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Characterization Investigations of Mechanically Alloyed and Sintered W- 8 wt% VC-x wt% TiC- 1 wt% C (x=0, 2) Composites

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Abstract

Mechanical alloying (MA) processes were carried out in a Spex mixer/mill to synthesize W-8 wt% VC-x wt% TiC-C (x=0, 2) powders for 1 hour and 9 hours in argon atmosphere. Effects of milling duration and TiC addition on W-8 wt% VC-x wt% TiC-C (x=0, 2) composite powders and sintered samples were investigated. W-based composite powders were characterized with a combination of SEM and XRD analyses. MA'd powders were consolidated into green compacts by uniaxial cold press under 500 MPa. Then MA'd powders sintered at 1750˚C under hydrogen and argon atmospheres for 1h. The microstructural and mechanical characterizations of the sintered samples were carried out by using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analyses. Density measurements and hardness measurements of the sintered samples were also determined.

Keywords: Mechanical Alloying, W heavy alloy, W-VC-TiC Composites

INTRODUCTION

Refractory tungsten (W) matrix composites reinforced with carbide, boride and oxide particles are quite attractive for various structural applications and for some nuclear applications because of their superior physical, mechanical and microstructural properties such as high melting point, high elastic modulus, high thermal shock resistance and low coefficient of thermal expansion, at high temperatures and at severe service conditions [1-6]. Tungsten matrix composites possess good properties for nuclear applications especially as plasma-facing components (PFCs) due to the high melting point, low erosion, high thermal stress, high thermal conductivity and low swelling [5-8]. As dispersion strengtheners, refractory oxide, carbide and nitride phases, such as Y_2O_3, La_2O_3, ThO_2, ZrO_2, TiC, ZrC, HfC, TiN etc. have been mainly used to improve the mechanical properties of tungsten and its alloys [1, 9, 10].

In this study, vanadium carbide (VC) was used as a dispersion strengthener. VC possesses excellent high temperature strength, high chemical and thermal stability at high temperatures, high melting point (2830 °C) and high hardness (27.2 GPa) [1, 11] and it is largerly used in WC-Co hard materials as grain growth inhibitors [1, 12-15]. Titanium carbide (TiC) is used as a reinforcement in W composites not only because of its very high melting temperature (3067 ºC), high hardness, good corrosion resistance and good high temperature strength, but also the possibility of formation of a (Ti,W) C solid solution, which has better mechanical properties than TiC. Consequently, the composites will indicate much better mechanical properties [1, 16].

There exist no investigations pertaining to the W-8wt.%VC-1wt.%C W-8wt.%VC-2wt.%TiC-1wt.%C system in the universal literature. The number of publications on the effect of TiC on various properties of W-VC-C alloys are also very limited. For this reason, it is very worthwhile to investigate the W-VC-TiC-C composite system. Thus, the objective of the present study is to report the effects of VC and TiC additions and the effect of milling durations on the microstructural properties, mechanical properties and sintering behaviors of W.

MATERIALS and METHODS

W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites were used in the experiments. The composites were produced by mechanical alloying (MA) method at different alloying time values shown in Table 1. W (99.9% purity, 24 µm average particle size), as the matrix of the composite VC powders (99.9% purity, 16 µm average particle size), TiC powders (99.9% purity, 15 µm average particle size) were used as starting materials. Graphite (C) powders(99.9% purity, 21 µm average particle size) were used as process control agent (PCA). W, VC, TiC and C powders were blended to constitute the compositions of W-8 wt.%VC-1 wt.%C and W-8 wt.%VC- 2 wt.%TiC-1 wt.%C which were mechanically alloyed for 1h and 9h in a Spex™ DuoMixer/Mill 8000D with a speed of 1425 rpm was used. WC balls having a diameter of 6.35mm (1/4 inch) were used for milling in a tungsten carbide (WC) vial. The vials were sealed inside a Plaslabs™ glove box under Ar gas (99.995% purity) to avoid oxidation during MA. The ball-to-powder weight ratio (BPR) was 10:1. The composition of the sintered samples and MA times are given in Table 1. Mechanically alloyed powders were cold-pressed at a pressure of 500 MPa in an APEX™ 3010/4 uni-action hydraulic press. Pressed samples were sintered in a Linn™ high temperature hydrogen furnace at 1750 °C under inert Ar (introduced between room temperature to 800°C and 1100-1750 °C), and reducing H_2 (introduced between 800-1100 °C) gas flowing conditions for 1h (Figure 1).

