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Mechanical Alloying of W-Mo-V-Cr-Ta High Entropy Alloys

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Abstract. Recent years have seen the emergence of high-entropy alloys (HEAs) consisting of five or more elements in equi-atomic or near equi-atomic ratios. These alloys in single phase solid solution exhibit exceptional mechanical properties viz., high strength at room and elevated temperatures, reasonable ductility and stable microstructure over a wide range of temperatures making it suitable for high temperature structural materials. In spite of the attractive properties, processing of these materials remains a challenge. Reports regarding fabrication and characterisation of a few refractory HEA systems are available. The processing of these alloys have been carried out by arc melting of small button sized materials. The present paper discusses the development of a novel refractory W-Mo-V-Cr-Ta HEA powder based on a new alloy design concept. The powder mixture was milled for time periods up to 64 hours. Single phase alloy powder having body centred cubic structure was processed by mechanical alloying. The milling characteristics and extent of alloying during the ball milling were characterized using X-ray diffractiometre (XRD), field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). A single phase solid solution alloy powder having body-centred cubic (BCC) structure with a lattice parameter of 3.15486 Å was obtained after milling for 32 hours.

1. Introduction

High entropy materials have attracted the attention of researchers in recent years due to their exceptional combination of high strength, reasonable ductility, high temperature thermal stability, excellent hardness and mechanical properties. Development of conventional alloys during the last several decades were based on the concept of having one or two principal elements in to which other elements were added in small quantities for enhancing specific properties. In contrast, HEAs are alloys consisting of five or more elements in equi-molar or near equi-molar ratios with concentration of each element between 5 to 35 atomic percentages [1-4]. HEAs in general exist as simple solid solution having body-centred cubic (BCC) or face-centred cubic (FCC) structure rather than as intermetallic phases. The attractive mechanical properties exhibited by these alloys can be attributed to: (i) high configurational entropy during mixing of these elements, (ii) severe lattice distortion, (iii) sluggish diffusion and (iv) cocktail effect [5-13]. The commonly reported HEAs consist of combination of elements such as Fe, Co, Ni, Cr, Al, Cu, Ti and Mn, which generally crystallize with a face-centred cubic structure. The recent trend in development of HEAs is based on a new alloy design concept [14]. Recently HEAs consisting refractory metals such as W, Mo, V, Cr, Ti, Ta, Hf, Zr and Nb crystallize to form single phase BCC structure and posses excellent high temperature mechanical properties for use in high temperature applications [15-18] were reported. Senkov *et al*. reported WTaNbMo and WTaNbMoV high entropy alloys having high yield strengths of 405 MPa and 477

MPa respectively at 1600°C [19]. Guo *et al*. investigated the high yield strength property of refractory MoNbHfZrTi at elevated temperature [20]. Though HEAs exhibit attractive mechanical properties, processing of these alloys remains a challenge. Almost all the refractory HEAs reported were processed by vacuum arc melting technique [15-22] though few studies indicate processing by spark plasma sintering (SPS) technique [23]. The success of the use of HEAs for industrial applications will depend on the ease with which these materials can be processed in addition to the subsequent characterisation of the microstructure and mechanical properties. The high melting point and enthalpy of melting of refractory elements impose restriction on processing of HEA components by melting technique. Powder metallurgy technique appears to be a viable technique for processing of HEAs due to their inherent advantages. The advantages are mainly: (i) the alloy components are processed at temperature lower than the melting point of the constituent elements, (ii) elements with wide variation in melting points can be effectively mixed, (iii) uniform distribution of elements can be achieved without the formation of coring or segregation and (iv) close control of microstructure of the alloys.

The present work reports the processing and characterisation of a novel refractory HEA. Powder mixture with equi-molar ratios of W, Mo, V, Cr and Ta was prepared by mechanical alloying. The extent of alloying during ball milling of elemental powder mixture was investigated by various characterisation techniques and reported.

2. Experimental procedures

The starting materials used for the present study were elemental powders of tungsten (99.9 % pure), molybdenum (99.9 % pure), vanadium (99.5% pure), chromium (99.0 % pure) and tantalum (99.9% pure). 50 grams powder mixture having equi-molar ratio was ball milled in a mono ball mill (FRITSCH, Serial no - 06.2000/02725) with ceramic vial as the milling chamber. Zirconia balls of 10 mm diameter with ball to powder weight ratio of 6:1were used for the dry milling inside a ceramic vial. Milling was carried out at 250 RPM with a relaxation time of 15 minutes after each hour. Powders were ball-milled up to 32 hours. Sampling was carried out after 0.25 hours, 8 hours, 16 hours and 32 hours of milling. The details of the starting elemental metal powders are shown in Table 1.

