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Abstract

High entropy metal diborides (HEBs) represent a radically new approach to extend the chemical composition window of ultra-high temperature ceramics (UHTCs). In this work, arc-melting was used to produce dense HEBs starting from UHTC powders. In order to understand the influence of each individual diboride within the quinary system (HfB_2, ZrB_2, TiB_2, TaB_2 and CrB_2), we investigated five quaternary equimolar solid solutions *e.g.* Hf-Zr-Ti-Ta, Hf-Zr-Ti-Cr, Hf-Zr-Ta-Cr, Hf-Ti-Ta-Cr, Zr-Ti-Ta-Cr and the overall quinary equimolar combination. Arc-melting allowed a rapid screening of favorable and unfavorable combinations. The produced HEBs were free from undesired oxides and characterized by linear variation of lattice parameters typical of diborides and binary solid solutions. Because of evaporation during arc melting, CrB_2 was hardly found in the solid solution, suggesting that vapor pressure should be taken into account when designing HEB

compositions especially for operating temperatures exceeding 2000 ˚C. Finally, Vickers microhardness ranged between the typical values of starting diborides.

1. Introduction

Borides and carbides of transition metals such as, ZrB_2, TiB_2, HfC, TaC, are known as ultra-high temperature ceramics (UHTCs). Owing to their particularly chemical and physical properties, high melting temperatures above ~3000 °C, excellent high temperature strengths, high hardness, good thermal and electrical conductivity and ablation resistance [1], UHTCs can be used in extreme temperatures and chemically aggressive environments. UHTCs are difficult to densify because of their melting point higher than 3000°C resulting from strong covalent bonding [1,2]. Current UHTC applications in hypersonic flights and rocket propulsion have operation requirements exceeding bulk mono-phasic materials. Pure monolithic ceramics present a series of limitations, such as poor damage tolerance and critical oxidation resistance [3,4]. Several studies have demonstrated that combining UHTCs with other elements such as metals [5], carbides, borides, nitrides [6] and metal disilicides [7], can help to solve some of these major drawbacks.

In recent years, high entropy alloys (HEA) have attracted growing interest [8–10]. Starting from work on metals, these new alloys are composed of "*r*"-number of metal specimens, generally $r \geq 5$, to form a high entropy solution having increased entropy of mixing $\Delta S_{mix} = -nR \sum_{i=1}^{r} x_i \ln x_i$,where n is the total number of moles, R is the gas constant, x_i is the mole fraction of component i [9]. The theory supporting these new alloys relies upon the principle of Gibbs free energy minimization, $\Delta G = \Delta H - T \cdot \Delta S$. According to this principle, a system with an enhanced entropy (ΔS) is more stable ($\Delta G<0$) at high temperatures thanks to the contribution of the entropic term ($-T \cdot \Delta S$). HEAs have been shown to have improved properties compared to conventional alloys. Further necessary conditions for the existence of the substitutional solid

solutions are set by the Hume-Rothery solid solution rules. Indeed, in order to obtain substitute alloys, two or more metals must meet the following requirements: 1) atomic radii that do not differ by more than 15 %, 2) same crystal structure, 3) similar electronegativity, 4) same valence.

High entropy oxides [11–14], borides [15–19], carbides [20–23] and silicides [24] have been obtained using different synthesis/sintering techniques such as spark plasma sintering and pressureless sintering. For instance, Gild et al. [13] have successfully synthesized high-entropy fluorite oxides (HEFO), with hardness comparable to 8 mol. Y_2O_3-stabilized ZrO_2 and low electrical and thermal conductivities. Castel et al. [21] have shown a significant enhancement in hardness of high entropy carbides material compared to the value calculated according to the rule of mixtures from the reference monocarbides and in comparison to the hardest monocarbide. Tallarita et al. [17] have produced high entropy borides starting from the respective oxides and boron, through a two-step processing method of Self-propagating High-temperature Synthesis (SHS) followed by SPS. This approach avoided the need for intense mechanical milling of individual borides. Although reactive sintering by SPS may be faster than hot pressing and pressureless sintering, it still requires costly equipment, high temperatures (>2000 °C) and high pressures (tens of MPa) to promote atomic diffusion of different elements to obtain solid solutions. Alternatively, Zhang et al. [25] have obtained solid solutions of binary and ternary carbides in a very short time (10-20 seconds) using the arc melting technique. This technique, already known in the metallurgical field, is able to reach very high temperatures, and therefore, melting materials with high melting point, close to 4000 °C, in a short time (a few seconds). In this way it was possible demonstrate the formation of solid solutions of binary, ternary carbides.