Table 1. The compositions of W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites.

Materials ID	W (wt.%)	VC (wt.%)	TiC (wt.%)	C (wt.%)	MA duration (h)
VC-1	89	8	-	1	1
VC-9	89	8	-	1	9
VCTiC-1	91	8	2	1	1
VCTiC-9	91	8	2	1	9

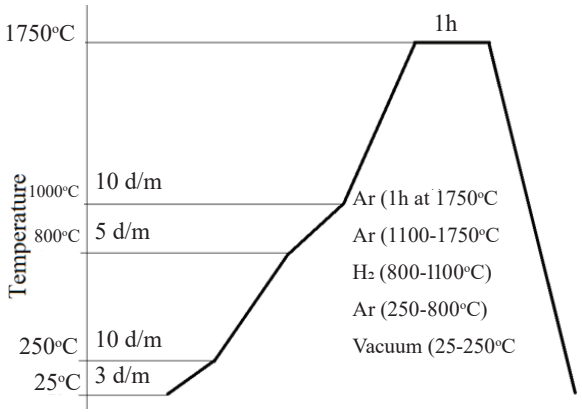
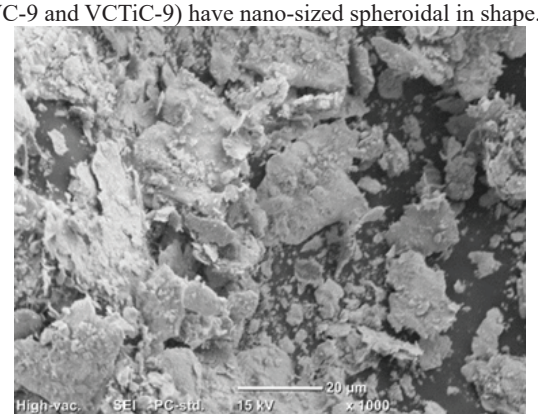


Figure 1. Sintering conditions of the pressed composites.

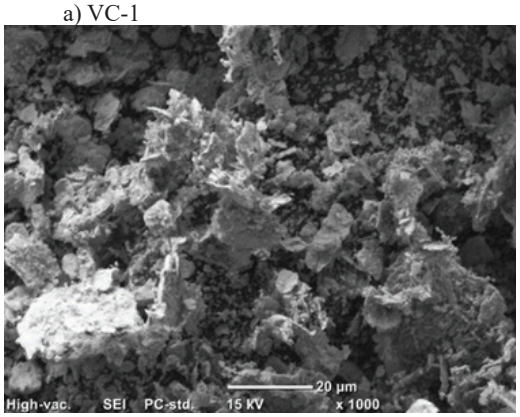
Microstructural characterizations were carried out using a Bruker™ D8 Advance XRD (Cu Kα Radiation) and a Jeol™JCM-6000 Benchtop Scanning Electron Microscope equipped with Jeol WX-36210DPP EDS apparatus. Bulk densities were measured in a Micromeritics™ AccuPcy II 1340 Gas Pycnometer.

RESULTS and DISCUSSIONS

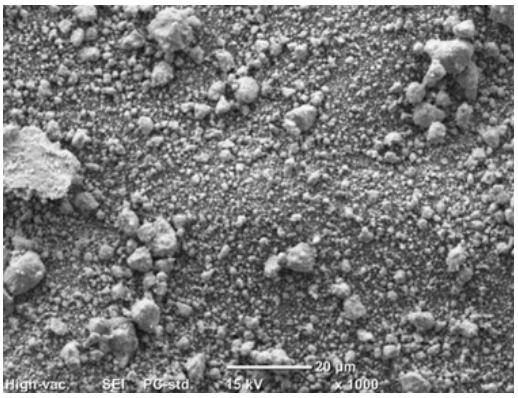
Mechanically alloyed (MA'd) powder properties and bulk properties were examined by using several characterization methods. First of all, SEM images of the MA'd powders were obtained. They are shown in Figure 2. After 1 h of MA, powders exhibit large irregular shapes, and their particle sizes decrease sharply after 9 h MA duration. While 1h MA'd powders (VC-1 and VCTiC-1) are large (micron sized) flat and shapes, 9h MA'd composite powders (VC-9 and VCTiC-9) have nano-sized spheroidal in shape.



