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MICROSTRUCTURAL CHARACTERIZATIONS OF SINTERED W-VC-C COMPOSITES AND THEIR ELECTROCHEMICAL BEHAVIOURS IN 1 M H_2SO_4 AQUEOUS SOLUTIONS

ABSTRACT

The effects of alloying duration on the microstructural and corrosion properties of Tungsten (W) matrix composites were investigated in this study. As blended W-2VC-1C (wt.%) powders were mechanically alloyed using a high energy ball mill at different milling times (1, 3, 6, 12 and 24 h) under inert Argon. Characterization of the sintered composites carried out using a scanning electron microscope (SEM) and X-ray diffractometer (XRD). Corrosion tests were performed in aqueous 1 M H_2SO_4 solutions to determine the effects of different alloying duration on the corrosion resistance of the composites.

Keywords: Mechanical Alloying, W Matrix Composites, VC, Corrosion, Polarization

SİNTERLENMİŞ W-VC-C KOMPOZİTLERİN MİKROYAPISAL KARAKTERİZASYONU VE 1 M H_2SO_4 SULU ÇÖZELTİSİ İÇERİSİNDEKİ ELEKTROKİMYASAL DAVRANIŞLARI

ÖZ

Bu çalışmada alaşımlama süresinin, tungsten (W) matrisli kompozitlerin mikro yapısal ve korozyon özelikleri üzerine olan etkisi incelenmiştir. Harmanlanan W-2wt.%VC-1wt.%C tozların mekanik alaşımlama işlemi farklı alaşımlama sürelerinde (1, 3, 6, 12 ve 24 s) Argon atmosferinde yüksek enerjili öğütücü kullanılarak yapılmıştır. Sinterlenen kompozitlerin karakterizasyon çalışmaları, taramalı elektron mikroskobu (SEM) ve X-ışınları difraktometresi (XRD) kullanılarak yapılmıştır. Korozyon testleri; değişik alaşımlama sürelerinin kompozitlerin korozyon direncini belirlemek için, 1M H_2SO_4 sulu çözelti içerisinde yapılmıştır.

Anahtar Kelimeler: Mekanik Alaşımlama, W Matrisli Kompozitler, VC, Korozyon, Polarizasyon

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1. INTRODUCTION

Tungsten (W) has the highest melting point of all elements except carbon. W is also among the heaviest metals (19.4 g/cm^3). W matrix composites reinforced with oxide, carbide and boride particles are quite attractive for different structural applications such as nuclear applications at high temperatures and at severe service conditions [1 and 4]. In this study, vanadium carbide (VC) was used as a dispersion strengthener. VC have excellent high temperature strength, high chemical and thermal stability at high temperatures, high hardness and high melting point [2 and 5] and it is largely used in WC-Co hard materials as grain growth inhibitors [2, 6 and 8]. In order to determine chemical properties of W-VC-C composites used to produce different alloying duration. For this purpose, W-VC-C composites were produced by mechanical alloying (MA) and conventional sintering. The effects of alloying duration on the corrosion behaviors of the sintered W-2VC-1C (wt.%) composites were investigated.

2. RESEARCH SIGNIFICANCE

Metal matrix composites (MMCs) are widely used in aerospace, defense, automotive industries and electronics/thermal management industries. Market demand will be over 350 USD million and 8.000 tons until 2019 according to market reports and industry experts. By the way, tungsten (W) matrix composites reinforced with carbide, boride or oxide particles are unique candidate quite attractive for different structural applications and for some nuclear applications at high temperatures and at severe service conditions. Fabrication and mechanical properties of the composites are well documented in literature. However, the corrosion behaviour and its microstructural response in the composites are immature and an emerging research topic [9 and 15]. Therefore, the effects of VC and TiC addition on the microstructural, mechanical and corrosion properties of W matrix composites were investigated in the presented study. Thus, the objective of the present study is to report the effects of VC and the effect of milling durations on the electrochemical and microstructural properties and sintering behaviors of W.

3. EXPERIMENTAL METHOD-PROCESS

W-2VC-1C (wt.%) composites were used in the experiments. The composites were produced by mechanical alloying (MA) method at different alloying times (1, 3, 6, 12 and 24 h). W (99.9% purity, 28 µm average particle size), as the matrix of the composite VC powders (99.9% purity, 8 µm average particle size) were used as starting materials. Graphite (C) powders (99.9% purity, 19 µm average particle size) were used as process control agent (PCA). The ball-to-powder weight ratio (BPR) was 10:1. WC balls having a diameter of 6.35 mm 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 process. W, VC and C powders were blended to constitute the compositions of W-2VC-1C which were mechanically alloyed (MA'd) in a Spex™ DuoMixer/Mill 8000D with a speed of 1425 rpm was used. The composition of the sintered samples and MA times are given in Table 1. MA'd powders were cold-pressed at a pressure of 500 MPa in an APEX™ 3010/4 uni-direction hydraulic press. Pressed samples were sintered in a Linn™ high temperature hydrogen furnace at 1750°C under inert Ar (introduced between room temperature to 600°C and 1100-1750°C), and reducing H_2 (introduced between 600-1100°C) gas flowing conditions for 1h.