The aim of this work is to demonstrate the feasibility of high entropy borides (HEB), mixing equimolar composition of HfB_2, ZrB_2, TiB_2, TaB_2 and CrB_2, through the arc-melting technique. Moreover, since this technique allows rapid fabrication of large number of samples, we prepared 6 compositions (one quinary and five quaternaries) to study the effect of each single boride on the formation of HEB solid solutions.

2. Experimental

Five commercial powders of transition metal diborides of HfB_2 (Treibacher, D_{50} 2.56 μm, impurities (wt.%): 0.23 C, 0.01 N, 0.23 O, <0.001 S), TaB_2 (Materion, purity 99.5%, impurities (wt.%): 0.04 Al, < 0.0007 Cd, < 0.0005 Cr, 0.07 Fe, 0.02 Nb, <0.0004 Pb), TiB_2 (H.C. Starck, Grade F, D_{90} 4.0 -7.0 μm, D_{50} 2.5-3.5 μm, impurities (wt. %): 0.4 C, 2.5 O, 0.5 N, 0.1 Fe), ZrB_2 (H.C. Starck, Grade B, D_{90} 4.0 -6.0 μm, D_{50} 1.5-3 μm, impurities (wt. %): 0.2 C, 1.5 O, 0.25 N, 0.1 Fe, 0.2 Hf), CrB_2 (H.C. Starck, Grade B, D_{90} 4.0 -6.0 μm, D_{50} 1.5-3 μm, impurities (wt. %): 0.3 C, 0.6 O, 0.5 Fe) were used to prepare six mixtures. One with all five equimolar elements and five equimolar combinations of 4 out of 5 borides: e.g (HfB_2, ZrB_2, TiB_2, TaB_2), (HfB_2, ZrB_2, TiB_2, CrB_2) (HfB_2, ZrB_2, CrB_2, TaB_2), (HfB_2, CrB_2, TiB_2, TaB_2), (CrB_2, ZrB_2, TiB_2, TaB_2). The six compositions are listed in Table 1. The starting equimolar powders were mixed using mortar and pestle and rotary milled with no milling media. All mixtures were pre-sintered in a Spark plasma sintering furnace (Chenhua 10–20 SPS furnace, China), at 1600 °C in low vacuum (5 Pa) under a pressure of 25 MPa, heating rate of 80 °C/min and dwelling time of 10 minutes, in order to clean borides from oxide impurities as much as possible. From each of the 6 pre-sintered pellets, 10 smaller pieces with a volume of about 40 mm^3 were obtained for the arc-melting experiments in order to have similar heating and cooling rates.

All samples were melted on a water-cooled copper crucible using arc melting by TIG-200P (AC/DC) (Dongguan Hanhuang Welding and Cutting Equipment Co., Ltd, China) under argon flow, with purity of 99.999 %, applying a current of 100 A for 10-20 seconds. The argon flow was maintained for 10 seconds after switching off the current in order to protect the samples from the oxidation during the free cooling. The samples were re-melted 5 times in order to homogenize the mixture as much as possible during melt formation.

Bulk densities were measured by the Archimede method, using ethyl alcohol instead of water. Several specimens were measured for each composition and the results were averaged. The microstructure was analyzed on polished cross sections, using diamond discs up to 0.25 μm, by field-emission scanning electron microscopy (FESEM, mod. ΣIGMA, ZEISS NTS Gmbh, Oberkochen, Germany) equipped with energy X-ray dispersive microanalysis (EDS, Model INCA energy 300; Oxford Instruments, UK). Crystalline phases of the samples, obtained from the melt, were identified by X-ray diffraction (XRD, mod. D8 Advance - Bruker, Germany) with Cu Kα radiation, step size of 0.04 and 0.5 s counting rate in the 20–100° 2θ range. The hardness was measured by Vickers indentation method applying a load of 1.96 N (200 g), 4.90 N (500 g) and 9.8 N (1000 g) (Innovatest Falcon 505, Rupac, Netherlands) for 15 seconds.

