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Arc plasma synthesis of IV-V groups transition metals high-entropy carbides cubic phases

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Abstract. The paper presents the results of experimental studies on the production of high-entropy carbides of transition metals of IV-V groups. In the course of experimental studies, three phases of high-entropy carbides $ZrNbHfTaC_4$, $VZrNbHfTaC_5$, $TiVZrNbHfTaC_6$ were obtained. These materials are characterized by a cubic structure of the NaCl type, the lattice parameters correspond to the known data on these high-entropy carbides. According to the data of scanning electron microscopy with energy dispersive analysis, the chemical elements are uniformly distributed in the obtained crystals of multicomponent carbides. A feature of the synthesis method used is the implementation without the use of vacuum and gas equipment.

1. Introduction

High-entropy carbides (HEC) are relatively new multicomponent, usually equimolar compounds [1]. Considering the fact that they contain transition metals that form ultra-refractory carbides, we should expect new results in the field of creating materials for extreme operating conditions. There are many theoretically predicted combinations of 4–6 metal combinations of elements that form high-entropy carbides [2]. Some of them have been successfully synthesized. A strategy of such materials synthesis is usually based on a relatively long exposure of the feedstock at high temperatures. This approach requires a lot of time, energy, and the use of expensive furnace and vacuum equipment. In this regard, the issue of developing new and improving existing methods for the synthesis of HECs in order to simplify the procedure for their synthesis is topical. Electric arc methods can be useful in the synthesis of such materials under the action of high temperatures of electric arc plasma [3, 4]. In the last few years, the direction of science has been developing associated with the rejection of vacuum equipment in plasma arc reactors. This approach was successfully used for the synthesis of the following HEC $TiZrNbHfTaC_5$ [5]. The so-called non-vacuum electric arc method has not previously been applied to the synthesis of high-entropy carbides of various compositions.

2. Methods and materials

2.1. Experimental setup

A series of experiments was carried out on an atmospheric laboratory arc reactor with an original design [5]. The arc discharge was initiated in air. The synthesis of non-oxide materials in air is possible due to the special design of the electrodes. Carbon oxides CO and CO_2 are formed during the initiation of an arc discharge because of anode erosion, and act as a protective atmosphere. A cloud of these gases, shielding the reaction zone, prevents the ingress of atmospheric oxygen into the synthesis products and prevents them from being oxidized. The anode is made of graphite in the form of a rod 8 mm in diameter and 10 mm long, the graphite cathode is made in the form of a crucible with an outer diameter of 25 mm, an inner diameter of 20 mm and a height of 25 mm. We used commercial electrodes with a purity of at least 99.9% (QiJing Trading Co, China). Mixtures of initial powders were loaded onto the bottom of a graphite cathode and covered with a graphite felt pad. A Condor Colt 200 welding transformer with a maximum current of 200 A was taken as a power source. The arc discharge was ignited inside the cathode. At the initial moment of time, the arc gap was set to no more than 1 mm.

The operating modes of the arc reactor necessary for the implementation of the synthesis of HES, using the example of the $TiZrNbHfTaC_5$ phase, were studied earlier in our previous work [5].

2.2. Materials used and their preparation

Powders of metals Ti, V, Zr, Nb, Hf, Ta with a purity of at least 99.9% (Rare Metals Corp., Russia) with an average particle size of up to 10 μm and X-ray amorphous carbon with a purity of at least 99% (Hi-Tech Carbon Corp., China).

The powders were mixed in an equimolar ratio in a Mixer/Mill 8000 M Horiba Scientific ball mill for 6 hours at a weight ratio of balls and powder of 4:1. A grinding jar and tungsten carbide balls were used.

