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Production of a Reinforced Refractory Multielement Alloy via High-Energy Ball Milling and Spark Plasma Sintering

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Abstract: Refractory high entropy alloys have shown potential to be developed as structural materials for elevated temperature applications. In the present research, the multielement alloy Fe2TiVZrW0.5 was produced by high-energy ball milling of elemental powders in the air to promote the formation of reinforcing oxide and nitride particles followed by spark plasma sintering consolidation. The sintering temperature was optimized to achieve a full-density material that was characterized from the microstructural and mechanical points of view. Hardness and KIC were measured in the as-sintered condition as well as after thermal treatment at 1100 °C. TEM observations showed the presence of a fine distribution of ZrO_2 and Ti(V)-N in the microstructure mainly constituted by the bcc Fe-V and Fe-V-W phases. The fine distribution of ceramic particles in a metallic multielement matrix is responsible for the consistent hardness and thermal stability of this alloy.

Keywords: refractory high entropy alloys; ZrO_2; high-energy ball milling; mechanical alloying; spark plasma sintering

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1. Introduction

Among the different families of HEAs, refractory ones show very interesting properties. Refractory high-entropy alloys (RHEAs) contain at least four of the nine refractory elements: Cr, Hf, Mo, Nb, Ta, Ti, V, W, and Zr, and have outstanding mechanical strength at extremely high temperatures. They generally have bcc microstructures constituted by elements that have this crystal structure [1,2]. High interest and a great number of studies have recently focused on this class of alloys [1,3–8]. They exhibit remarkable mechanical properties up to 1000 °C and above, and can therefore be considered a valid substitution for Ni-based superalloys as new high-temperature structural materials [9–13]. Refractory HEAs can possess either a single-phase bcc/B2 structure or multi-phase structures in which some intermetallic compounds are dispersed in the bcc/B2 matrix [14–16]. For the production of HEAs, mechanical alloying through a high-energy ball milling process can be used [11,17–21] since the high-energy ball–powder collisions enable the alloying effect among different powders, together with reducing the grain size. Moreover, using the powder metallurgy route, all the problems related to casting (segregations, dendritic microstructure, porosity) can be avoided. To keep the grain size as fine as possible, which ensures high mechanical strength, Spark Plasma Sintering (SPS) can be used to consolidate the powders. SPS is a field-assisted sintering technique similar to conventional hot pressing. However, instead of external heating, a pulsed direct current flows through a graphite die and two graphite punches, which contain the powder, whilst mechanical uniaxial pressure is applied. On increasing temperature under a small pressure (the minimum required to establish the electrical contact between punches and powder), densification is progressively promoted by rearrangement of the powder particles, localized deformation at the contact points, and bulk deformation of the particles [22]. SPS is a suitable method to sinter milled powders since it does not require long times at high temperatures, which could delete the refining effect obtained through the milling process. Therefore, SPS is a consolidation technique that is used for sintering milled HEA powders since it works with different classes of materials, leading to homogeneous microstructures and high densification in short times [23–26]. The application of the pressure is important to obtain a suitable densification of the compact during the sintering cycle and it was seen that it is more effective if it is applied after powder degassing when the powder particles start to plastically deform [27,28].

One of the main issues concerning materials prepared via ball milling is that they are very sensitive to process conditions (milling type, energy input, type and amount of process control agent, atmosphere, etc.). Specifically, the role of the milling atmosphere is considered of main importance. Several authors have investigated the influence of the milling atmosphere on the formation of secondary phases, on the powder refinement, and on the microstructural evolution of the milled powders [11,17,29–34]. In particular, they have studied the effect of oxygen and nitrogen uptake in the case of milling in air, considering the oxygen adsorption not as a contamination, but as a source of oxides, together with the process control agent and the oxide layers of the initial powders. The intentional oxygen uptake, leading to the formation of oxides, was first developed by Benjamin [35] in the preparation of oxide-dispersion-strengthened superalloys, using a sealed air atmosphere in an attritor mill. Other authors reported that mechanical milling in air promoted the formation of oxides, nitrides, and oxynitrides uniformly dispersed into a metal matrix [11,17,30–34,36]. These compounds are not necessarily harmful to the alloy system since they can contribute to the material dispersion strengthening leading to higher hardness and strength. Moreover, it should be considered that milling in the air is easier and cheaper than using a protective atmosphere; therefore, it is promising for industrial applications.