Table 1. Starting compositions, density values, and quantitative EDS mapping of samples core

			EDS analysis*				
Label	**Starting composition mol%**	**Bulk density g/cm^3**	**Hf**	**Zr**	**Ti**	**Ta**	**Cr**
			mol %				
1 - all	$(Hf_{0.20}, Zr_{0.20}, Ti_{0.20}, Ta_{0.20}, Cr_{0.20})B_2$	7.9 ± 0.2	25	22	23	27	1
2 - CrB_2	$(Hf_{0.25}, Zr_{0.25}, Ti_{0.25}, Ta_{0.25})B_2$	9.3 ± 0.5	27	24	22	25	-
3 - TaB_2	$(Hf_{0.25}, Zr_{0.25}, Ti_{0.25}, Cr_{0.25})B_2$	6.9 ± 0.2	39	30	30	-	1
4 - TiB_2	$(Hf_{0.25}, Zr_{0.25}, Cr_{0.25}, Ta_{0.25})B_2$	9.4 ± 0.2	32	30	-	36	0.8
5 - ZrB_2	$(Hf_{0.25}, Cr_{0.25}, Ti_{0.25}, Ta_{0.25})B_2$	8.5 ± 0.2	37	-	29	31	2
6 - HfB_2	$(Cr_{0.25}, Zr_{0.25}, Ti_{0.25}, Ta_{0.25})B_2$	5.6 ± 0.4	-	33	32	33	1

*error within 3% measured using EDS

3. Results and discussion

3.1 X-ray diffraction spectra.

Fig. 1 shows X-ray diffraction spectra: all samples display the primitive hexagonal unit cell typical of the isomorphous starting diborides. Principal diffractions are usually surrounded by small peaks (< 2% of highest peak, see bottom enlarged spectra below each diffraction pattern), which accounts for phase separation, as discussed in sections 3.2 and 3.4.

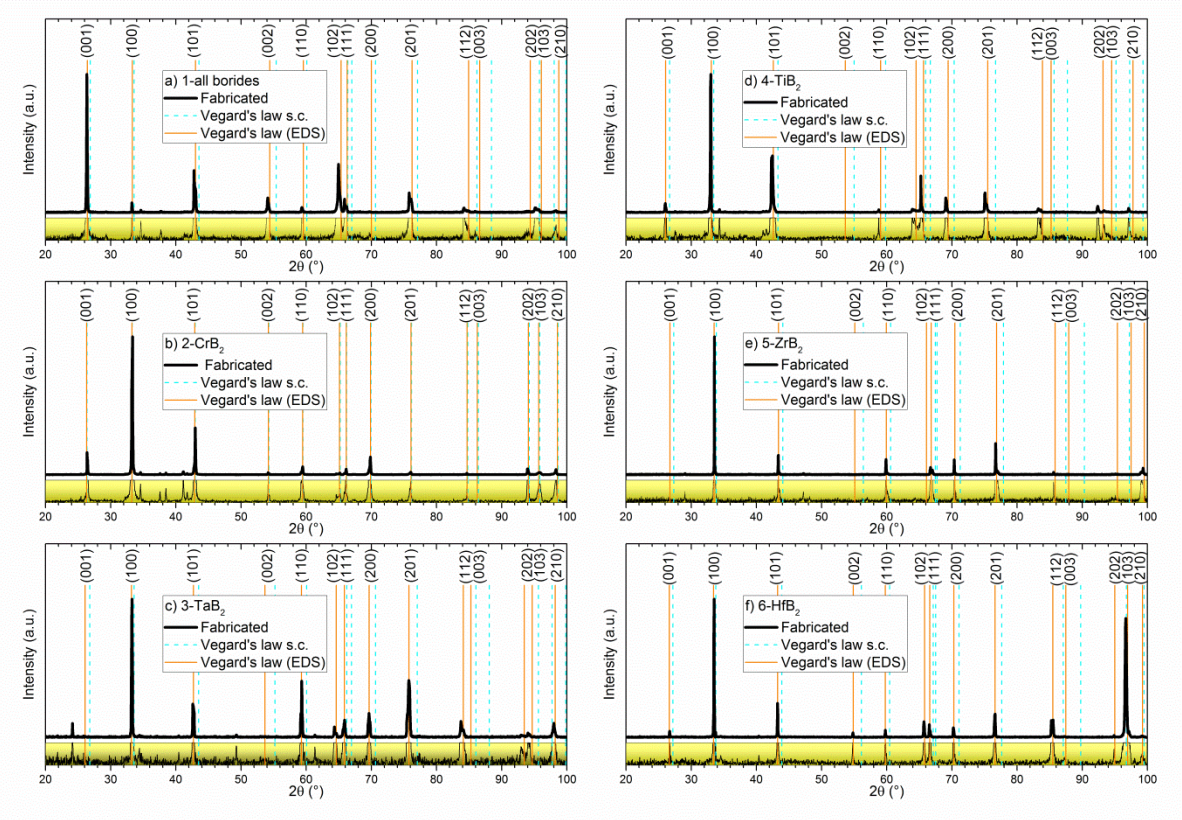

Figure 1: Normalized X-ray diffraction patterns for the 6 mixtures and expected peaks' position of high entropy metal diborides (HEBs) calculated with the Vegard's law considering the starting compositions (s.c.) and the compositions detected by EDS. All scales of the insets zoom range from 0 to 0.02.

