Distribution of impurities in ceramics based on zirconium nitride obtained using the oxidative constructing approach

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Abstract. The localization of impurity phases in ceramics created by direct nitridation of zirconium rolled metal was established. For ceramics synthesized at temperatures above the melting point of the metal, the impurity phases are localized along grain boundaries and at macrodefects. In a composite heterostructure of the composition ZrN – (ZrN1/α – solid solution of nitrogen in metal/ZrN) – ZrN, impurity phases are predominantly localized in an α-solid solution of nitrogen with their subsequent displacement to grain boundaries and macrodefects at the end of the nitridization process.

1. Introduction

Metal nitrides of the titanium subgroup have found application in various branches of technology: thin films in microelectronics [1–3], protective and hardening coatings [4–6], and functional ceramics [7–9]. Methods of creating a product from transition metal nitrides are based on classical technologies of molding nitrides of simple forms from powders with subsequent sintering; or on compaction of metal powders with nitriding of the manufactured compact. However, high requirements for the purity, granulometry and phase composition of metal and nitride powders suitable for compacting, as well as the complexity of the processes of forming thin-walled products and products of complex geometry, high sintering temperatures significantly limit the proposed range of ceramic products [10–12]. The oxidative engineering approach allows you to create ceramic products of various forms by direct single-stage oxidation of metal billets [13], including the nitridation process above the melting point of metal [14] due to the formation of a shell from a refractory nitride layer at the initial stage. In this case, the synthesis of ceramics passes through the stages of formation of Zr\text{solid solution/ZrN1 - s/ZrN} heterostructures [15–17].

The initial zirconium and nitrogen contain impurities, the composition and quantity of which correspond to the chemical qualification of the reagent, which can affect the composition and properties of the synthesized ceramics. The aim of this work is to study the distribution of impurity phases formed in the process of high temperature zirconium nitridation.
2. Experimental part

E-110 grade zirconium (TU 95.166-83) in the form of a 0.30 mm thick foil and a bar 4.0 mm in diameter were used as the starting material. Zirconium nitridation was carried out at a temperature of 2400 °C in an atmosphere of nitrogen classification “ultrapure”, 99.999% (table 1). During nitridation, the nitrogen pressure in the reactor was maintained at the level of (1.5±0.1) × 10^5 Pa. The temperature of the sample was determined by a Luma Sense IMPAC ISR 50-LO optical pyrometer. Synthesized ZrN, ceramics with different degrees of nitridation (x = 0.33-1), preserving the size of the original metal billet.

Table 1. The content of impurities in volume percent for Zr grade E-110 and gaseous nitrogen classification “ultrapure”, 99.999%.

| Impurities, % | ZrE-110 grade zirconium | Gaseous nitrogen classification “ultrapure”, 99.999% |
|--------------|------------------------|------------------------------------------------------|
| Nb           | 0.9-1.1                | 0.002                                                |
| Al           | 0.008                  | 0.005                                                |
| Be           | 0.003                  | 0.005                                                |
| C            | 0.02                   | 0.1                                                  |
| Fe           | 0.05                   | 0.05                                                 |
| Si           | 0.02                   | 0.02                                                 |
| Ca           | 0.03                   | 0.02                                                 |
| Cu           | 0.005                  | 0.005                                                |
| Mn           |                        |                                                      |
| Ti           |                        |                                                      |
| Pb           |                        |                                                      |
| O₂           |                        |                                                      |
| H₂           |                        |                                                      |
| Hydrocarbons |                        |                                                      |
| (CH₄)        |                        |                                                      |

The phase composition was studied on an XRD-6000 X-ray diffractometer (Shimadzu) in monochromatized copper radiation. X-ray diffraction patterns were obtained from the surface layer (5–7 μm) of the synthesized samples and from powder samples prepared by grinding ceramic fragments.

The surface cleavage morphology was studied by scanning electron microscopy (SEM) (Carl Zeiss microscopes with energy dispersive microanalysis systems from Oxford Instruments: LEO 1420, with INCA Energy 300; LEO 430i with ISIS 300; CrossBeam 1540EsB, with INCA Energy 350XT).

3. Results and discussion

The diffraction patterns characterizing the initial structure of zirconium rolled metal and the synthesized zirconium nitride ceramic are shown in figure 1. It follows from this analysis that after the complete nitridation process, the surface and volume of the ceramic consist exclusively of stoichiometric zirconium nitride ZrN (diffraction patterns 2 and 3).

Figure 1. X-ray diffraction patterns of the studied samples: I - initial zirconium; 2 - surface of zirconium nitride; 3 - powder sample of zirconium nitride.
A typical image of the free surface of a completely nitridized zirconium sample is shown in Figure 2. Relief outlines of the grain boundaries appearing on the surface appear; randomly located pores with sizes up to several microns are present.

![A typical image of the free surface of a completely nitridized zirconium sample](image)

**Figure 2.** A characteristic image of the free surface of nitride: without annealing (a), annealing for 1.5 hours (b) and 24 hours (c).