In the present investigation, powder milling in the air was used to produce a multielement alloy composed of Ti, V, Zr, W, and Fe to take advantage of this milling atmosphere to promote the formation of dispersed reinforcing oxide and nitride particles. Milled powder was spark plasma sintered and characterized in terms of microstructure, hardness, and fracture toughness.

2. Materials and Methods

Five initial high-purity powders (Fisher Scientific, Darmstadt, Germany) were used to produce the alloy Fe2TiVZrW0.5. The particle size, amount % in weight, and atomic fraction of the initial powders are summarized in Table 1. W powders used have a very small particle size to promote a fine W dispersion into the alloy since in preliminary laboratory experiments it was seen that bigger particles do not allow a complete dissolution of W, even after a prolonged milling time. For the same reason, the alloy composition was not designed in equiatomic proportion (0.2 atomic fraction of each element) but W was reduced to a lower amount, correspondingly increasing the amount of Fe.

Table 1. Initial powders.

Element	Particle Size (μm)	Purity Level (%)	Weight (wt.%)	Atomic Fraction (-)	VEC (-)
Fe	<74	99.00	28.4	0.35	8
Ti	<149	99.90	12.2	0.18	4
V	<44	99.50	13.0	0.18	5
Zr	<44	99.50	23.1	0.18	4
W	0.6–0.9	99.95	23.4	0.1	6

According to the definition proposed by Yeh [37], the ideal configurational entropy of mixing of an alloy (S^{SS},ideal) is calculated with the Formula (1):

$$S^{SS,ideal} = -R\Sigma c_i \times \ln(c_i) \quad (1)$$

with c_i = atomic fraction of element i.

The S^{SS},ideal must be higher than 1.5 in order to have a high-entropy alloy. Calculation of S with the atomic fractions reported in Table 1 gives S = 1.511.

Another important parameter used to identify high-entropy alloys is the Valence Electron Concentration (VEC). It is used to predict the formation of solid solution phases. The empirical VEC rule was first proposed by Guo et al. [38,39] based on their experimental observation of around 20 multi-component systems such as AlxCrCuyFezMnNi, AlxCoyCrzCu0.5FevNiw, MoNbTaVW, and CoCrFeMnNi, etc. It was found that FCC is stable at VEC $\geq$ 8, BCC is stable at VEC $\leq$ 6.87, and a mixture of FCC and BCC phases exists at 6.87 $\leq$ VEC $\leq$ 8. The calculation of the alloy VEC is based on the VEC values reported in Table 1, and it is carried out through Equation (2) [1]:

$$VEC_{(HEA)} = \sum_{i-1}^{n} C_i (VEC)_i \quad (2)$$

where C_i and $(VEC)_i$ are the atomic fraction and the VEC of element I, respectively. The present alloy has the following VEC:

$$\text{VEC} = \sum c_i \times \text{VEC}_i = 5.6 \quad (3)$$

indicating the formation of a bcc solid solution, which is the desired phase for refractory alloys [7,33].

The production of the alloy was carried out through high-energy ball milling and SPS. Ball milling was carried out in a Fritsch Pulverisette six-ball mill (Fritsch, Idar-Oberstein, Germany) with steel vials and balls. A rotation speed of 400 rpm and a ball-to-powder ratio (BPR) of 10 were used. Milling was stopped every 5 h in order to check the powder alloying and refinement. The milling process was carried out in the air to promote oxygen uptake and subsequent oxide formation. To avoid any powder overheating, each milling cycle comprised 20 min of milling followed by a 10 min pause.

Sintering was carried out through Spark Plasma Sintering (DR. SINTER 1050® SPS (Sumitomo Coal and Mining Ltd., Tokyo, Japan) at three different temperatures (1050 °C, 1250 °C, and 1350 °C) with a holding time of 5 min at the maximum temperature and applying a pressure of 30 MPa from 650 °C up to the end of the sintering cycle. The heating rate was 50 °C/min. During sintering, the temperature was monitored through a pyrometer recording the temperature from 570 °C.

Thermal treatment was carried out in a tubular laboratory furnace under Ar atmosphere for 1, 4, and 8 h at 900 °C and 1100 °C since the majority of refractory alloys exhibit interesting mechanical properties up to the range 800–1000 °C, showing marked decreases in properties above this temperature [40–42]. Moreover, 1100 °C is considered the highest application temperature of state-of-the-art Ni-based superalloys [43,44], which is a reference alloy category for the RHEAs.