Nevertheless, considering main peaks ascribed to hexagonal phase, experimental lattice parameters obtained from XRD patterns are shown in Table 2 together with those calculated by means of Vegard's rule [26]. The calculation was done using powder diffraction files (PDF) n. 65-0878, 65-1073, 65-1883, 65-3389, and 65-3387 for TaB_2, TiB_2, CrB_2, HfB_2, ZrB_2, respectively, and the actual atomic percentage obtained using EDS analysis explained below. As it can be seen from Fig. 1, the deviation from Vegard's rule is minimized if compositions determined by EDS analysis are taken into account instead of the starting equimolar ones. In Fig. 2 we plotted a series of observed lattice parameters of various diborides and binary solid solutions taken from Ref. [27], along with those of the HEBs solutions developed in this work. As can be seen, there is an excellent agreement

between a linear interpolation of observed c/a ratio vs. atomic radii of metal atom, r_m and the plotted values, the only unexpected outlier is 3-TaB_2.

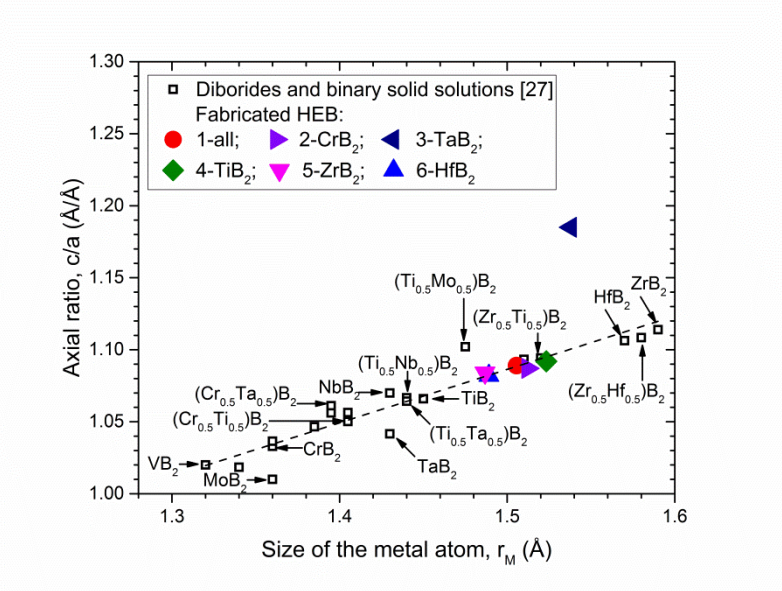

Figure 2: Observed tetragonality, c/a ratio, *vs.* atomic radii of metal atom, r_m, for diborides and binary solid solutions taken from Ref. [27], along with those of the high entropy metal diborides (HEBs) developed in this work. The dotted line was obtained by linear fitting ($R^2 = 0.90$) the values of diborides and binary solid solutions.

The reason for the large deviation (8%) in the length of the *c*-axis is not known, and to date, such anomalies were observed in other studies as well [27] but no explanation has been found so far. In summary, XRD results suggest that (i) there is a negligible or no amount of Cr in solid solution, and (ii) metal-to-metal replacement to form solid solution occurred readily in the Hf, Zr, Ti, and Ta diborides.

Table 2. Lattice constants *a*, and *c* (Å) obtained from observed (100) and (001) peaks, respectively, compared to the one calculated using Vegard's rule and the actual atomic percentage obtained using EDS analysis. *c* values of sample 5 were extrapolated from (101) peak.

	***a* XRD**	***a* Vegard**	***c* XRD**	***c* Vegard**	***c/a* XRD**	***c/a* Vegard**
1- all	3.109	3.102	3.387	3.370	1.089	1.086
2-CrB_2	3.101	3.107	3.372	3.382	1.087	1.089
3-TaB_2	3.107	3.115	3.683	3.413	1.185	1.096
4-TiB_2	3.132	3.125	3.421	3.415	1.092	1.093
5-ZrB_2	3.082	3.085	3.340	3.330	1.084	1.080
6-HfB_2	3.086	3.091	3.338	3.344	1.082	1.082

3.2 Sample morphology and EDS analysis

Fig. 3 shows the cross section of the samples obtained from the arc-melting process of the six materials listed in Table 1. From SEM analyses of the microstructures it was ascertained that all materials reached a good level of densification, with the exception of 4-TiB_2, (missing TiB_2) that exhibited small distributed porosity in the center and voids in the edges (see supplementary section). Bulk densities measured with the Archimede method (Table 2) ranges from 5.6 to 9.4 g/cm3, depending on the composition and residual porosity. Due to evaporation phenomena and new phase formation during arc-melting (section 3.4), the starting composition was strongly modified, therefore an exact calculation of theoretical and relative densities was not possible.

