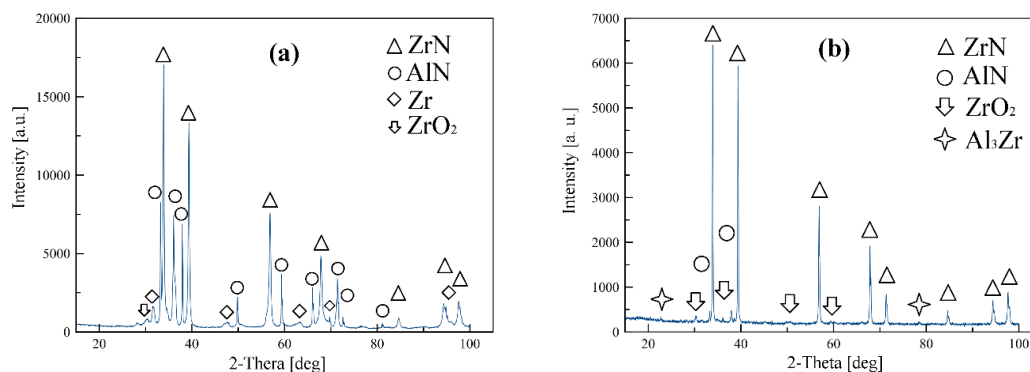


The surface of the obtained sample was light gray in color, while the lower part of the charge in the crucible was brown. The results of X-ray phase analysis of the surface layers of the sample are presented in Figure 1 (a). The main 3 phases present in the sample are aluminum nitride (53.2 mol.%), Zirconium nitride (32.8 mol.%) And unreacted metal zirconium (8.8 at.%), And zirconium oxide peaks are observed as an impurity. (5.2 mol.%). The presence of zirconium oxide is due to the fact that, due to the fire hazard, metal zirconium powder is supplied in a container in water, as a result of which zirconium metal is hydrolyzed and ZrO<sub>2</sub> is formed during subsequent heating.



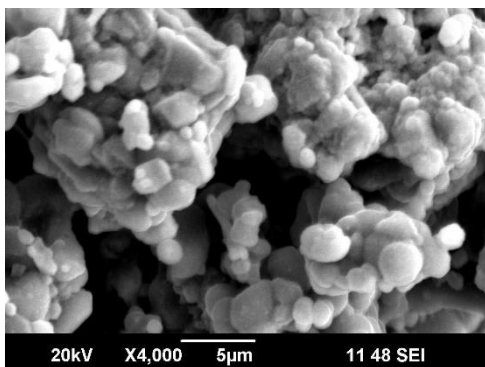
A significant amount of non-interacting metallic zirconium (8.8 at %) is worth noting, despite carrying out the synthesis in a nitrogen atmosphere. That clearly indicates the difficulty of diffusion of nitrogen into the mixture, which may indirectly confirm the solid-phase nature of the reaction of formation of zirconium nitride. It is also important to note the high content of aluminum nitride in the surface layer - in the initially mixed mixture, the AlN content was 33.3 mol. %, and in the surface layers of the sample the content of aluminum nitride is 53.2 mol. %, which can be explained by the reaction

(1): when aluminum nitride interacts with zirconium metal, molten aluminum metal is formed. The density of the melt is  $2.5 \text{ g/cm}^3$ , while the density of the remaining substances is much higher ( $\text{AlN} - 3.26 \text{ g/cm}^3$ ,  $\text{Zr} - 6.45 \text{ g/cm}^3$ ,  $\text{ZrN} - 7.3 \text{ g/cm}^3$ ), thereby aluminum metal is partially extruded into the layer on the surface of the sample. X-ray phase analysis of the lower part of the charge (figure 1 b), which has a brown tint, confirmed this assumption. There is a lower content of aluminum nitride (18.3 mol.%), while zirconium nitride is present in a clear excess (74.9 mol.%). The content of a small amount of intermetalide  $\text{ZrAl}_3$  (4.2 mol.%) confirms the fact of the solid-phase reaction (1). An admixture of zirconium oxide (2.5 mol.%) from the initial zirconium powder is also present in the sample. The absence of obvious peaks of aluminum oxide indicates the absence of the reaction of aluminothermy zirconium oxide, which could explain its low content in the sample.



**Figure 1.** X-ray phase analysis of samples (a) - sample 1: the surface of the obtained product, (b) sample 2: lower part of the product.

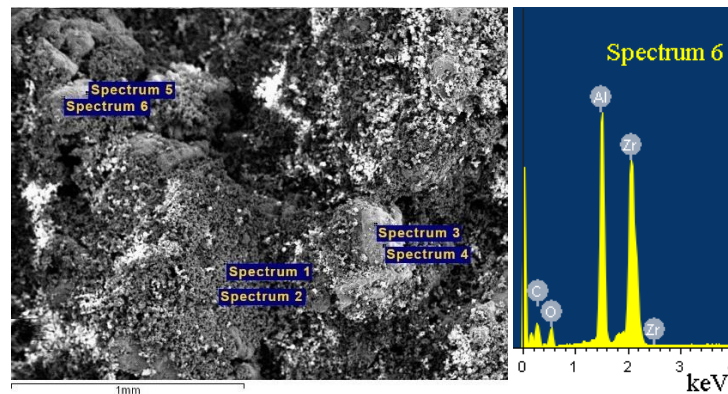
To study the surface of the obtained samples and examine the nature of the solid-phase interaction, studies were performed using an electron microscope (figure 2), which showed that the average particle size of the obtained zirconium nitride is  $3\text{--}4 \text{ }\mu\text{m}$ . During the solid-phase reaction, a change in the morphology and size of metallic zirconium particles occurred when interacting with aluminum nitride.



