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The use of high-energy shock wave treatment as pre-activation of sintering high-entropy solid solutions of transition metal borides and carbides

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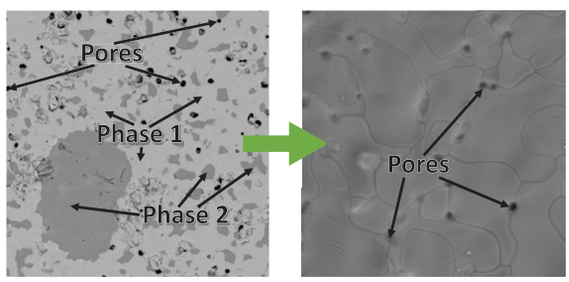
Synthesis of solid solutions of transition metal borides (NbB_2, TaB_2, HfB_2 and ZrB_2) and carbides (NbC, TaC, HfC, ZrC and VC) was carried out *via* sintering the individual components without applying pressure. To activate the interaction of the components, the initial powders were processed by high-energy shock wave treatment (HESWT). HESWT enables the formation of homogeneous solid solution for a mixture of carbides; however, this method did not give the desired results for a mixture of transition metal borides, likely due to the higher strength of borides crystal lattice in comparison with carbides.



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High-entropy ceramics (HEC) are the type of ultrahigh-temperature materials based on the solid solutions of transition metals (IV–VI groups of the Periodic Table) – carbides, nitrides, borides and silicides. In comparison with the individual components, these materials possess a number of unique properties such as increased strength and hardness, reduced energy of formation, *etc*.

The effect of reducing the energy of formation of a complex product compared with the individual carbides, borides, *etc*., is known for this kind of materials. In addition to the thermodynamic effects, associated primarily with the synthesis processes, high-entropy solid solutions have a number of specific properties that are related, among other things, to the characteristics of structure formation. For example, polyelement diborides of various composition (general formula is $Me^{d}_{0.2x5}B_2$) have a unique layered (quasi-2D) high-entropy crystal structure that differs from the hexagonal structure of individual diborides. Due to the above structure, polyelement complex diborides possess high values of hardness and oxidation resistance exceeding the average value for the five individual d-metal diborides.[1]

Good mechanical properties of the ultrahigh-temperature ceramic materials based on the polycomponent solid solutions of transition metal diborides have been achieved in earlier works.[1–5]

Another technique described recently[2,3] was to obtain the materials *via* carbo/boro-thermal reduction of individual transition metal oxides followed by hot pressing. The drawback of this method of material preparation is formation of the by-product of the synthesis, B_4C, that has a negative impact on the hardness of solid solution of transition metals diborides. Similar materials were obtained[4] in the form of a coating deposited by magnetron sputtering. It was found that the hardness of the (Hf, Ta, V, W, Zr)B_2 films did not decrease when heating up to 1400 °C.

Certain properties of the high-entropy solid solutions of transition metals carbides have been investigated in works.[5,6] These materials showed high relative density (up to 99%) and high hardness (up to 36.1 GPa). Also, noteworthy is the chemical homogeneity of materials obtained by spark plasma sintering.[5] However, chemical decomposition of solid solution has been observed for these materials in some areas after sintering[5] and after oxidation.[6]

In the above studies, HEC based on carbides and borides solid solutions were mainly produced by sparking plasma sintering. Here, the main aim was to obtain similar materials from individual carbides and borides by high-temperature sintering without pressure applied. To activate the interaction between individual compounds during sintering, initial powder mixtures have been processed by high-energy shock wave treatment (HESWT).

Using HESWT for ceramic powders is one of the promising methods of formation the composite materials. This method consists in the accumulation of structural defects in the crystal lattices of the initial substances due to high-energy activation.[7] When forming products under pressures exceeding the dynamic yield strength of ceramic materials (up to 10 GPa) the structural and phase transformations as well as chemical reactions proceed, that is, the mechanical activation of fast solid-phase processes (physicochemical and mechanical) occurs. Under such conditions many solids begin to behave like ‘pseudofluids’. Thus, due to the strong deformation of the particles and accumulation of structural defects in the crystal lattices the materials acquire completely new properties.[8]