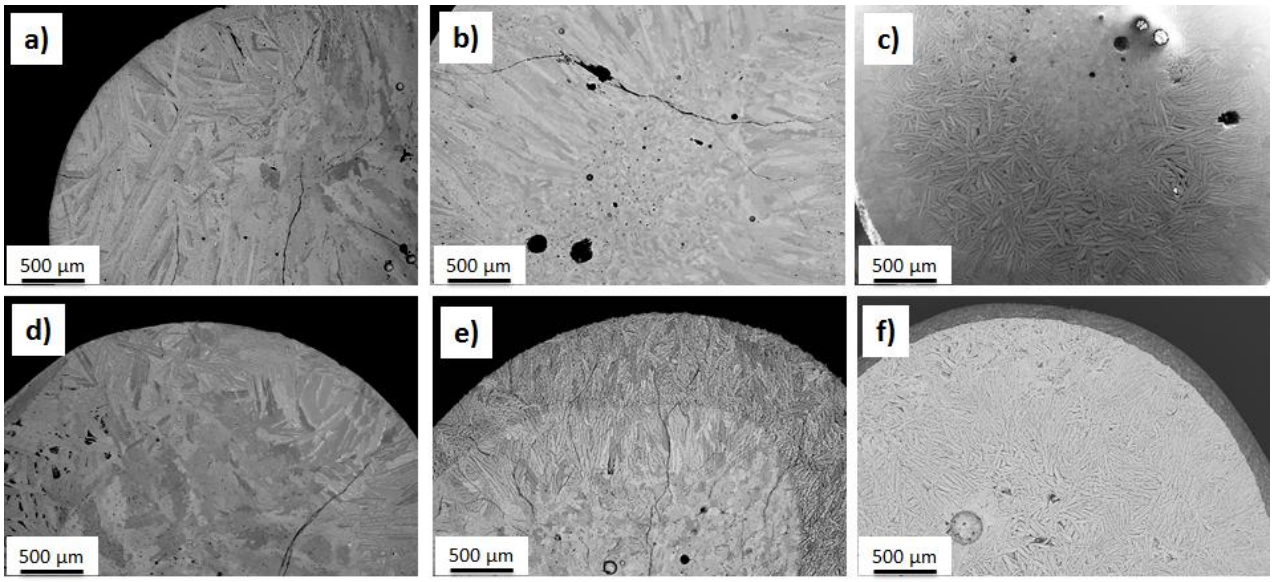

Figure 3. Cross section of spherical HEB samples:
a) 1- all, b) 2- CrB_2, c) 3- TaB_2, d) 4-TiB_2, e) 5- ZrB_2, f) 6- HfB_2.

Dense specimens were often found to be affected by cracks due to thermal shock/strong temperature gradient experienced during arc-melting treatment. They all exhibited the typical anisotropic microstructure of metallic materials obtained from melting [28,29]. During cooling down, the surface cooled much faster than the core, which generated a strong radial temperature gradient. As a result, an anisotropic structure was created, with rounded/coarsened grains in the (hot) core that gradually changed to elongated and dendritic-like grains towards the rapidly cooling surface. Approximately, the transition from rounded to elongated grains occurred at a distance of 2 mm from the center. According to EDS analyses, a single solid solution phase was detected in the core grains constituting the inner part of the molten samples, in agreement with the phases detected by X-ray diffraction and in agreement with the large mutual solubility range of diborides observed by other authors [30]. Moreover, grain boundaries were found to be clean in this portion of material, at least at SEM resolution. Shifting from the core to the edge, compositions and morphology of the grains changed and liquid phase separation was observed in the grain boundary regions.