Table 1. Specification of powders

Elements	Purity	Size	Source
Tungsten	99.0%	325 mesh	Loba-chemie
Molybdenum	99.9%	150µm	Sigma-aldrich
Vanadium	99.5%	325 mesh	Sigma-aldrich
Chromium	99.0%	60-100 mesh	Loba-chemie
Tantalum	99.9%	60-100 mesh	Sigma-aldrich

The milled powders were analyzed using X-ray diffractometer(XRD), Field emission scanning electron microscope (FESEM) attached with energy dispersive X-ray spectroscope (EDS) and field emission transmission electron microscope (FETEM). XRD analysis was carried out using Rigaku make model: TTRAX-IIIXRD set up with Cu-kα radiation (λ=1.540Å) operating at 50 KV/100mA. Scanning was carried out for 2θ angles in the range 20° to 100° at scan rate of 0.067°/second with step size of 0.02°. The crystal structure was analysed and the lattice parameter of the milled powder was determined. The FESEM used was of Zeiss, model: Sigma. FETEM was of JEOL, model: JEM-2100F, operated at 200 kV.

3. Results and discussions

Figure 1 shows the XRD pattern of the powder mixture milled for various time periods. The XRD pattern of the powder milled for 0.25 hours shows the reflections from planes corresponding to the starting elements viz. Ta, W, Cr, V and Mo. The high intensity of the peaks corresponding to these elements decreased after milling for 8 hours. Analysis revealed increase in the peak width indicative of

decrease in crystallite size during the milling process. The XRD pattern obtained for powder mixture milled for 32 hours revealed disappearance of few peaks corresponding to reflections from the planes of the starting metal powders. The peak width increased continuously with milling time. Milling of the powder mixture for 32 hours resulted in elimination of the reflections from the starting powders. Simultaneously appearance of new peaks was evident indicating the formation of new alloy. Analysis of the XRD pattern revealed the formation of single-phase body centred cubic structured alloy powder. Lattice parameter determination revealed that the peaks were corresponding to reflections from (110), (200), (211) and (220) planes with interplanar spacing of 2.227Å, 1.578Å, 1.286Å and 1.117Å. The lattice parameter for the BCC alloy powder after milling for 32 hours was determined to be3.15486 Å.

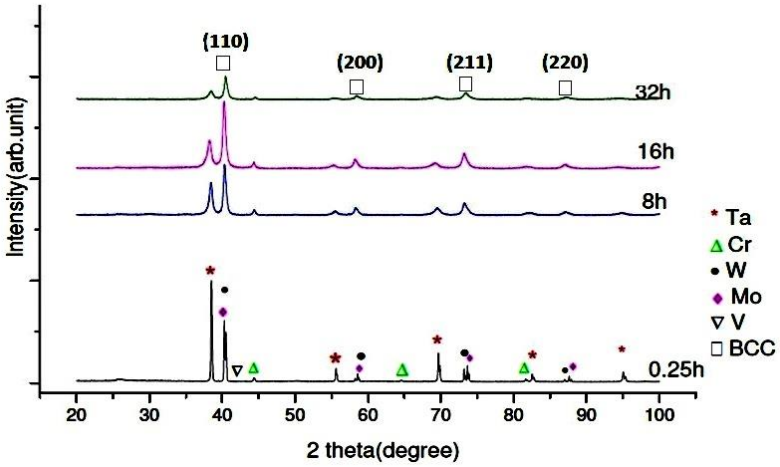


Figure 1.XRD patterns of W-Mo-V-Cr-Ta HEA milled with varying milling time.

FESEM images of milled powders are shown in Figure 2. The morphology of the powder mixture milled for 0.25 hours indicate a mixture of coarse and fine powder particles with irregular morphology. The coarse particles seen at the initial stages of milling is not evident after milling for 8hours (Figure 2 (b)) and indicates fracturing of the particles. The features also indicate cold welding of individual powder particles after 8 hours of milling. With further milling, the powder size decreases due to the continuous process of fracturing and cold welding of the constituents of the powder mixture. Milling for 32 hours resulted in fine powder mixture with almost spherical size (Figure 2(d)).

Figure 3 (a) to (c) shows the EDS spectrum of the powder mixture milled for different time periods. The quantitative analysis of the EDS spectrums presented in Table 2. The results reveal the following: (a) the powder mixture after milling for 8 hours showed only small amounts of tungsten and chromium; (b) subsequent milling of the powder mixture results in increase in atomic percentage of tungsten and chromium; (c) almost equi-atomic composition of the elements after milling for 32 hours. However vanadium content was slightly high with a concomitant decrease in chromium. During the milling process, tungsten and chromium are fractured and are embedded inside the tantalum and vanadium powders forming a composite powder. Due to the impact of the powders between the milling balls, Ta and W powders undergoes severe plastic deformation resulting in cold welding. The severe plastic deformation during milling results in the powder becoming more brittle. The brittle powders with further milling fractures and simultaneously gets re-welded. The process of cold welding, fracturing and re-welding continues till the individual elements are uniformly distributed at the atomic level leading to mechanical alloying.

