Low temperature synthesis of an equiatomic (TiZrHfVNb)C₅ high entropy carbide by a mechanically-induced carbon diffusion route

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Abstract.

A novel, homogeneous, nanostructured and equiatomic (TiZrHfVNb)C₅ High Entropy Carbide (HEC) was successfully synthesised in a powder form by a mechano-synthesis process from the elemental mixture. This synthesis method for HECs, not previously reported, is simple, reproducible and carried out at room temperature. During milling, the transition metals (Ti, Zr, Hf, V and Nb) alloying and the diffusion of carbon (introduced as graphite) into the alloy structure are simultaneously induced, obtaining the expected (TiZrHfVNb)C₅ HEC. The room temperature method employed contrasts with those reported in the bibliography from binary carbides that are carried out at a very high temperature (1800-2200 °C), with the consequent energy savings.

Keywords: High Entropy Alloy; High Entropy Carbide; Carbide; Ceramic; Mechanical Milling; Mechanosynthesis.

INTRODUCTION.

High Entropy Materials (HEMs), which cover the most highly developed High Entropy Alloys (HEAs), along with the less developed High Entropy Carbides (HECs),

1 High Entropy Borides (HEBs) and High Entropy Nitrides (HENs), among others, are
2 currently attracting the attention of researchers due to their unique composition and
3 outstanding properties [1-3], which make them suitable for a large number of potential
4 applications. In this sense, a search made on the web of science (WOS) using the term
5 “*High Entropy*” gives more than 2100 results in the last five years (2015-2019), while
6 until 2014, the results were only 470.

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8 The term “*High Entropy Materials*” refers to a group of advanced materials
9 formed by five or more principal elements in equal or near equal atomic proportion.
10 According to the criterion of Yeh et al [4], the concentration of each principal element
11 must be between 35 and 5 at. % of the total amount. This high number of elements
12 causes the entropic stabilisation of random solid-solutions against the formation of
13 ordered compounds. Properties of HEM are in general superior when compared to
14 similar simple or complex materials. For example, for the most widely studied HEAs, it
15 has been shown that they present higher strength, ductility, hardness, fracture toughness
16 and corrosion resistance than conventional alloys [5-7]. All these interesting properties
17 make them suitable for structural, functional and high temperature applications in
18 several fields, such as aerospace engineering, civil transportation, energy industries, etc.

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20 HECs are one of the most interesting HEMs that are in an incipient state of
21 study. In them, the stabilization by an entropic effect is also a key parameter, since they
22 are formed by at least five disordered metal cations in the cationic sublattice combined
23 with carbon that occupies the atomic positions in the anionic sublattice. The first studies
24 on HECs based on the IVB (Ti, Zr, Hf) and VB (V, Nb, Ta) transition metals seem to
25 show that they have higher hardness, better extreme heat, oxidation and wear resistances
26 and, even, higher biocompatibility than single carbides [8-12]. These carbides, which
27 are part together with the borides and nitrides of the same transition metals of the so-

called Ultra High Temperature Ceramics (UHTCs), are suitable for thermal protection coatings in aerospace applications, as high-performance drill bits and cutting tools in the mining industry and also as coatings in the bone replacement implants industry.

Up to now, the few studies on HECs have reported their synthesis mainly in bulk form from the corresponding single carbides. These carbides are mixed by a wet ball-milling process, subsequently, compacted/shaped by uniaxial or isostatic pressing and, finally, subjected to reactive sintering by Spark Plasma Sintering (SPS) and/or Hot-Pressing at relatively high temperatures, usually between 1800-2200 °C. Specifically, (TiZrHfNbTa) C_5 , (TiZrNbTaW) C_5 and (TiHfVNbTa) C_5 have been obtained using this methodology [7-9, 13]. More recently [13], the use of both metallic powders or metal oxides and graphite as the raw materials has been proposed, although worse results were obtained in terms of homogeneity of the elemental distribution. Moreover, the synthesis of the (TiZrHfNbTa) C powder has also been reported by a two-step process consisting of the carbothermal reduction of the single oxides at 1600 °C, leading to the formation of the single carbides, followed by the solid solution formation after annealing at 1900-2000 °C [14]. However, the extremely high temperatures required to synthesise HECs, besides inducing a high energy consumption, do not allow obtaining powders with the most adapted microstructure to be used in coatings technology or powder metallurgy processes [15].