Hereby, we focused on the obtaining HEC by high-temperature sintering from powder mixture of individual transition metals carbides and diborides processed by HESWT. The following compositions of high-entropy borides (MeB_2): NbB_2, TaB_2, HfB_2 and ZrB_2; and carbides (MeC): NbC, TaC, HfC, ZrC and VC with equimolar ratio of individual compounds were chosen. Content of the main component in all the initial powders was at least 98.5%. Compositions MeC and MeB_2 were grinded and mixed in a vibration mill with hard-alloy grinding bodies (grade ‘WC8’) for 40 h (grinding bodies wear was about 3 wt%). The high hardness

of this hard-alloy material allowed us to grind MeC and MeB_2 compositions. Then one part of the powder was processed by HESWT using a copper storage ampoule placed in a steel shell, which was wrapped in a sheet explosive, and it was detonated in water. HESWT was carried out under the following conditions: detonation velocity 7.8 km s^{-1}, detonation pressure 23.6 GPa, exposure 0.85 μs, impact impulse 470.6 GPa^2 μs. After HESWT the compacted powders were grinded by the crushing mold. All powder samples have been compressed into discs under pressure of 100 MPa using paraffin (3 wt%) as a plasticizer. Sintering was carried out in a graphite furnace in vacuum at 2300 K. The resulted materials were characterized by X-ray diffraction and scanning electron microscopy.

The cell parameters of the materials were calculated using the peaks corresponding to the *P*6/*mmm* and *Fm*-3*m* space groups for borides and carbides, respectively. Niobium boride and carbide have been used as a model phase for the calculation, inasmuch as the peaks positions of the solid solution are the closest to the ones of the corresponding niobium compounds known from crystallographic databases.

X-ray diffraction (Figure 1) shows the broadening of the peaks of the initial components after HESWT. For both compositions, the peaks of the individual components disappear after sintering, which indicates the formation of a solid solution.

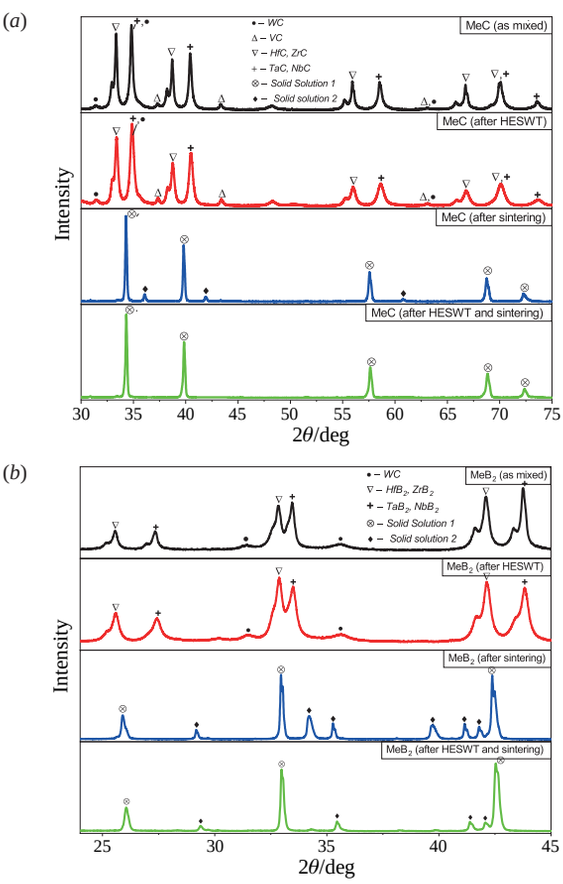

Figure 1 XRD spectra on different stages of the process for: (*a*) MeC and (*b*) MeB_2.

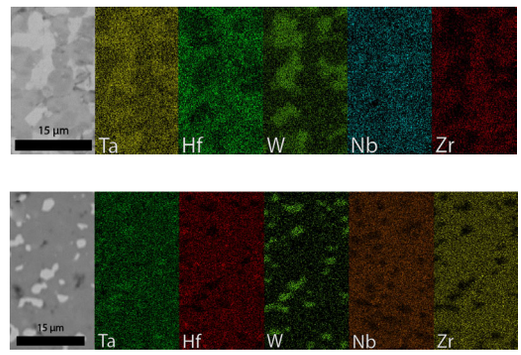

Figure 2 EDXS mapping of MeB_2 samples (*a*) after sintering and (*b*) after HESW treatment and sintering.