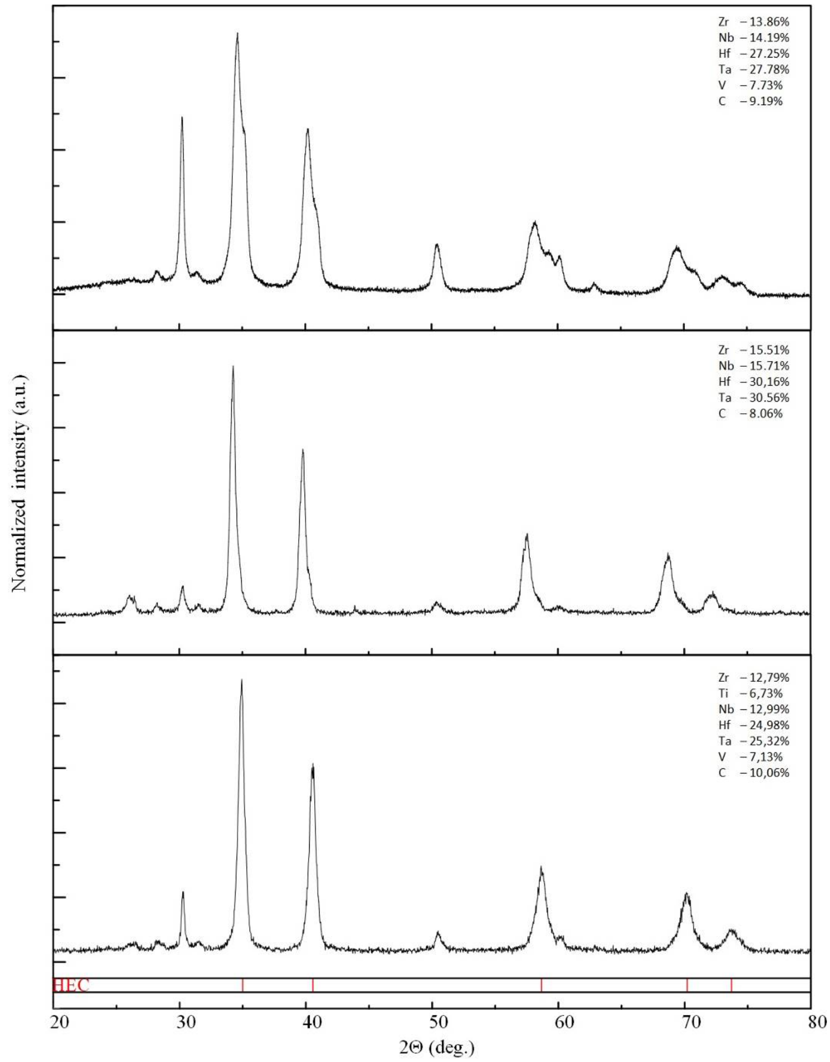

Fig.1. Typical X-ray diffraction patterns of powders containing HEC phases $VZrNbHfTaC_5$, $ZrNbHfTaC_4$, $TiVZrNbHfTaC_6$.

2.3. Analytical methods

The obtained materials were analyzed by X-ray diffraction (Shimadzu XRD 7000 s, $\lambda = 1.54060$ Å, Shimadzu standard software), scanning electron microscopy on a Tescan Vega 3 SBU scanning electron microscope equipped with an Oxford X-Max 50 X-ray fluorescence energy dispersive analysis (EDS) attachment with Si /Li crystal detector, transmission electron microscope on a JEOL JEM 2100F transmission electron microscope equipped with EX-24063JGT for EDS.

3. Results and discussion

Fig.1 shows typical X-ray diffraction patterns of obtained HEC samples. Structures of the NaCl type are identified, corresponding to the HEC phases: $ZrNbHfTaC_4$, $VZrNbHfTaC_5$, $TiVZrNbHfTaC_6$ with lattice parameters 4.486 Å, 4.446 Å, 4.529 Å. Such results correspond to the literature data within the limits of possible errors. Peaks are also identified, which may correspond to minor impurities of graphite and metal oxides.

According to scanning electron microscopy with energy dispersive analysis, it was found that the synthesis products contain objects of various morphologies, including particles with longitudinal dimensions of ~35 μm and transverse dimensions of ~15 μm, which have a loose surface (Fig.2), objects of the microroll type (Fig.3), dense particles with a size of about 80 μm, characterized by the presence of internal cavities (Fig.4). According to the data of energy dispersive analysis in the mapping mode, it can be seen that the atoms of the corresponding metals are distributed uniformly in HECs crystals, which indirectly proves the presence of high-entropy carbides phases.

