Investigation of the formation and distribution of elements in the production of Al-Ti-V-Zr-Nb alloys by the aluminothermic method

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Abstract. The results of testing the method for synthesis of a high-entropy AlNbTiVZr alloy using metallothermic reduction of group IV and V metals from their oxides are presented. At the first stage, a joint aluminothermic recovery of metals in a resistance furnace was performed. Then, to achieve uniformity and remove harmful impurities, the metal was melted in a vacuum furnace with an inert atmosphere. The alloy obtained after the second remelting was subjected to x-ray diffraction and electron microprobe (EMA) analysis. The results of the analysis revealed the presence of a solid solution of Zr (Nb, V) with TiAl inclusions, which confirms the prospects of using metallothermic synthesis to produce a high-entropy alloy with a single-phase structure.

1. Introduction

High-entropy alloys with an equiatomic distribution of elements are very promising materials for use in various fields of technology, and in the last decade they have attracted the attention of researchers. The first mention of a high-entropy alloy was made in 2004 [2]. The idea behind these alloys was their high mixing entropy, which suggested a departure from traditional alloying methods, when one or two main base elements are present in the alloy. The new approach provided a transition to the concept of multicomponent alloys, where all elements are present in equiatomic or close to equiatomic ratio to each other. The development of high-entropy refractory alloys is aimed at creating so-called heat-resistant and heat-resistant compositions.

Work on finding rational ways to obtain high-entropy alloys has been carried out for more than fifteen years, all over the world. However, there is still no clear opinion on what methods are most appropriate to produce them. The most well-known methods for producing high-entropy alloys include vacuum arc melting [3], mechanical alloying [4], and laser surfacing [5]. These methods are based on mixing and fusing components with a chemical purity of 99.99%, which implies the high cost of obtaining these alloys in industrial production. To improve the economic performance of the technology for obtaining alloys, it is possible to use the stage of aluminothermic reduction of metals from relatively inexpensive oxides. In this paper, this approach was tested in the synthesis of a high-entropy AlNbTiVZr alloy in a resistance furnace.

The aim of this work was to study the phase and chemical composition of the AlNbTiVZr alloy sample obtained by aluminothermic reduction of Nb, Ti, V, and Zr oxides under controlled temperature
conditions in a resistance furnace. Samples of melting products synthesized in corundum crucibles were examined.

2. Materials and methods of research
Synthesis of the alnbtivzr alloy was performed in a resistance furnace followed by metal remelting in a vacuum furnace with an inert atmosphere. The charge for aluminothermic reduction of niobium, titanium, vanadium and zirconium oxides to metals is calculated using the reaction stoichiometry, taking into account the reducing capacity of each of the elements.

X-ray phase analysis of the samples was performed on an x-ray diffractometer "XRD 7000 diffractometer (Shimadzu)". The samples were taken in filtered monochromated CuKα radiation. Diffractograms were decoded using JCPDS and ASTM databases.

Electron microprobe analysis (EMA) was performed on polished samples using a Carl Zeiss EVO 40 scanning electron microscope and Inca X-Act EMA prefix.

3. The results of research and their discussion
The phase and elemental composition of metal samples obtained by aluminothermic reduction of Nb2O5, TiO2, V2O5 and ZrO2 oxides in corundum crucibles was studied using the example of an alloy after remelting in an inert atmosphere of Ar with the chemical composition, at.%, 53.2 Al, 9.14 Nb, 14.53 Ti, 16.32 V, 6.79 Zr and mass%, 0.12 O, 0.009 N. To achieve the equiatomic composition, it is necessary to adjust the charge mixture and improve the experimental method previously tested in [6, 7].