a) VC-1



b) VCTiC-1



c) VC-9

d) VCTiC-9

Figure 2. SEM images of the W-8wt.%VC-1wt.%C and W-8wt.%VC-2wt.%TiC-1wt.%C 1h and 9h MA'd powder composites a) VC-1, b) VCTiC-1, c) VC-9, d) VCTiC-9.

As seen in Figure 3, only W peaks can be seen in XRD patterns because of very low weight percentage of carbide phases. Moreover, with increasing MA duration and TiC content, the peak intensities decreased and their full width half maximum (FWHM) values increased. Positions of the peaks shift to lower 2θ values. After 1 h MA duration, with the effect of increasing TiC content, the peak intensities of W decreased. On the other hand, V_8C_7 peaks are more clear for the VCTiC powder composites (Figure 4). It is clear that, due to the increasing MA duration and TiC content, the peak intensities of the solid solution phase decreased and their full width half maximum (FWHM) values increased. As seen in Figure 5, after 9 h MA duration, vanadium carbide phase is more clear for the VCTiC powder composite than VC powder composite. Furthermore, after 9 h MA duration, WC phase occurred, probably either C atoms came in to W lattices with increasing alloying time or WC contamination happened from the grinding media due to the high alloying duration.

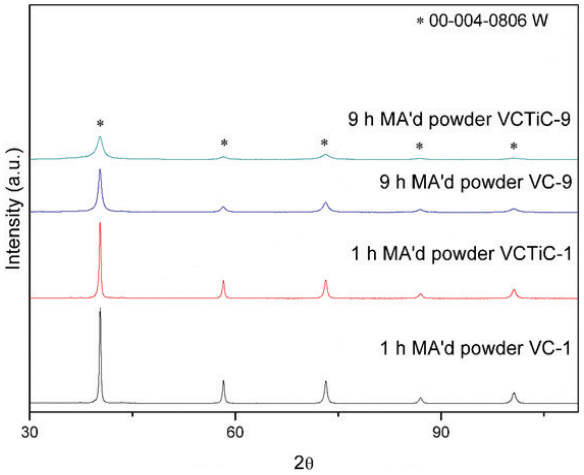


Figure 3. XRD patterns of MA'd W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C powders for 1 h and 9 h MA duration.

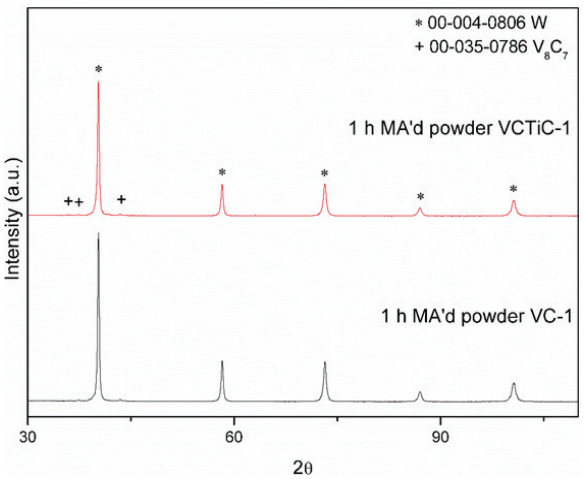


Figure 4. XRD patterns of MA'd W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C powders for 1 h MA duration.