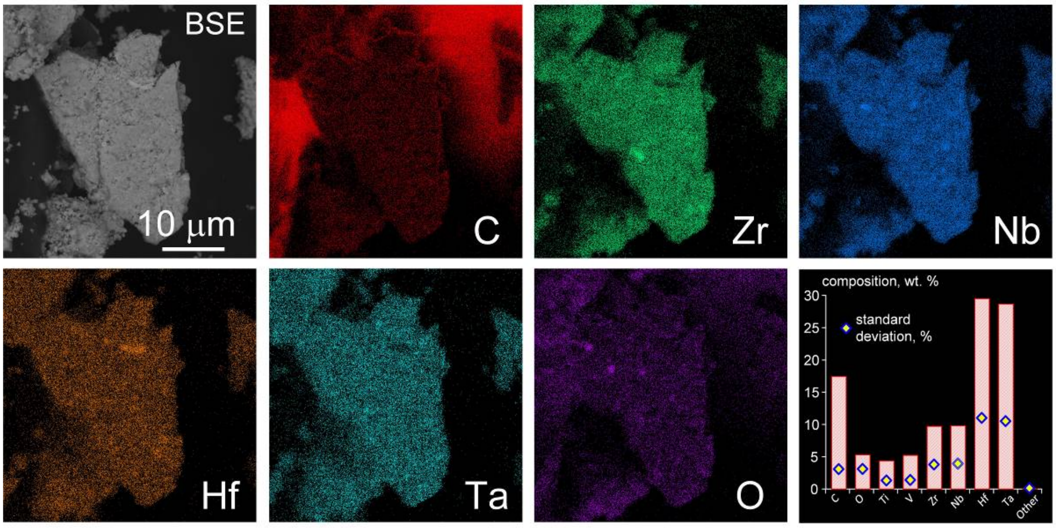

Fig.2. Typical results of scanning electron microscopy of synthesized HEC $ZrNbHfTaC_4$.

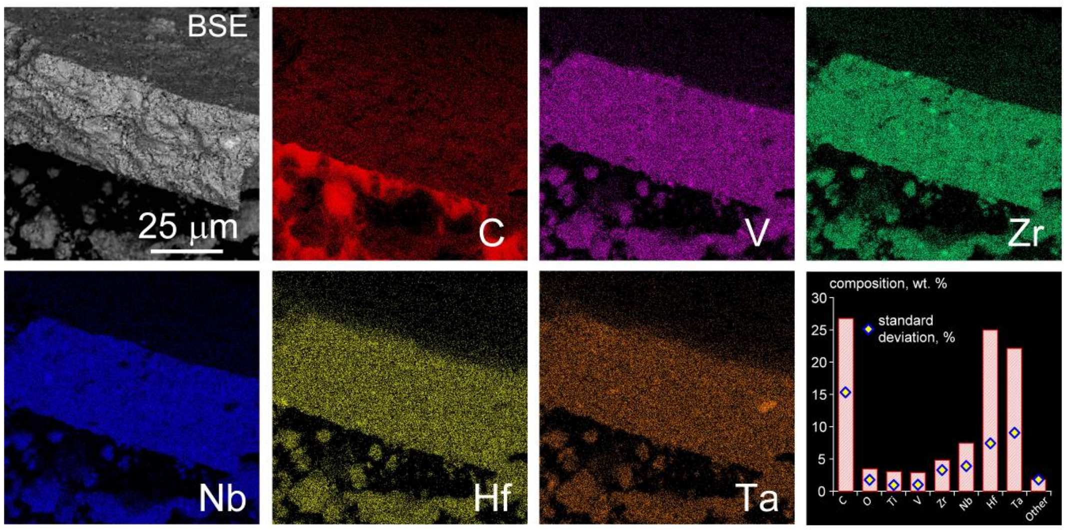

Fig.3. Typical results of scanning electron microscopy of synthesized HEC $VZrNbHfTaC_5$.

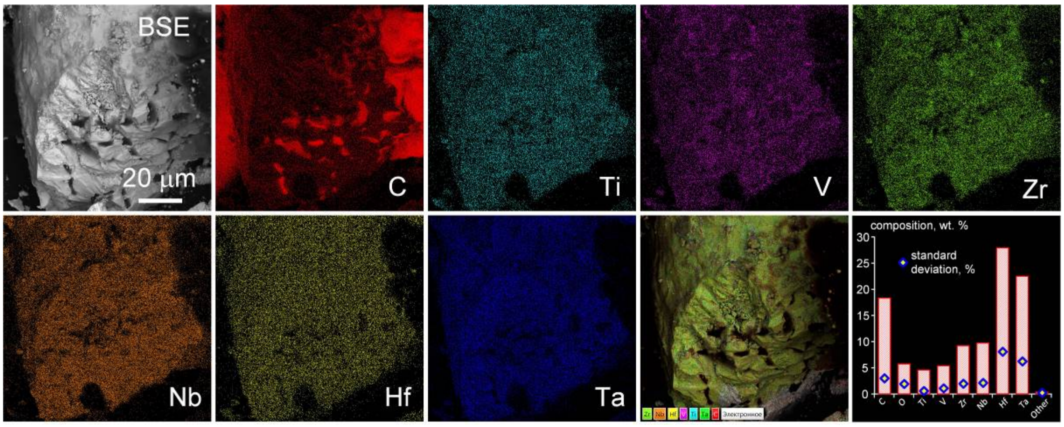

Fig.4. Typical results of scanning electron microscopy of synthesized HEC $TiVZrNbHfTaC_6$.