Figure 2b shows a typical view of the free surface of nitridized zirconium samples with an additional exposure (annealing) time in a nitrogen medium after completion of the main nitridization process. The microstructure of the surface did not undergo significant changes; however, the formation of local regions containing inclusions of a different elemental composition and located along grain-boundary regions was noted (Figure 2b, c). By the time of annealing at 24 hours, the impurity phase is formed crystals 1-3 microns in size.

This distribution of oxygen-containing phases differs from the phase distribution described in [18] for zirconium nitride annealed in the presence of oxygen.

A study of the transverse cleavage of a ceramic sample of zirconium nitride obtained by nitridation of a zirconium rod for 6 days indicates a structural heterogeneity of the obtained material. The cleaved surface morphology is represented by three different nitride layers (figure 3).

In the outer stoichiometric ZrN layer with a thickness of about 400 μm along the grain boundaries that make up the nitride layer, no defects in the form of pores and inclusions were detected. On a transverse cleavage of a layer of zirconium nitride below it (~ 1200 μm thick), which has a nitrogen deficiency of 2-12 at. % [15–17], grain-boundary segregation of the impurity phase was detected.

| Spectrum  | N      | O      | Sr | Zr  |
|-----------|--------|--------|----|-----|
| Spectrum 1| 47.39  | 0.00   | 0.00 | 52.61 |
| Spectrum 2| 45.54  | 11.89  | 0.00 | 42.57 |
| Spectrum 3| 52.26  | 11.54  | 0.53 | 35.66 |
The nature of the distribution of volume inclusions over the cleaved surface indicates intergranular destruction of nitride during cleavage, and local elemental analysis allows the impurity phase to be identified as zirconium oxide.

Figure 3. SEM image of a half transverse cleavage of a zirconium nitride sample obtained within 6 hours.

Figure 4. The oxide phase in the volume of non-stoichiometric zirconium nitride.
An inner ceramic layer is located in the central part of the sample with a diameter of ~ 2000 μm, a feature of which is the brooky pattern of the surface morphology (figure 5). Apparently, the hand-made relief is caused by amorphization of the nitride phase, or by the supersaturation of the impurity component (in this case, according to elemental analysis, with oxygen).

![SEM image](image)

**Figure 5.** SEM image of a brooky morphology pattern of the central part of the transverse cleavage of a ceramic sample after 6 days of nitridation.

| Spectrum   | Spectrum 9 |
|------------|------------|
| N          | 4.92       |
| O          | 47.71      |
| Zr         | 47.37      |
| Total      | 100.00     |
*mass. %

A typical image of the transverse cleavage obtained for a sample of 300 μm foil is shown in figure 6. The internal volume of zirconium nitride exhibits a polycrystalline structure, the crystallite size reaches hundreds of microns and is limited in one direction by the thickness of the sample.

![Typical image](image)

**Figure 6.** A typical image of a cleaved nitride sample obtained from a 300 μm zirconium foil for 120 min at 2400 °C.
A cavity partially occupied by phases based on impurity elements was found on one of the chips in the central part of the sample. The formation of cavities during the nitridation of titanium and zirconium was described in [17]. Ceramics synthesized by direct nitridation of a foil are characterized by the absence of a concentration of impurity phases over the entire cross section of the sample. This can be explained by the high degree and rate of nitridation. Since the complete nitridation of a zirconium foil 300 μm thick at 2400 °C with the formation of stoichiometric ZrN nitride occurs in 30 minutes [16], the time is 120 minutes. It turns out to be enough to complete the process of recrystallization of the entire internal volume. This factor, as well as the low solubility of impurity elements in the nitride phase, close to the stoichiometric composition, caused their runoff and accumulation near the macrodefect (figure 7).

![Figure 7](image)

**Figure 7.** Micrograph of the cleaved surface of zirconium nitride obtained with pronounced localization of impurity elements near the macrodefect.

### 4. Conclusion

In the process of zirconium nitridation, impurities contained in the parent metal and nitrogen form independent phases. The localization of impurity phases is determined by the structure of nitride ceramics: the outer layer of stoichiometric nitride, below it is the region of non-stoichiometric nitride and in the center the region of the α-solid solution of nitrogen in the metal. At a temperature above the melting point of the metal, a liquid phase forms, which is retained in the bulk of the sample by a layer of pure refractory stoichiometric nitride. With the appearance of a melt inside the nitride shell, nitride formation occurs both in the liquid phase and on the inner surface of the outer nitride layer, which leads to an increase in the thickness of pure nitride and an increase in the concentration of impurities in the melt. This explains the increased concentration of impurities in the region of the α-solid solution. Upon completion of nitridation at a temperature \( T > \frac{1}{3} T_{sl} \), a recrystallization process takes place in the ceramic with the formation of a coarse-grained nitride structure. This contributes to the additional displacement of impurity phases. Thus, to the impurities previously localized in the α-solid metal solution, phases displaced during recrystallization are added. All impurity phases are concentrated along the grain boundaries and in the regions of macrodefects of the structure.

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