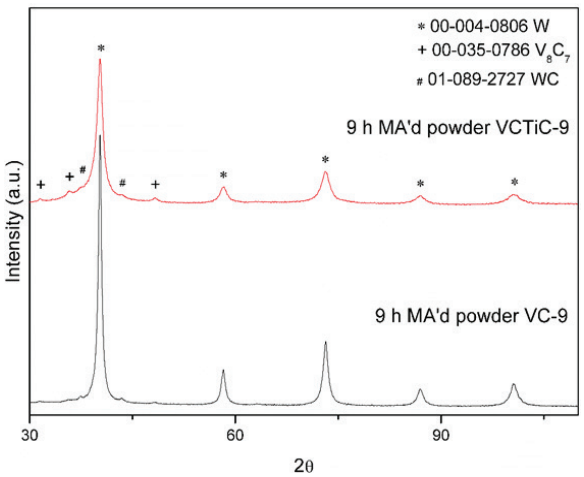
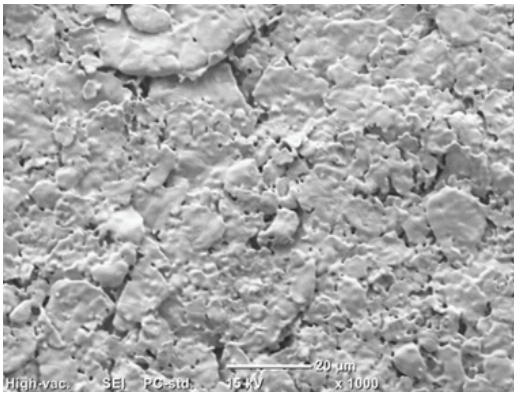
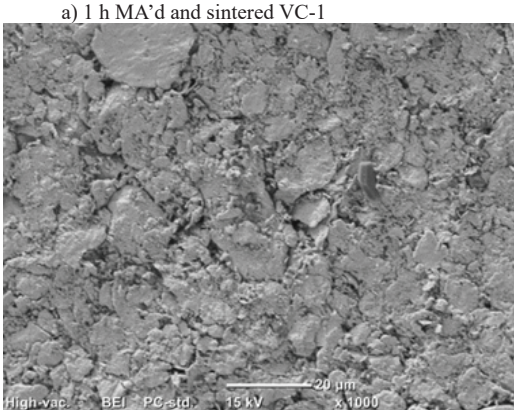


Figure 5. XRD patterns of MA'd W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C powders for 9 h MA duration.

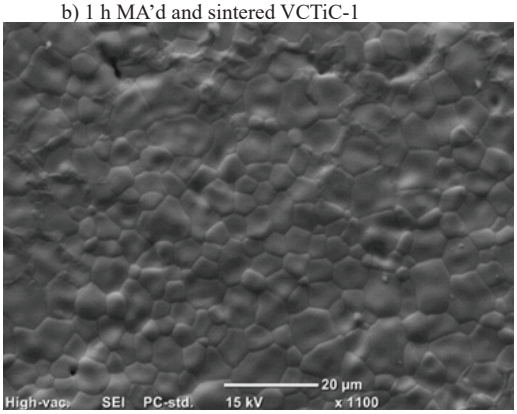
Figure 6 shows representative SEM micrographs of MA'd and sintered VC and VCTiC composites . It is evident from Figs. 6a and 6b, that 1 h MA duration is insufficient in sintering both VC and VCTiC sintered composites, since their microstructures exhibit irregular grain structure and intergranulate porosity and voids. On the other hand 9 h MA'd and sintered VC and VCTiC composites have sound and dense microstructures consisting of equaxed grains (Figs. 6c and 6d). Whereas the grain sizes vary between 5 and 12 µm for the 9 h MA'd and sintered VC-9 composite, those of the VCTiC-9 composite are much smaller (3-7 µm)



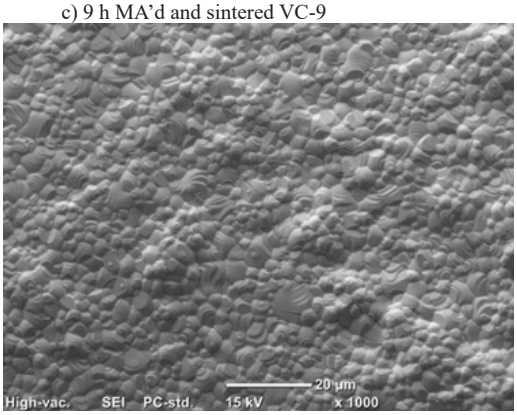
a) 1 h MA'd and sintered VC-1



b) 1 h MA'd and sintered VCTiC-1



c) 9 h MA'd and sintered VC-9



d) 9 h MA'd and sintered VCTiC-9

Figure 6. SEM/EDS analyses of MA'd and sintered W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites.