Bright field and dark field TEM images and high resolution transmission electron microscope (HRTEM) image of the 32 hours milled powder are shown in Figure 4(a), (b), and (c), respectively. Analysis of the selective area electron diffraction (SAED) pattern shown in Figure 4(d) reveals BCC crystal structure for the 32 hours milled powder. From SAED pattern, the inter-planar spacings were

determined to be 2.21Å, 1.59Å, 1.29Å and 1.12Å corresponding to the (110), (200), (211) and (220) planes respectively. These values are in good agreement with the values obtained from XRD data. The results indicate a single phase BCC structured solid solution W-Mo-V-Cr-Ta high entropy alloy powder can be obtained by mechanical alloying.

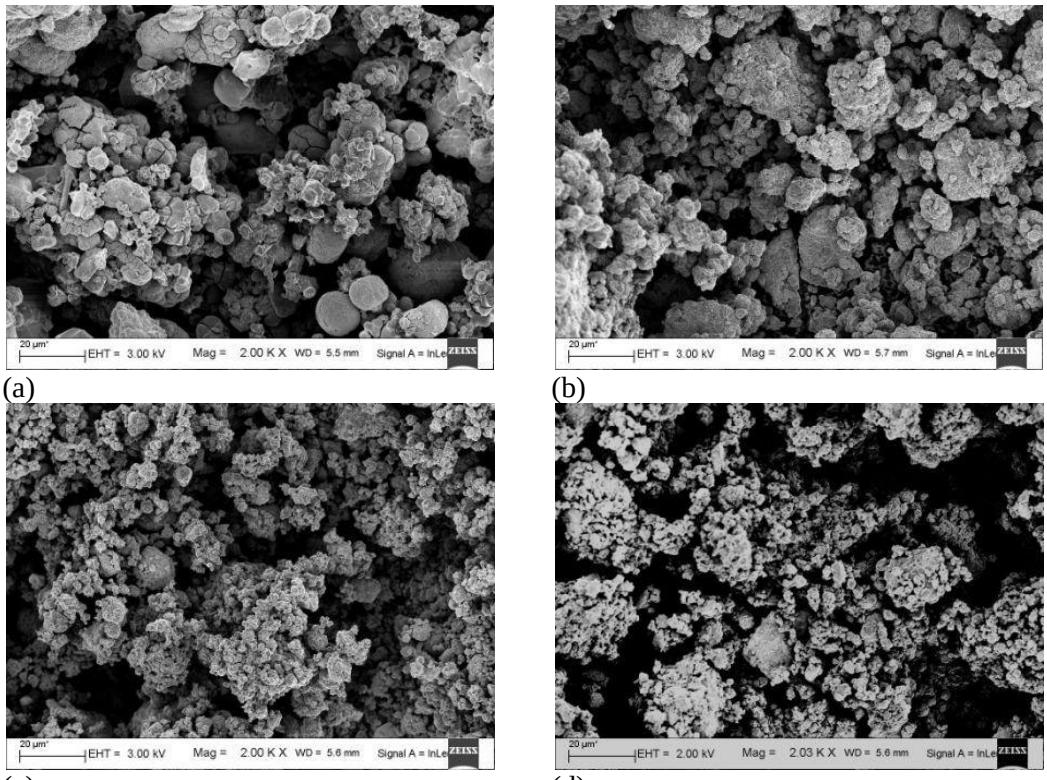
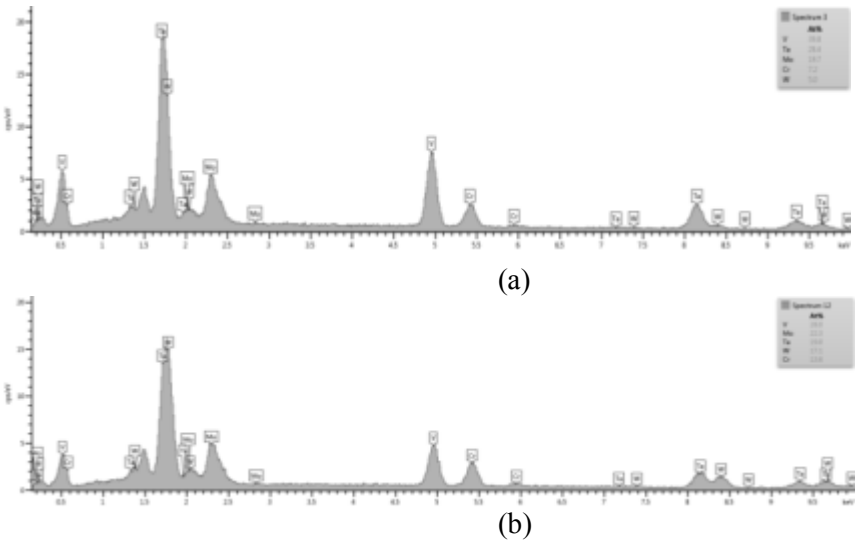
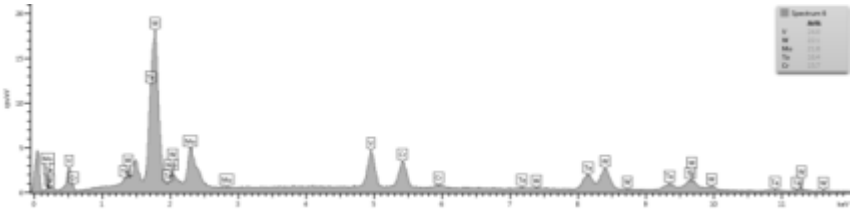