**Figure 2.** Sample 2 shot of a mixture of aluminum nitride with metallic zirconium.

Corral-like formation growths on particles (figures 3-5) becomes obvious. The appearance of those formations can be explained by local sparks between several metallic zirconium particles due to microwave radiation, which leads to the formation of characteristic marks on the surface.

Analysis of the surface of the reaction product particles (figure 3) showed a high content of a solid solution of zirconium with oxygen and nitrogen [13] on the surface of the samples under study (table 1, spectrum 1, 3, 4, and 5). In this case, in the spectrum of 1, there is a large amount of dissolved aluminum, while in the other areas studied, the content of metallic aluminum ranges from 0.28 to 1.92 at. % Also, the content of the intermetallic compound (spectrum 2, 6) is large on the surface of the particles, which may be caused by a lack of nitrogen due to the difficulty of diffusion into a densely loaded mixture.



**Figure 3.** Sample 1 surface.

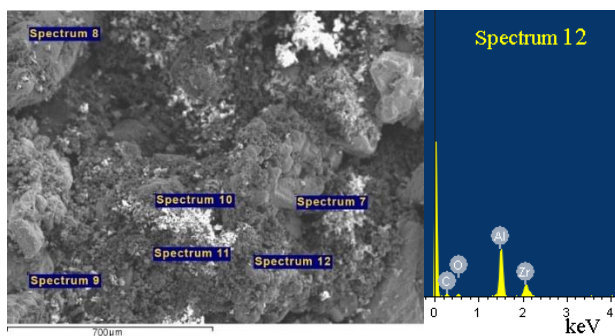
**Table 1.** Sample 1 surface analysis results.

Spectrum	N	O	Al	Zr
Spectrum 1	11.40	14.87	14.27	59.46
Spectrum 2		8.59	30.39	61.01
Spectrum 3	5.64	10.27	0.28	83.81
Spectrum 4	8.12	12.71	0.49	78.68
Spectrum 5	9.30	14.34	1.92	74.44
Spectrum 6		13.88	21.75	64.37

With further approximation (figure 4), it is obvious that the particles under study contain a large amount of zirconium, thus being remnants of reacted metallic zirconium. Elemental analysis of spectra 7–9 (table 2) shows a low aluminum content (around 1 at.%) With the main solid solution of zirconium with nitrogen (spectrum 7, 8) and oxygen (spectrum 7–9).

Coral-like growths in turn (spectra 10–12) contain an increased aluminum content, which can be interpreted as residues from the original aluminum nitride after solid-phase reaction with metallic zirconium.

Obviously, there has been an active transfer and the concentration of oxygen impurities on the surface of the particles, and if the total oxygen content in the sample from the surface of the mixture is not more than 5.2 at. %, then on the surface of particles its concentration sharply increases to 15 - 20 at. % (table 1, 2). The transfer can be explained by different solubilities in the formed zirconium nitride and metallic zirconium, as a result of which impurity oxygen is concentrated in the residue of metallic zirconium during the reaction of the formation of ZrN, thus forming a solid solution, thereby leaving the surface of metallic zirconium particles.

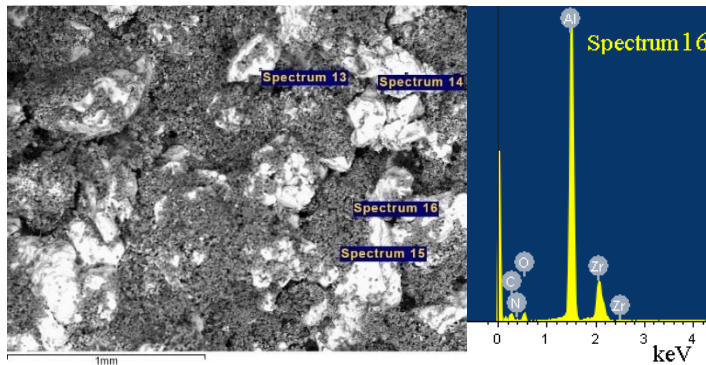


**Figure 4.** Sample 1 surface.

**Table 2.** Sample 1 surface analysis results.

Spectrum	N	O	Al	Fe	Zr
Spectrum 7	11.55	19.18	1.09		68.17
Spectrum 8	9.20	19.31	0.72		70.77
Spectrum 9		12.96	0.69		86.35
Spectrum 10	15.95	15.44	18.26		50.35
Spectrum 11	11.38	11.32	42.84	1.66	32.80
Spectrum 12		19.72	38.05		42.23

Similar results are observed for sample 2 from the lower part of the product obtained (Fig. 5): a high content of metallic zirconium (table 3, spectrum 13, 14) with an increased concentration of oxygen. The growths on the grains of the initial zirconium are a product formed as a result of reaction 1 with coral-like growths characteristic of the formation of molten aluminum metal (spectrum 15, 16).

**Figure 5.** Sample 2 surface.**Table 3.** Sample 2 surface analysis results.

Spectrum	N	O	Al	Zr
Spectrum 13	10.15	17.04	0.33	72.48
Spectrum 14		6.73	1.52	91.74
Spectrum 15	10.88	13.78	43.49	31.85
Spectrum 16	10.46	10.96	48.48	30.10

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