However, after sintering both compositions revealed the peaks that should be identified as a secondary solid solution phase (solid solution 2). Apparently, two different types of solid solutions are formed during the sintering process. In the case of MeC there are no peaks of solid solution 2 after HESWT, this indicates the formation of pure and homogenous high-entropy solid solution.

Using the HESWT technique results in a slight change in the parameters *a* and *c* of the MeB_2 hexagonal cell and the parameter *a* of the MeC cubic lattice (see Table 1). However, in both cases HESWT leads to the accumulation of microstrain in the lattice. Moreover, in the case of the MeB_2 mixture, a significant growth of the crystallite was likely due to the absorption of most of the explosion energy on friction, heating and consolidation of the material *via* diffusion. In the process of sintering the relaxation of the accumulated strains and a predictable increase in the size of crystallites occured in both systems.

SEM and EDSX data for MeB_2 samples (see Figure 2) show that formation of solid solutions occures after sintering. However, for MeB_2 there is disintegration into two areas: the first, enriched with W and Ta and depleted of Zr and Hf and the second, showing the opposite trend in the elemental composition. At the same time, niobium atoms are evenly distributed in both areas. After HESWT, niobium atoms are leaving the areas enriched with tungsten and tantalum. Apparently, minor amounts of tungsten (up to 4 at%), which have been implemented into the material during grinding, become the points of initiation of decomposition of the main high-entropy solid solution.

In the case of a carbide mixture (Figure 3), for materials not treated with HESWT the desintegration of the solid solution into two areas has been observed as well: the first area is enriched with V and depleted of Hf and Z and the second area shows opposite trend in elemental composition. After HESWT this material reveals chemical homogeneity.

Comparing the X-ray diffraction data of the mixtures after HESWT and sintering, the following conclusion should be made: the energy of HESWT in the case of borides is expended in the accumulation of strains and the lattice distortion. In the case of carbides, energy is expended in both the accumulation of defects of crystal lattice and the reduction of crystallites. Different behavior of carbides and borides mixtures is associated with the strength of the crystal lattice and the energy of the

Table 1 Crystallographic parameters of MeC and MeB_2.

Conditions	MeB_2 (*P*6/*mmm*)				MeC (*Fm*-3*m*)		
	a = *b*/Å	*c*/Å	Crystallite size/Å	Microstrain (%)	*a* = *b* = *c*/Å	Crystallite size/Å	Microstrain (%)
Initial mixture	3.143	3.482	189	0.153	4.45	338.8	0.079
HESWT	3.141	3.486	455.2	0.593	4.45	276.4	0.328
Sintering	3.134	3.436	1213	0.073	4.524	895	0.111
HESWT + sintering	3.125	3.408	758.7	0.108	4.519	939	0.138

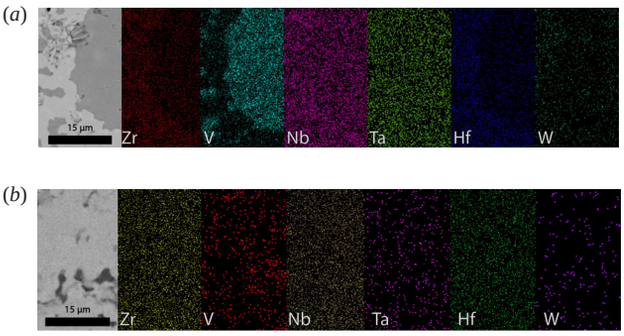

Figure 3 EDXS mapping of MeC samples (*a*) after sintering and (*b*) after HESW treatment and sintering.

chemical bonds. This correlates with the reference values of the thermodynamic parameters (ΔH_f, ΔG_f), elastic constants and microhardness.[9] At the same time, for a mixture of MeB_2 the formation of two types of solid solutions for the material processed by HESWT is probably attributed to a high level of residual microstrains and less diffuse mobility in the sintering process. These phenomena have not been detected for the mixture of MeC after HESWT.

Thus, solid solutions of transition metal carbides and borides have been obtained *via* high-temperature sintering. Without pre-activation by HESWT two different kinds of solid solutions were formed, whereas treating the powders of the initial components by HESWT allowed us to obtain a homogeneous high-entropy solid solution of transition metals carbides. This treatment did not ensure the same result for a mixture of transition metal borides, it is likely due to the stronger crystal lattice of these compounds compared with carbides.

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