According to the data of transmission electron microscopy (Fig.5), particles with characteristic sizes from 50 to 300 nm are identified in the synthesis products. According to the electron diffraction patterns, one can make sure that the particles are characterized by a cubic lattice of the NaCl type, with parameters corresponding to the reference ones for $ZrNbHfTaC_4$, $VZrNbHfTaC_5$, $TiVZrNbHfTaC_6$. The interplanar distances determined from HRTEM images corresponds to the reference value for each of the obtained HEC phases within the error.

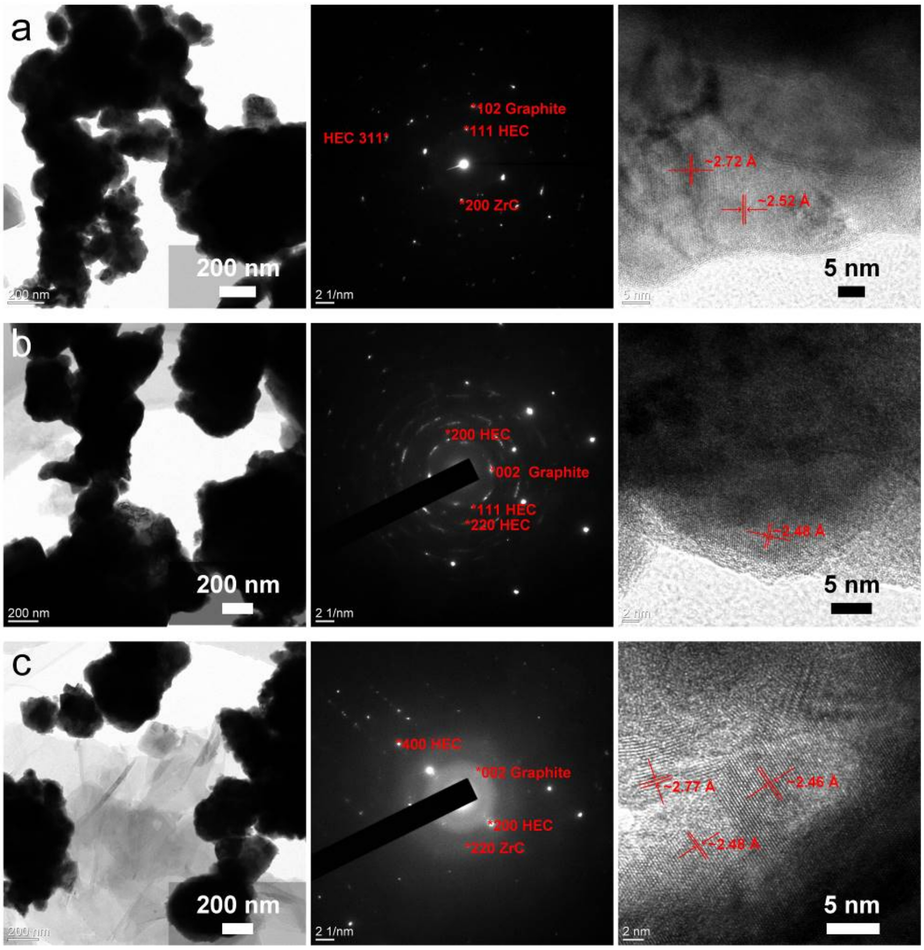

Fig.5. Typical TEM images, SAED and HRTEM images of obtained $ZrNbHfTaC_4$ (a), $VZrNbHfTaC_5$ (b), $TiVZrNbHfTaC_6$ (c).

4. Conclusion

The paper presents the results of experimental studies on the synthesis of high-entropy carbides of various compositions ($ZrNbHfTaC_4$, $VZrNbHfTaC_5$, $TiVZrNbHfTaC_6$) by the original non-vacuum electric arc method. The obtained powders contain cubic phases of the NaCl type, the parameters of which correspond to the known ideas about the structure of HEC of the corresponding composition. According to scanning electron microscopy, the synthesis products contain microsized particles in which metals are uniformly distributed, which indirectly confirms the presence of HEC phases. Transmission electron microscopy data prove the successful synthesis of the indicated phases of high-entropy carbides. The possibility of obtaining phases $ZrNbHfTaC_4$, $VZrNbHfTaC_5$, $TiVZrNbHfTaC_6$ by the non-vacuum electric arc method has been shown for the first time.

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5. References

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