Therefore, in this work, we present an alternative synthesis method for a novel powdered (TiZrHfVNb) C_5 HEC, which can be extended to other compositions including transition metals of the IVB and VB groups and tries to solve the limitations of the above-mentioned synthesis methods. The procedure consists of a room temperature mechanosynthesis process involving the simultaneous alloying of metals and carbon diffusion into the metal alloy. The selected elements, i.e, Ti, Zr, Hf, V and

Nb, were chosen because their corresponding single carbides are used as UHTCs or additives in ceramic-metal composites to improve some specific properties [16-19]. Since the carbide formation of these transition metals from elemental mixtures is a highly exothermic reaction [20], the control of the occurrence or non-occurrence of combustion processes during milling, which are denoted as mechanically induced self-sustaining reaction (MSR), must be taken into account. In MSR, the reactants are instantly transformed into products after a critical milling time called the ignition time. MSR contrasts with conventional mechanochemical processes, in which the conversion into products gradually proceeds with milling time as a result of diffusional solid state reactions between the reactants. Either mechanochemical mechanisms, MSR or gradual, have been observed for the same reactant mixture depending on the milling intensity regime [21].

EXPERIMENTAL PROCEDURE.

Equiatomic mixtures of Ti, Zr, Hf, V and Nb powders, together with the corresponding stoichiometric amount of graphite powder (all of them supplied by Alfa Aesar, 325mesh and purity higher than 99.6 %), were used to form a hypothetical $(\text{TiZrHfVNb})\text{C}_5$ High Entropy Carbide. Thus, 5 g of these mixtures were placed in a 45 ml tempered steel vial (67HRC) together with 5 ($\varnothing=15$ mm, $m=13.6$ g) or 17 ($\varnothing=10$ mm, $m=4.0$ g) tempered steel balls. This number of balls was selected to maintain the same Powder-to-Ball-Ratio (PBR of 1/13.6) for the two synthesis routes carried out in the present work. Both mixtures were milled at a spinning rate of 300 rpm in a planetary ball mill (PULVERISETTE 4, Fritsch) under 5 atm of an inert high-purity argon atmosphere (supplied by Air Liquide). Although the same PBR was used regardless of

the diameter of balls, the energy of impacts with 15 mm balls are greater than with 10 mm balls. The use of different ball sizes was intended to try to synthesize the expected (TiZrHfVNb)₅ HEC by both MSR or gradual mechanochemical mechanisms. In addition, the planetary ball mill was modified to detect when an exothermic MSR process occurred and allowed stopping the milling procedure at exactly this moment. An in-depth description of the planetary mill modification can be found elsewhere [22]. The as-synthesized powders obtained were labelled as *MSR-route* (15 mm diameter ball used) and as *Diffusion-route* (10 mm diameter ball used), respectively. Thus, the milling process for the *MSR-route* sample was stopped after 700 min, when the ignition time for the MSR reaction was detected, and for the *Diffusion-route* sample, milling was extended until 3000 min (50h), which it was enough time to ensure the inhibition of the MSR reaction and the complete formation of the HEC expected instead of mix of different carbides.

The X-Ray Diffraction (XRD) patterns were obtained with a PANalytical X'Pert Pro instrument equipped with a θ/θ goniometer using Cu K α radiation (40 kV, 40 mA), a secondary K β filter, and an X'Celerator detector. The diffraction patterns were scanned from 25° to 80° of 2 θ in a step-scan mode at a step of 0.02° and a counting time of 275 s/step. Lanthanum hexaboride, LaB₆ (Standard Reference Material 660c, NIST), was used for calibration of the diffraction positions. The space group symmetry as well as the interplanar distances and the lattice parameter of the synthesised phase were calculated from the XRD diagrams using the X'Pert HighScore Plus software. The elucidated structures were compared with those in the PDF-4+ database from the International Centre for Diffraction Data (ICDD).

Scanning Electron Microscopy (SEM) images were obtained on a Hitachi S-4800 SEM-FEG microscope, in secondary mode at an acceleration voltage of 5kV. The

quantification of the transition elements and carbon was carried out by point analysis and mappings using an Energy-Dispersive X-Ray Spectroscopy (EDS) detector coupled in the SEM microscope at an acceleration voltage of 30 kV.

Transmission Electron Microscopy (TEM), High Resolution TEM (HRTEM), Selected Area Electron Diffraction (SAED) and High-Angle Annular Dark-Field (HAADF) images as well as point and mapping EDS were obtained by using a FEI TalosTMF200S scanning/transmission electron microscope at an acceleration voltage of 200 kV (point resolution=0.25 nm). This microscope is equipped with a HAADF detector with 0.16 nm point resolution (Fischione Instruments, USA) and an INCA ZX-max 80 silicon drift detector (SDD) for the EDS measurements. The micrograph analysis, lattice spacing, Fast Fourier Transform (FFT) and phase interpretation were performed with the Gatan Digital micrograph software (Gatan Inc., USA). The powder samples were dispersed in ethanol and droplets of the suspension were deposited onto PELCO[®] copper grid with pure carbon film.