Table 1. The composition of the studied W-2VC-1C (wt.%) composites

Materials ID	W (wt.%)	VC (wt.%)	C (wt.%)	MA duration (h)
WV1	97	2	1	1
WV3				3
WV6				6
WV12				12
WV24				24

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-36210 DPP EDS apparatus. Therefore, electrochemical investigations of the composites were checked with potentiodynamic scanning (PDS) technique in aqueous 1 M H_2SO_4 electrolyte at room temperature. An Ag/AgCl and platinum (Pt) wire electrodes were used as a reference and auxiliary electrode, respectively. Firstly, the specimens were immersed into the solution until reaching a steady open circuit potential (OCP) before the corrosion tests. After equilibration, polarization started at a rate of 1 $mV \cdot s^{-1}$. The PDS began at the cathodic over potential of -400 mV vs. E_{ocp} and the scan was stopped when the specimens reached an indicated anodic potential (>2V). The diameter of the corrosion test specimens was about 1 cm and all data have been normalized according to the surface area.

4. RESULTS AND DISCUSSIONS

Figure 1 show the XRD patterns of the sintered W-2VC-1C (wt.%)and mechanically alloyed for 1, 3, 6, 12 and 24 h. Only W peaks are detected in all composites because of the very low weight percentage of carbide phases. W characteristic peaks almost same 2Θ degree at all MA duration.

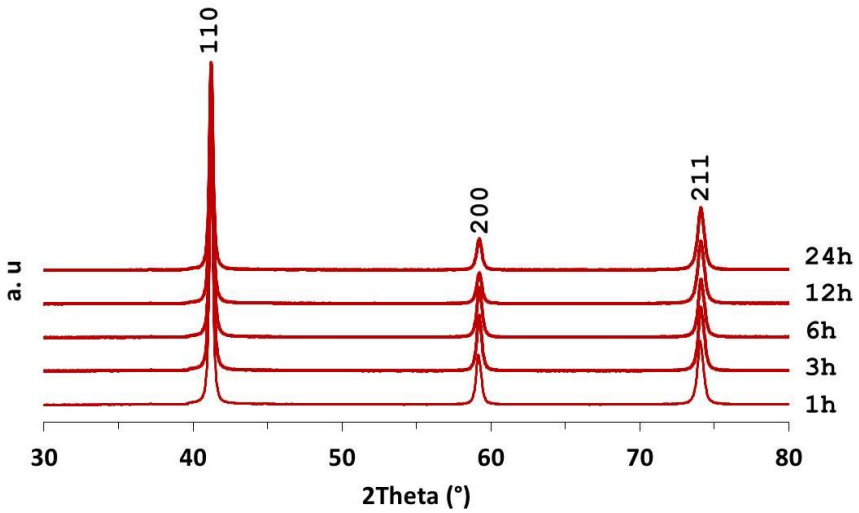

Figure 1. XRD analyses of the sintered composites

Figure 2 show representative SEM micrographs of MA'd and sintered composites before corrosion tests. SEM analyses used to figure out the VC phases dispersed in W matrix. It supported that increasing with milling time dispersed the carbide phases more homogenously. As seen in Figure 2, VC phase has dispersed very homogenously increasing with MA time for sintered W-2VC-1C composites. Increasing with MA time, porous structure is decrease for the sintered W-2VC-1C composites up to 12h. After 6 h milling time, equiaxed grains have been obtained and

can be clearly seen in Figure 2. Furthermore, it is evident from Figures 2a and b, that 1 and 3 h MA duration is insufficient in sintering for W-2VC-1C sintered composites, since their microstructures exhibit irregular grain structure and inter-granulate porosity and voids.