![Figure 1. X-Ray analysis results: 1 - Zr(Nb, V); 2 - TiAl)](image)

According to the results of x-ray phase analysis presented in figure 1, the main identified phases in the sample were Zr (Nb,V) and TiAl. According to the EMA results, the microstructure of the alloy (figures 2 and 3, tables 1 and 2) was the base of a solid solution evenly distributed in it, with non-metallic inclusions. The image of the Scanning electron microscope (SEM) shown in figure 2 had an middle position relative to the sample under study. The base of the plume was in the form of a uniform structure with needle-shaped dendrites. The chemical composition of the spectra is shown in table 1. The solid solution on the cross-section of the sample has an area of about 30 -50 microns located under the spectra 1, 2, 7, 9. Under the spectra 3, 6, 8 there are dendrites that have a needle-like structure with a length of
2 - 25 and a width of 1 - 5 microns and have carbon in their composition. The gray areas under the spectrum 4, 5 have a size of 5 - 10 microns, carbon and silicon are present in the composition.

Figure 2. SEM image (middle of the test sample): 1, 2, 7, 9 - solid solution; 4, 5 - a mixture of solid solution of carbides and silicides; 3, 6, 8 - carbides of solid solution.

Figure 3. SEM image (edge of the test sample): 1 - aluminum oxide; 2, 3, 5, 8, 9, 10 - solid solution; 4 - a mixture of solid solution of carbides and silicides; 6, 7 - carbides of solid solution.

Table 1. Chemical spectral analysis for figure 2 (spectrum-chemical composition in at.%).

| №  | Al   | Nb  | Ti  | V   | Zr  | P    | Si  | C   |
|----|------|-----|-----|-----|-----|------|-----|-----|
| 1  | 61.67| 11.03| 11.87| 12.90 | 2.53 |
| 2  | 51.19| 10.04| 11.93| 21.96 | 2.57 | 2.30 |
| 3  | 27.94| 11.02| 23.86| 13.27 | 2.34 | 21.57 |
| 4  | 14.68| 12.57| 13.04| 18.45 | 2.89 | 13.32| 25.05 |
| 5  | 17.53| 10.78| 13.00| 16.64 | 2.59 | 10.36| 29.11 |
| 6  | 24.03| 7.73 | 18.33| 9.86  | 1.30 | 38.76 |
| 7  | 52.71| 8.21 | 11.72| 22.45 | 2.72 | 2.19 |
| 8  | 19.91| 8.19 | 18.43| 11.49 | 2.45 | 39.53 |
| 9  | 61.43| 10.87| 11.85| 12.98 | 2.87 |

Figure 3 shows a SEM image taken at the edge of the sample under study. The image shows a uniform structure with non-pronounced dendrites and the presence of non-metallic inclusions. The chemical composition of the spectra is shown in table 2. The solid solution has the same area as in Figure 1, about 30 - 50 microns, located under the spectra 2, 3, 5, 8, 9 and 10. The dark region under spectrum 1 has oxygen and aluminum in its composition, which indicates the presence of Al₂O₃. The light gray regions under spectrum 4 and the dark gray regions under spectra 6, 7 are represented by a mixture of carbon, silicon and carbon, respectively. Drawing an analogy with figure 1, we can say that it is possible to form carbides in the metal. Carbides can be formed due to CO/CO₂ gases in the resistance furnace. It is possible to exclude the formation of carbides when replacing heating elements made of carbon, for example, molybdenum or tungsten.

Table 2. Chemical spectral analysis for figure 3 (spectrum-chemical composition in at.%).
When comparing the test sample in the middle and at the edge, using a SEM, differences in the structure and the presence of non-metallic inclusions in the form of aluminum oxide were observed. To eliminate oxides in the final alloy, it is necessary to perform additional remelting in a vacuum-arc furnace to ensure uniformity and separation of the metal and oxide phases.

Conclusions
The results of the study show that the formation of a high-entropy alloy is possible with the combined aluminothermic reduction of Nb, Ti, V and Zr. In the synthesized alloy, the formation of a solid solution based on Zr (Nb, V) with the presence of intermetallic inclusions of AlTi was achieved. Also, electron microprobe analysis showed that the alloy contains non-metallic inclusions in the form of carbides and oxides, which may not favorably affect the final product.

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