In all the compositions containing Cr, this element was preferentially detected along the grain boundaries as a secondary phase, though a tiny percentage was also found in solid solution (see

quantitative analyses in Table 1). Indeed, observing the EDS compositional maps of sample 1-all $(Hf_{0.20}, Zr_{0.20}, Ti_{0.20}, Ta_{0.20}, Cr_{0.20})B_2$, Fig. 4, and except those contain Cr, they presented a quasi-equimolar solid solution of HfB_2, ZrB_2 TiB_2 and TaB_2. This feature is even more evident in sample 2-CrB_2 where CrB_2 was not included the original mixture.

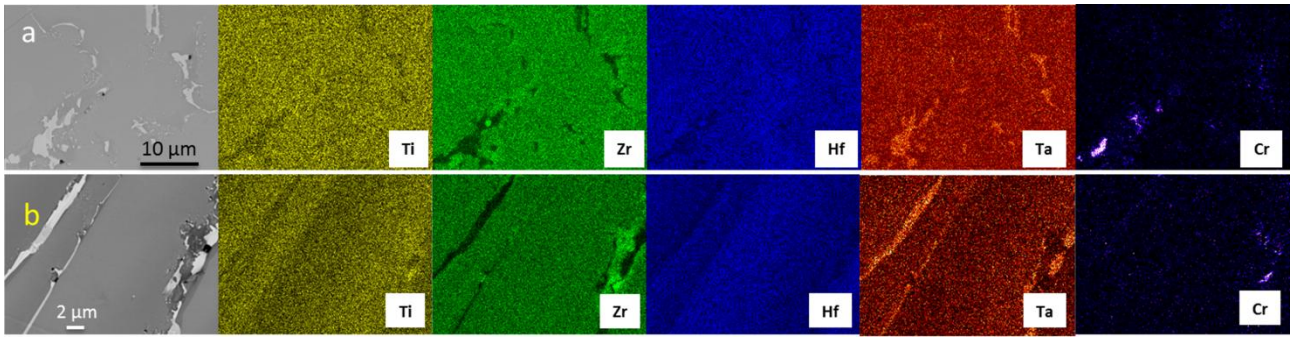

Figure 4. EDS compositional maps of a) inner part and b) external part of the sample 1-all b, containing all borides. CrB_2 phase separation was observed, the remaining borides formed a complete solid solution

Noteworthy, in sample 2-CrB_2 $(Hf_{0.25}, Zr_{0.25}, Ti_{0.25}, Ta_{0.25})$ B_2, missing Cr, Ta segregation between the grains was observed, as shown in Fig 5 b)..

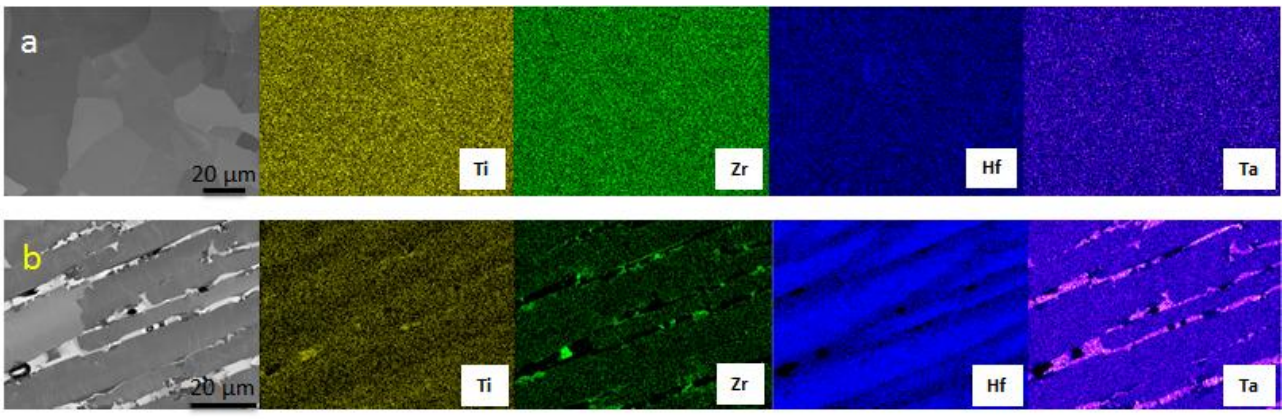

Figure 5. EDS compositional maps of a) inner part and b) external part of the sample 2-CrB_2.

For mixtures 3, 4, 5 and 6, figures are reported in the supplementary material. Sample 3, ($Hf_{0.25}$, $Zr_{0.25}$, $Ti_{0.25}$, $Cr_{0.25}$)B_2, was characterized by a solid solution with almost equal atomic content of Hf, Zr, and Ti, but much smaller content of Cr. Cr was preferentially detected at the grain boundaries. Towards the edge of the pellet, we noticed that elongated grains composed of Hf, Zr, and Ti were surrounded by ZrB_2 rounded agglomerates and CrB_2 phases (see Fig. A1 a) and b)).