Figure 7, 8 and 9 show the X-ray diffraction (XRD) patterns of sintered composites. 1h MA'd and sintered composites have more sharp W peaks than those of the 9 h MA'd and sintered composites. Similar to the as-blended composite powders, free carbon and CV_2 phases are still present in 1 h MA'd and sintered composite VC samples, inferring that 1 h MA is insufficient for sintering. However, V_8C_7 phase emerges and C and CV_2 phases disappeared in the microstructures of 9 h MA'd and sintered VC composites.

As seen in Figure 9, 1h MA'd and sintered VCTiC composites have W, V8C7 and Ti phases. This shows that TiC began to decarburize in 1h. 9 h MA'd and sintered VCTiC composites have W, TiV, Ti, V_8C_7 and Ti-W solid solution phases, suggesting that, both vanadium carbide and titanium carbide phases were decarburized at 9 h MA duration, XRD analyses show that TiC was more decarburized than vanadium carbide, especially at high milling durations. W and TixW(1-x) peaks were overlap in X-ray diffraction analyses. This is supported by Ti atom diffusion into W lattice after decarburization of the TiC [3]. Thus it can be stated that C and Ti atom diffusion into W lattice increase with increasing milling time.

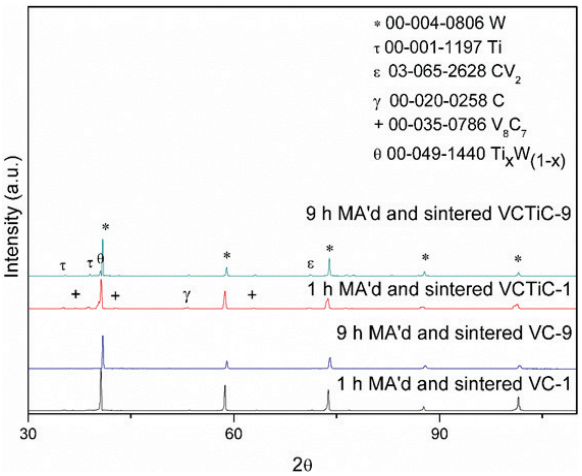


Figure 7. XRD patterns of sintered W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites for 1 h and 9 h MA duration.

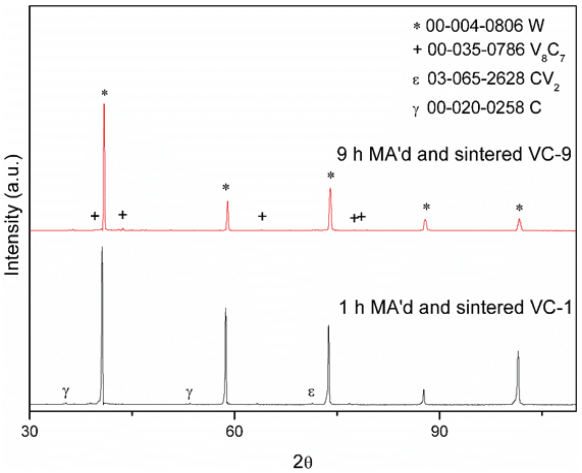


Figure 8. XRD patterns of sintered W-8 wt.%VC-1 wt.%C composites for 1 h and 9 h MA duration.