RESULTS AND DISCUSSION.

The XRD patterns for both *MSR-route* and *Diffusion-route* samples are shown in Fig 1. The *MSR-route* sample was formed by a set of different carbides, marked as *a*, *b*, *c*, *d* and *e* in Fig.1, with cubic structure and *Fm-3m* space group symmetry, analogous to the corresponding single TiC (00-032-1383), ZrC (00-035-0784), HfC (00-039-1491), VC (01-073-0476) and NbC (00-038-1364) carbides. However, attending to Fig.1b, which is a magnification in the 2θ range of 31° - 43° , it is possible to corroborate that the position of the XRD peaks does not match exactly with that of the single carbides. Therefore, they correspond, in fact, to different complex solid solution carbides (as usual observed by MSR-route from mixtures of different elemental

transition metals and graphite [23]), but not to the single (TiZrHfVNb)₅ HEC expected.

As opposite, when the milling process was carried out at lower energetic conditions (*Diffusion-route* sample) by decreasing the diameter of milling balls and, consequently, the impact energy, the XRD pattern (Fig.1a) showed the formation of a single face centred cubic phase (fcc) with the *Fm-3m* space group symmetry, analogous to the abovementioned single carbides. The presence of any other secondary phase containing any of the raw elements was not observed. Only, a slight peak at approximately 44.7° (2θ) was detected that could be assigned to the (110) crystallographic plane of the ferrite (α-Fe). This element, coming from the milling media, is the consequence of the long milling time employed (50 h). Anyway, the low intensity of this peak suggests a low Fe contamination. Despite the long milling time employed, the low spinning rate used (300 rpm), together with the presence of an optimal lubricant, such as graphite, prevents a high Fe contamination from the milling media. This aspect was also corroborated in a previous work [24].

The interplanar distances and the lattice parameter determined by the XRD peak refinement for the fcc phase are shown in table 1. The obtained value of 0.450 nm is in concordance with the value calculated by assuming the Vegard's law [25] (0.449 nm, table 1) for the hypothetical (TiZrHfVNb)₅ from the lattice parameters of single carbides: TiC (0.433 nm), ZrC (0.469 nm), HfC (0.464 nm), VC (0.417 nm) and NbC (0.447 nm). In addition, the magnification of the XRD pattern between 31° and 43° (2θ) clearly showed that the XRD peaks corresponding to the (111) and (200) crystallographic planes of the fcc phase are perfectly symmetrical. Therefore, it can be concluded that this fcc phase synthesised at low temperature is the expected (TiZrHfVNb)₅ HEC

By other hand, the large broadening of the XRD peaks suggests a nanostructured character of the synthesized HEC. An average crystal domain size (D) of 2.5 nm was determined by the Williamson-Hall (W-H) method [26], corroborating this aspect. In addition, the microstrain (ϵ) determined by the same W-H method was 4.5 %. These low D and high ϵ values are direct consequence of the long milling time required to complete the formation of the $(\text{TiZrHfVNb})\text{C}_5$ HEC by a conventional mechanochemical diffusion route. As opposite, the D and ϵ values determined for the complex carbides observed in the *MSR-route* sample were 29 ± 5 nm and 0.5 ± 0.1 %. These larger crystal domain size and lower microstrain values in comparison with the *Diffusion-route* sample are due to the MSR reaction that causes an increase in temperature and even the formation of a transient liquid phase [24].

To confirm the formation of a single $(\text{TiZrHfVNb})\text{C}_5$ HEC, the *Diffusion-route* sample was characterised microstructurally. The SEM images (Fig. 2) mainly show the presence of submicrometric particles and the EDS-SEM maps a homogeneous elemental distribution. In some areas of maps (marked in black square in Fig. 2), the presence of Fe coming from the milling media was detected. Semi-quantitative EDS analyses carried out on 30 random points of these maps revealed average atomic percentages of 10.6 ± 1.0 % at. Ti, 10.3 ± 0.4 % at. Zr, 9.1 ± 0.9 % at. Hf, 9.2 ± 1.2 % at. V, 10.3 ± 1.2 % at. Nb and 50.5 ± 2.3 % at. C. These values agree with the expected equiatomic composition for the $(\text{TiZrHfVNb})\text{C}_5$ HEC.