Figure 2.FESEM images of W-Mo-V-Cr-Ta milled powders after (a) 0.25hours (b) 8 hours (c) 16 hours and (d) 32 hours.



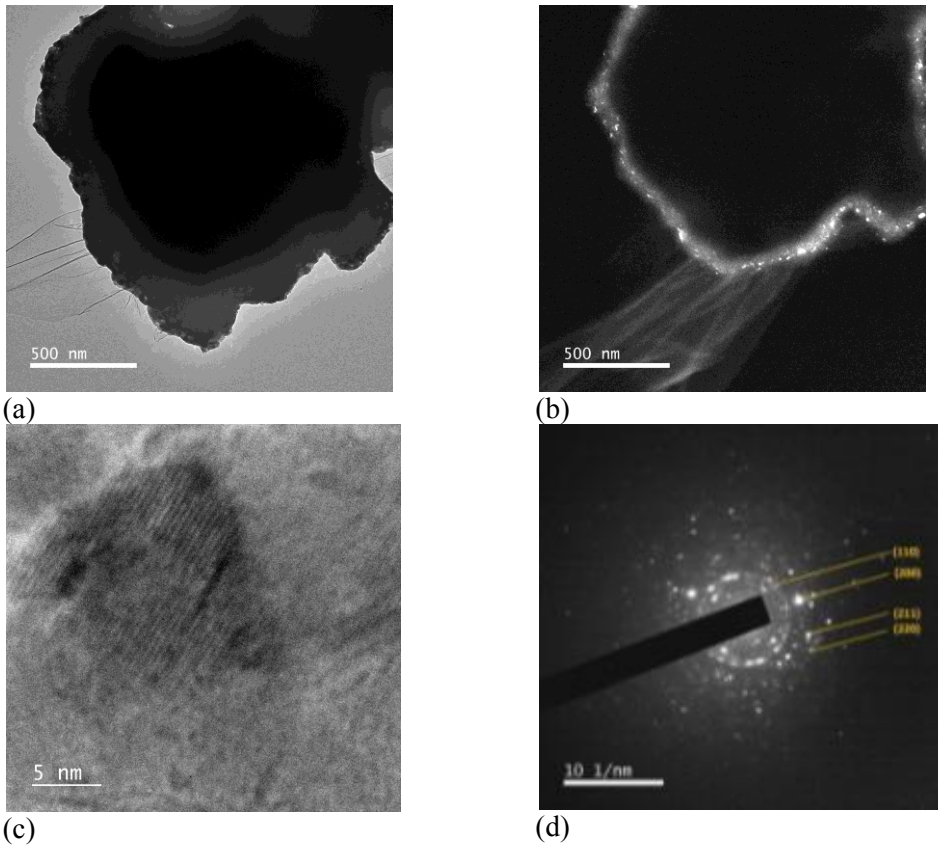


(c)

Figure 3.EDX of milled powder of (a) 8 hours (b) 16 hours and (c) 32 hours

Table 2. Chemical composition of powders determined by EDS

Milling Hour	W (at%)	Mo (at%)	V (at%)	Cr (at%)	Ta (at%)
8 hr	5.0	19.7	39.8	7.2	28.4
16 hr	17.1	22.3	28.0	13.6	19.0
32 hr	22.1	21.8	24.0	15.7	16.4



(a) (b)

(c) (d)

Figure 4.TEM images of 32 hours milled powder (a) Bright field (b) Dark field (c) HRTEM image (d) SAED pattern.

4. Conclusions

The conclusions of the present work are as follows:

(i) A novel refractory W-Mo-V-Cr-Ta high entropy alloy powder can be obtained by mechanical alloying technique.

(ii) 32 hours of milling of the elemental powders results in a single phase BCC structured HEA having lattice parameter of 3.15486 Å.

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