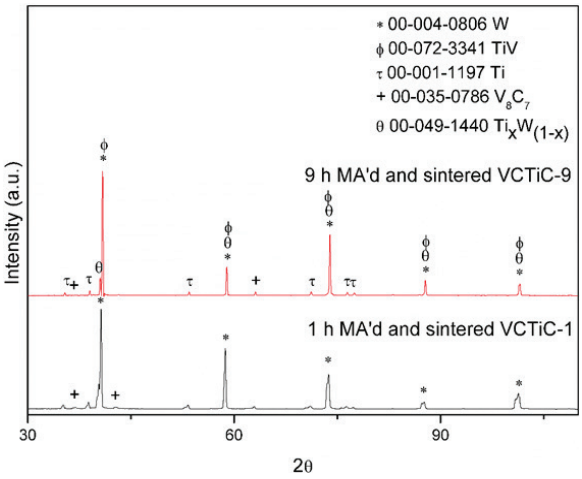


Figure 9. XRD patterns of sintered W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites for 1 h and 9 h MA duration.

Bulk density and relative density (%) values of the MA'd VC and VCTiC composites are given in Table 2. While the relative (%) density values of the 1 h MA'd and sintered VC and VCTiC composites are in unacceptable limits (78.69% and 68.13%), increasing MA duration, increases the relative densities for both composites. 9 h MA'd and sintered VC and VCTiC composites reached acceptable relative (%) density values, 96.5 % and 97.8 % respectively. On the other hand, W matrix composites that includes TiC reached maximum density of 97.8 % for 9 h MA duration.

Table 2. The densities of the mechanically alloyed W-8 wt.%VC-1 wt.%C and W-8 wt.%VC-2 wt.%TiC-1 wt.%C composites.

Material ID	Bulk Density	Relative Density (%)
VC-1	13.42	**78.69**
VCTiC-1	11,05	**68,13**
VC-9	16.45	**96.46**
VCTiC-9	15.86	**97.77**

Hardness is one of the major properties of tungsten alloys. Especially using carbide phases as grain growth inhibitors, hardness values usually increases [5, 6, 16]. Relative density and microhardness values of the VC and VCTiC bulk composites MA'd 1 h and 9 h are plotted in Figure 10. The minimum hardness values (1.21 GPa) was obtained after 1h MA'd and sintered VCTiC. Hardness values are proportional with the MA duration. The hardness values of the 9h MA'd and sintered VC and VCTiC are very similar to each other and 9h MA'd VCTiC has the maximum hardness value (7.6 GPa).

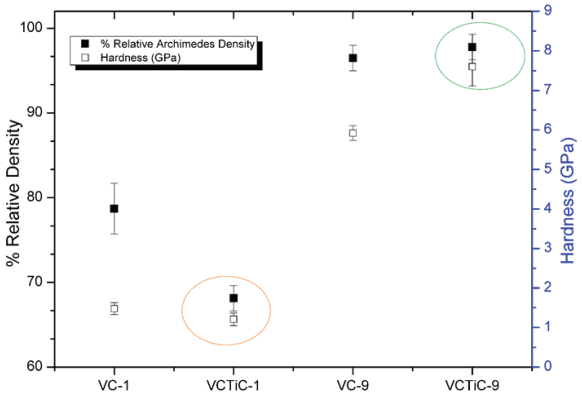


Figure 10. Microhardness and relative density values of the sintered VC and VCTiC composites.

CONCLUSIONS

On the basis of the results reported in the present investigation, the following conclusions can be drawn :

1- Adding VC and TiC increases amorphization rate of the MA'd W powders. The intensities of the characteristic the W peaks decreased with increasing alloying time.

2- XRD results show that, after 9h MA duration, VC phase is more clear at VCTiC powder composite. With increasing MA duration and TiC content, the W peak intensities decreased and their full width half maximum (FWHM) values were increased. The positions of the peaks shift to lower 2θ values.

3- After 1h MA time, the powders are large and exhibit large irregular shapes, and then their particle sizes were dramatically changed after 9 h MA duration. After 9h MA duration , WC phase occurred, probably either C atoms came in to W lattices with increasing alloying time or WC contamination happened from the grinding media due to the high alloying duration.

4- 1h MA duration is insufficient for sintering at 1750 °C. as proven by the SEM and XRD investigations and hardness and density measurements.

5- 9h MA'd and sintered VCTiC composites have W, TiV, Ti, V_8C_7 and Ti-W solid solution phases, indicating that TİC and VC were partially decarburized.