A representative TEM image of the *Diffusion-route* sample is shown in Fig. 3. A heterogeneous particle size distribution and the presence of agglomerates, below 100 nm and up to 300 nm, are observed. However, the fact that the corresponding SAED pattern (Fig. 3) is formed by diffuse rings, instead of discrete points, suggests that the particles are formed by nanocrystalline domains, in agreement with the XRD results.

1 All the electron diffraction rings and their interplanar distances correspond to the
2 crystallographic planes of the single fcc phase (table 1). By using the plane (200) as
3 reference, the lattice parameter determined (0.450 nm) is in total agreement with the
4 calculated by XRD (also in table 1).
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10 Fig. 4 shows some HRTEM images performed in different areas of the
11 *Diffusion-route* sample, in which some oriented nanocrystalline domains (around 5 nm)
12 with interplanar spacings, belonging to the (111) and (200) planes (0.260 and 0.228 nm,
13 respectively) of the fcc structure, are displayed. In this case, the Fast Fourier Transform
14 (FFT) carried out on the HRTEM image corroborated the fcc structure, attending to the
15 reflection observed, again the (111), (200) and (220) crystallographic planes. The
16 corresponding interplanar distances determined are also displayed in table 1. In
17 addition, due to the high milling time required, some amorphized areas between the
18 nanodomains were detected, as can be observed in Fig. 4.4.
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32 Finally, EDS maps were carried out in HAADF-STEM mode on a group of
33 agglomerated particles (Fig. 5). Here, a high level of homogeneity for the different
34 transition metals, i.e, the Ti, Zr, Hf, V and Nb, is observed at the nanoscale, confirming
35 the synthesis of the anticipated (TiZrHfVNb) C_5 HEC.
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45 CONCLUSIONS

46 An stoichiometric (TiZrHfVNb) C_5 High Entropy Carbide was successfully
47 synthesized by a mechanosynthesis method, from elemental transition metals and
48 graphite powders as raw materials, consisting in the simultaneous metal alloying and
49 carbon diffusion into the alloy structure. It was crucial the use of low energetic milling
50 conditions and the stabilisation of the transition metals by alloying to inhibit the usual
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MSR exothermic reaction that produces a mixture of complex carbides with an heterogeneous chemical composition.

This mechanosynthesis route for HECs was carried out at room temperature, in contrast to the usual high temperature methods based on reactive sintering processes from the mixture of single carbides. This allows that HECs can be obtained in a powder form, with a nanometric character and a minimum energy requirement. This is a clear advantage to develop potential composite materials based on HECs by powder metallurgy processes.

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FIGURE CAPTIONS.

Figure 1. a) XRD patterns of *MSR-route* and *Diffusion-route* samples. b) Magnification of the XRD patterns of the *diffusion-route* sample in the 31–43° 2 θ range showing the (111) and (200) lines of the single fcc phase and the set of different complex carbides for the *MSR-route* sample. (●)TiZrHfNbC₅ High Entropy Carbide; (a, b, c, d e) Different complex carbides; (□) α -Fe; Continuous lines: the (111) and (200) reflections for the TiC, ZrC, HfC, VC and NbC single cabides.

Figure 2. SEM image and EDS-SEM mappings for the *Diffusion-route* sample. Colours: Red=Titanium; Green=Zirconium; Purple=Hafnium; Yellow=Vanadium; Light blue=Niobium; Black squares: α -Fe particles coming from the milling media.

Figure 3. Bright Field TEM and SAED images for the TiZrHfVNbC₅ High Entropy Carbide synthesized by the *Diffusion route*.

Figure 4. High Resolution TEM and the corresponding Fast Fourier Transform (FFT) images for the TiZrHfVNbC₅ High Entropy Carbide synthesized by the *Diffusion-route*. Numbers of each HRTEM images correspond to the magnification areas marked in the main TEM image.

Figure 5. High-angle annular dark-field (HAADF) image and EDS-mappings for the TiZrHfVNbC₅ High Entropy Carbide synthesized by the *Diffusion-route*. Colours: Red=Titanium; Green=Zirconium; Purple=Hafnium; Yellow=Vanadium; Light blue=Niobium.

TABLE CAPTIONS.

Table 1. Interplanar distances and lattice parameters for the single (TiZrHfVNb)C₅ synthesized by the *Diffusion-route*.

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Table 1. Interplanar distances and lattice parameter for the single (TiZrHfVNb)C₅ synthesized by the *diffusion-route*.

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