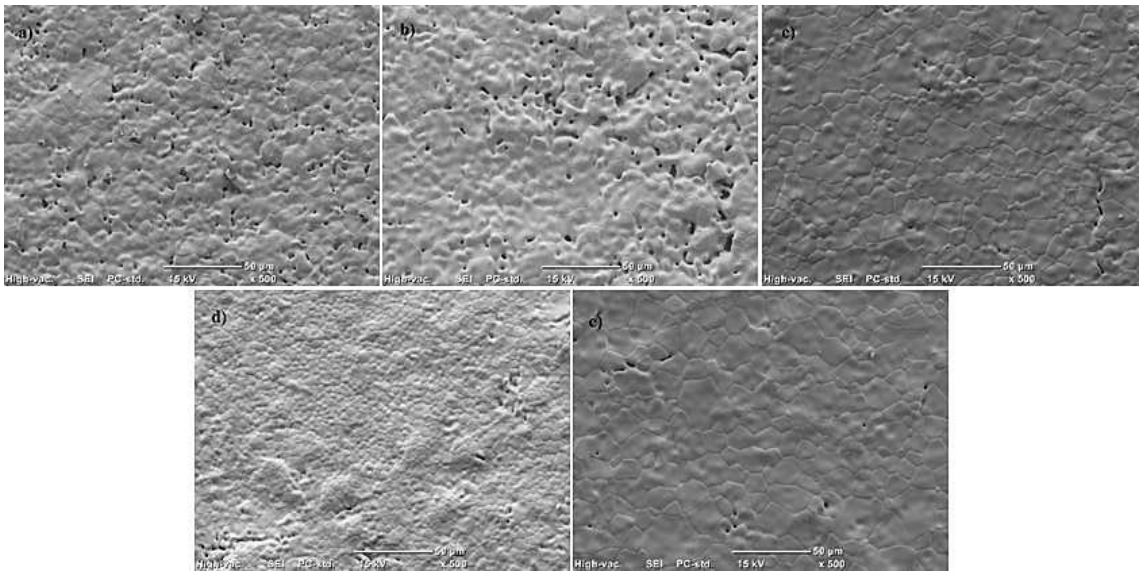

Figure 2. SEM micrographs of the sintered W-2VC-1C composites a)WV1, b)WV3, c)WV6, d)WV12 and e)WV24

On the other hand, after 6 h MA duration and sintering, WV6, WV12 and WV24 composites have dense microstructures consisting of equiaxed grains (Figures. 2c, d and e). Whereas the grain sizes vary between 7 and 25 µm for the WV6 and WV24, those of the WV12 are much smaller (3-15 µm). While pore sizes are decrease up to 6 h MA duration for sintered composites, after 6 h MA duration, increasing with MA duration pore sizes increase. The potentiodynamic polarization curves of the composites were given in Figure 3.

The figure shows the effect of milling time on the corrosion resistance of the composites reinforced with VC particles in 1 M H_2SO_4 acidic aqueous solution, as comparatively. According to the Figure 3, the PDS curves of the composites have the some regime and showed significant passivation behavior in 1 M H_2SO_4 solutions. Some fluctuations were observed in the passivity region of the composites, but any fluctuation was not seen for 24h mechanical alloyed composite. It is probably related to composite microstructure and grain sizes before the corrosion tests. According to Figure 2 c and e, 6 and 24 h MA'd composites have very similar microstructure but the grain size of the 24 h MA'd composite is more regular than 6 h MA'd composite. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) values of the composites calculated from the PDS curves are given in Table 2. It is well known that current density is directly related to electrode potential and it can provide more realistic results related to the electrochemical behavior of the composites. For example, maximum I_{corr} values measured the MA'd and sintered composite for WV24 as 47.8µA·cm^{-2} (Table 2), which is higher than that of 6 h MA'd and sintered composite (31.6µA·cm^{-2}). In other words, the corrosion resistance of the composite WV24 is lower than the others.

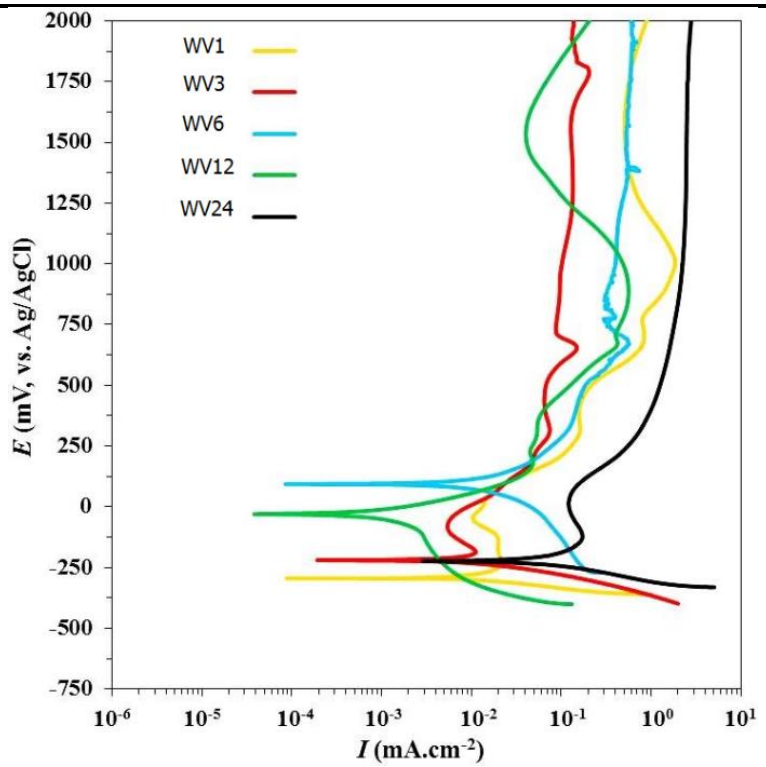

Figure 3. Potentiodynamic scanning (PDS) curves of the MA'd composites at different time in 1 M H_2SO_4 aqueous solutions