6- Increasing MA time also increases the relative densities. 9h MA'd and sintered VCTiC composite the has the maximum relative density of 97.8%.

7- Adding 2wt.% TiC increases the hardness values. 9h MA'd and sintered VCTiC composite has the maximum hardness value of about 7.6 GPa.

Anknowledgements

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REFERENCES

[1] Coşkun, Selim, Aziz Genç, and M. Lütfi Öveçoğlu. "Synthesis of W-3 wt% Mn-2 wt% VC composites by high energy milling and sintering." Metals and Materials International 19.3 (2013): 533-541.

[2] Tejado E., P.A. Carvalho, A. Munoz, M. Dias, J.B. Correia, U.V. Mardolcar, J.Y. Pastor, The effects of tantalum addition on the microtexture and mechanical behaviour of tungsten for ITER applications Journal of Nuclear Materials, In Press, Accepted Manuscript, 2015

[3] Jahangiri, H., & Öveçoğlu, M. L. (2016). Determination of crystallite size, strain and solubility in mechanically alloyed W-xTi (x= 0.5, 1.0, 4.0 and 10.0 wt%) powder alloys. Materials Letters, 178, 193-196.

[4] Jahangiri, H., Sönmez, S., & Öveçoğlu, M. L. (2016). Influence of Milling Media on the Mechanical Alloyed W-0.5 wt. Ti Powder Alloy. Indian Journal of Materials Science, 2016.

[5] Zibrov, M., Mayer, M., Gao, L., Elgeti, S., Kurishita, H., Gasparyan, Y., & Pisarev, A. (2015). Deuterium retention in TiC and TaC doped tungsten at high temperatures. Journal of Nuclear Materials, 463, 1045-1048.

[6] Tuğrul, A. B., Demir, E., Yılmaz, O., Sönmez, S., Öveçoğlu, M. L., & Büyük, B. (2016). An Investigation on the Mass Attenuation Coefficients of W-VC-C and W-VC-TiC-C Composites for Gamma Radioisotopes. Acta Physica Polonica A,129(4), 724-727.

[7] Rieth, M., Boutard, J. L., Dudarev, S. L., Ahlgren, T., Antusch, S., Baluc, N., ... & Domain, C. (2011). Review on the EFDA programme on tungsten materials technology and science. Journal of Nuclear Materials, 417(1), 463-467. Buyuk B., Tugrul A.B., Comparison of Lead and WC-Co materials against gamma irradiation. Acta Physica Polonica A, Vol.125, pp423-425, (2014).

[8] Lee, K. H., Yoon, J. K., Lee, J. K., Doh, J. M., Hong, K. T., & Yoon, W. Y. (2004). Growth kinetics of W 5 Si 3 layer in WSi 2/W system. Surface and Coatings Technology, 187(2), 146-153.

[9] Song, G. M., Wang, Y. J., & Zhou, Y. (2003). Thermomechanical properties of TiC particle-reinforced tungsten composites for high temperature applications. International Journal of Refractory Metals and Hard Materials, 21(1), 1-12.

[10] Pierson, H. O. (1996). Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps. William Andrew.

[11] Choi, K., Hwang, N. M., & Kim, D. Y. (2013). Effect of VC addition on microstructural evolution of WC–Co alloy: mechanism of grain growth inhibition.Powder Metallurgy.

[12] Luyckx, S., Osborne, C., Cornish, L. A., & Whitefield, D. (2013). Fine grained WC–VC–Co hardmetal. Powder metallurgy.

[13] Lin, C., Kny, E., Yuan, G., & Djuricic, B. (2004). Microstructure and properties of ultrafine WC–0.6 VC–10Co hardmetals densified by pressure-assisted critical liquid phase sintering. Journal of alloys and compounds, 383(1), 98-102.

[14] Lee, H. R., Kim, D. J., Hwang, N. M., & Kim, D. Y. (2003). Role of vanadium carbide additive during sintering of WC–Co: mechanism of grain growth inhibition. Journal of the American ceramic society, 86(1), 152-154.

[15] Suryanarayana, C., & Al-Aqeeli, N. (2013). Mechanically alloyed nanocomposites. Progress in Materials Science, 58(4), 383-502.