Similarly, sample 4 ($Hf_{0.25}$, $Zr_{0.25}$, $Cr_{0.25}$, $Ta_{0.25}$)B_2, displayed homogeneous distribution of Zr, Hf and Ta element in the center grains, with small segregated CrB_2 – based secondary phases at the grain boundaries On the contrary, going towards the edge, elongated grains were surrounded by mixed secondary phase with irregular morphology (see Fig. A2 a) and b)) containing inhomogeneous distribution of Zr, Hf, Ta mainly and Cr in small quantities. Samples 5 ($Hf_{0.25}$, $Cr_{0.25}$, $Ti_{0.25}$, $Ta_{0.25}$)B_2 and 6 ($Cr_{0.25}$, $Zr_{0.25}$, $Ti_{0.25}$, $Ta_{0.25}$)B_2, showed characteristics similar to sample 4 (see Fig. A3 a) and b) and A4 a) and b)).

3.3 Hardness

Indentations were collected indistinctly both in the samples core and close to the sample surface. Values were in the range 19-20 GPa, and slightly increased to 20-23 GPa reducing the load from 1 to 0.5 and 0.2 Kg, as shown in Fig. 6 and Table 2A, mainly due to the indentation size effect [31], [32].

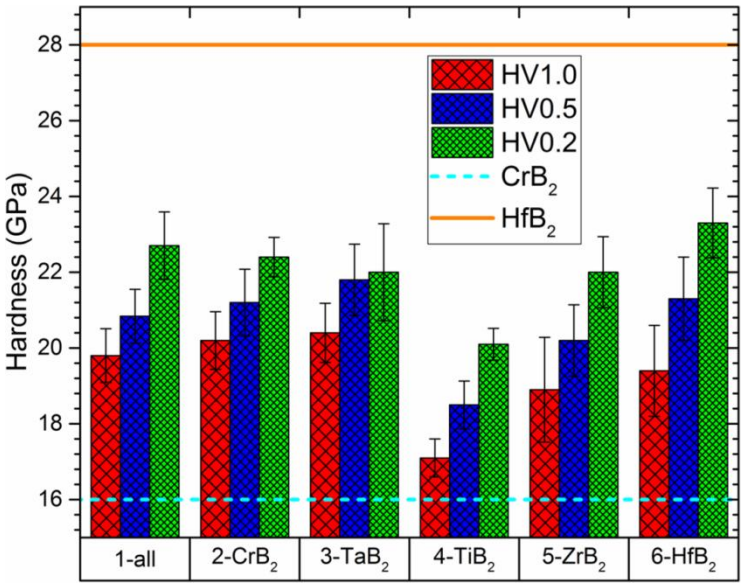

Figure 6. Hardness value measured with load 1, 0.5 and 0.2 Kg for quaternary and quinary borides. HfB_2 and CrB_2 lines are the hardest and softest borides as reference materials such indicated by Fahrenholtz et al. (HV1.0) [1] and Wang et al. (HV0.5) [33]

The lowest values were found for the mixture without TiB_2, a feature which can be attributed to residual porosity shown in figure 3 d). Amongst the other fully dense mixtures, the hardest one was sample 3, missing TaB_2 probably due to its finer microstructure. Table 1A shows physical and chemical properties of the transition metal diborides considered in this work. They all satisfy the Hume-Rothery solid solution rule, as demonstrated by [15].

3.4 Microstructural evolution

In their work, Gild et al. [15], demonstrated the formation of a high entropy phase including CrB_2 using the spark plasma sintering technique, despite the limited solid solubility of CrB_2 in both HfB_2 and ZrB_2 [27]. In our case, the formation of high entropy diboride should be easier because, in the molten state, the activation energy for diffusion is much smaller than in the solid state [34]. Compared to the starting compositions we observed a notable reduction of CrB_2 content in all mixtures and of TaB_2 in the case of 2-CrB_2, (e.g. the mixture missing CrB_2). Indeed, we

hypothesized that in the arc melting process, formation of solid solutions is not only affected by melting points of each constituent material, but also by their vapor partial pressure. In this work, CrB_2 has the highest vapor partial pressure followed by TaB_2, as shown in Table 1A.. Therefore, in samples containing CrB_2 (1, 3, 4, 5, 6) the peculiar microstructure obtained is affected by the fast vaporization and evaporation of CrB_2 from the center towards the surface. To a lower extent, TaB_2 also experienced the same phenomenon, because of its high vapor partial pressure. Broadly, microstructural evolution of compositions containing CrB_2 can be schematized as follows. During heating:

1) at least 2 melts form, with different melting points and composition. Since CrB_2 melting point << other borides, at temperature around 2000°C or below CrB_2 becomes liquid and partially dissolves other borides in the vicinity, forming the L1 liquid phase.
2) As the temperature continues to rise and melting proceeds towards the pellet interior, new L1 liquid phase is formed and evaporation of CrB_2 occurs on the surface.
3) Other molten liquids form (L2, with no CrB_2), with higher melting point than L1.
4) Progressive/fast extension of melting from the surface down to the core and progressive depletion of CrB_2 from the core.

During cooling:

1) the solid solution nuclei from L2 (most refractory) liquid type begin to solidify from the outer surface and grow forming columnar grains that develop in the direction of the temperature gradient present in the sample. These crystalline nuclei are mainly formed by solid solutions of the high melting elements, where HfB_2, ZrB_2, TiB_2 are quasi equimolar whilst TaB_2 is slightly lower due to partial evaporation.
2) CrB_2 vaporization is blocked in the proximity of the outer surface due to rapid closure of exit channels and the CrB_2-liquid phase (L1) remains trapped and solidifies along the grain boundaries, as observed by SEM-EDS.

3) CrB_2 secondary melt separation occurs because of different factors, including its reduced melting point compared to other borides, decreased solubility of other borides when the temperature decreases and extremely fast cooling (≈1000 ˚C/s).

Finally, in sample 2, missing CrB_2, TaB_2 is the lowest melting temperature phase, thus in this case, TaB_2 based liquid phase is formed and phase separation mainly involving TaB_2 occurs during cooling.

Mechanisms occurring during cooling are sketched in Fig. 7.

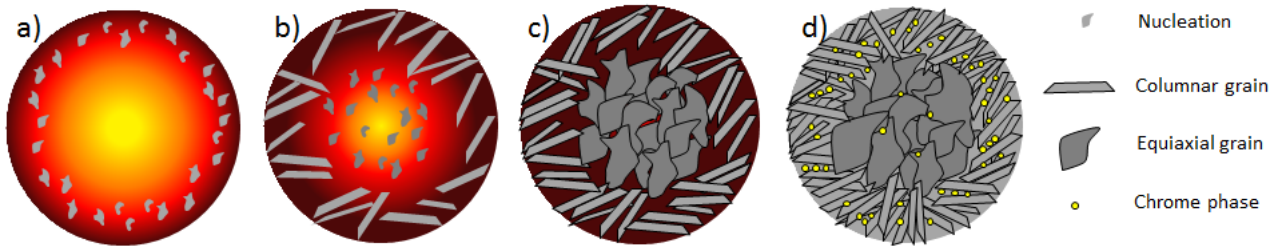

Figure 7. Solidification mechanism: a) first formation of crystalline nuclei in the outermost area formed by the high melting elements (HfB_2, ZrB_2, TiB_2, TaB_2), b) nuclei growth forming columnar grains that develop in the direction of the temperature gradient and formation of crystalline nuclei in the central part of the sample c) growth of the equiaxial grains in the innermost area of the material formed by an equimolar solid solution d) precipitation of Cr element among the grain boundary principally in the external part of the sample

Finally, future work is concerned with additional experiments to control the cooling rate. It is expected that producing larger samples has the effect to decrease the cooling rate, limiting or suppressing the formation of a core – shell structure, with the dense equiaxed core and elongated shell grains. This could be achieved by lowering the arc current gradually or using a heated stage.

4. Conclusions

High entropy metal diborides were obtained using the arc-melting technique staring from a powder mixture. HfB_2, ZrB_2, TiB_2 and TaB_2 formed equimolar solid solutions as confirmed by EDS analysis. Unlike solid state processing, the similarity in melting point and vapor partial pressure of each individual diboride is an essential requirement to achieve homogenous samples using arc-melting technique. CrB_2 did not form a solid solution because during processing its low melting point contributed to phase separation while its high vapor partial pressure induced almost complete sublimation. The XRD analysis confirmed that oxide phases were not present and the values of lattice parameters were in agreement with theoretical values. The influence of each element on the hardness values showed no large variations and lowest value was for the sample without TiB_2. The results obtained in this work demonstrates as arc-melting technique could allow a rapid screening of hundreds of high entropy borides compositions avoiding long reaction times needed in solid state processing.

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