A JEOL IT300 scanning electron microscope (JEOL Ltd., Akishima, Japan) operating at 20 keV accelerating voltage and equipped with an energy-dispersive X-ray spectroscope (EDXS) was used to examine the powders and the sintered alloys.

X-ray diffraction (XRD) analyses were carried out to evaluate the phase composition after milling and after sintering. The measurements were carried out with an ItalStructures IPD3000 diffractometer (GNR Analytical Instruments Group, Novara, Italy) using Co Kα radiation, and an Intel CPS120 detector (Inel, Artenay, France) that measured the signal concurrently throughout an angular range of 5°–120°. The acquired diffraction spectra were elaborated by Rietveld's method using MAUD software (Materials Analysis Using Diffraction [45].

In order to investigate the microstructure, the alloy was also observed with a high-resolution Scanning Transmission Electron Microscope (S/TEM), ThermoFisher Talos F200S (Thermo Fisher Scientific, Waltham, MA, USA) at the maximum accelerating voltage of 200 kV. The instrument is equipped with an EDXS system using two windowless Silicon Drift Detectors (SDD) with a total active area of 60 mm^2. Thin foils were prepared by starting from 1 mm thick alloy slices, followed by mechanical polishing on both sides down to a thickness of about 70 μm and surface roughness of 1 μm. Three mm discs were punched from the thin foil, and dimple-grinded in the central area down to 20 μm thickness.

The electron transparence was achieved through ion milling in a Leica RES102 apparatus (Leica Microsystems, Wetzlar, Germany) applying an accelerating voltage of 7 KV and a current of 2,6 mA, at a beam incident angle of 5 degrees.

Phase transformations occurring during the heating of the milled powders were studied by means of Differential Scanning Calorimetry (DSC) using a Netzsch STA 409 Luxx apparatus (Netzsch, Selb, Germany) under a protective flux of Argon (100 mL/min) in the chamber. The DSC heating was carried out at 10 °C/min up to 1350 °C, which is the maximum sintering temperature used.

The density of the sintered discs was measured by the water displacement method, and the oxygen content was measured by a LECO TC400 machine (LECO Corporation, St. Joseph, MI, USA). Image Analysis was carried out using the software Image J.

3. Results

3.1. Milled Powders

Powders milled for 5, 10, 15, and 20 h are reported in Figure 1a–d. Powders milled up to 15 h contained large particles formed by cold welding and plastic deformation of different powder particles. The big particles disappeared after 20 h of milling, when particle fragmentation prevails on cold welding [29]. Powder milling of 20 h is shown at a high magnification in Figure 2 with its EDXS. The amount of oxygen and nitrogen adsorbed during the milling process, measured through LECO analysis, are 5.5 %wt. and 6.1 %wt., respectively. As can be seen from Figure 2, powder particles are very fine (<5 μm). X-ray diffraction analysis on the same powder (Figure 3) indicates the presence of two cubic bcc structures, namely 1 and 2 on the XRD spectrum, with a large prevalence of phase bcc 1 (95%) with respect to phase bcc 2 (5%). Phase bcc 1 has a cell size parameter a = 3.178 Å and represents the most part of the alloy, phase bcc 2 has a lower cell size a = 2.905 Å and constitutes only 5% of the alloy. No oxides were detected by XRD thus suggesting that the oxygen detected by LECO is present as a supersaturated solid solution, created by the high-energy milling process, or, as reported by other authors, they are present as amorphous phases [30,46]. There were two sources of oxygen: the initial content of the elemental powders (less than 0.1 %wt. declared by each powder producer) and the atmosphere (air) under which milling was carried out.

3.2. Sintered Samples

3.2.1. Microstructural Analysis

The microstructures of samples sintered at 1250 °C and 1350 °C are shown in Figure 4. The specimen sintered at 1050 °C is not reported because of its excessively high amount of macro-porosity. The sample sintered at 1250 °C also shows the presence of some residual porosity, indicated by arrows in Figure 4a. The amount of porosity measured through Archimedes' method is 3.6 %vol. Instead, the alloy sintered at 1350 °C is almost full density (residual porosity evaluated through Image Analysis < 0.5 %vol.). The microstructure of both specimens, observed under a scanning electron microscope at high magnification (8000×) is very fine and constituted by a homogeneous mix of different light gray, dark gray, and white areas.