Table 2. The corrosion parameters of the MA'd and sintered composites calculated from PDS curves

Materials ID	MA Duration (h)	E_{corr} (mV)	I_{corr} (µA·cm^{-2})
WV1	1	-294	10.1
WV3	3	-220	8.7
WV6	6	94	31.6
WV12	12	-30	2.7
WV24	24	-223	47.8

Figure 4 presents Surface SEM images of the sintered composites exposed to 1 M H_2SO_4 aqueous solution after corrosion tests. Sintering processing alters both the bulk structure and the surface of a material, leading to changes in grain size and boundary density, orientation, and residual stress. These surface changes can have an impact on electrochemical behavior of the composites. It is well known that as much as noble potential and as low as possible current density is desired for corrosion protection. In addition, it was found that the pit size and number is proportional with corrosion current densities and milling time of the composites (Figure 4). As comparing the SEM images before corrosion tests (Figure 2), it is clear that corrosion behavior of the composites is influenced from milling time, porosities in the bulk structure and grain size.

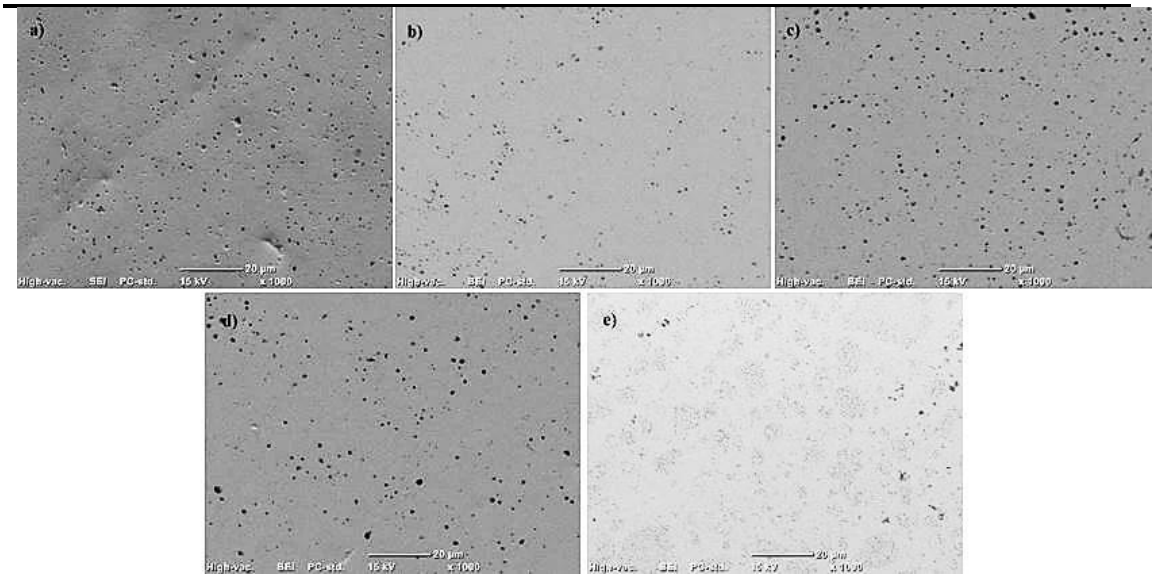

Figure 4. Surface SEM images of the sintered composites exposed to 1 M H_2SO_4 aqueous solutions after corrosion tests: a) 1 b) 3 c) 6 d) 12 and e) 24 h MA'd composites

5. CONCLUSIONS

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

- Only W characteristic peaks are detected in all composites because of the very low weight percentage of carbide and carbon phases. The same XRD results were obtained at before and after corrosion tests.
- Increasing with MA duration, porous structures are decrease for the sintered W-%2VC-%1C composites up to 6 h MA duration.
- While 1 h and 3 h MA duration is insufficient in sintering for WV1 and WV3 composites, WV6, WV12 and WV24 composites have dense microstructures consisting of equated grains.
- Sintering processing alters both the bulk structure and the surface of a material, leading to changes in grain size and boundary density, orientation, and residual stress. These surface changes can have an impact on electrochemical behavior of the composites.
- The corrosion resistance of the composite WV24 is lower than the others. At the same time WV6 is higher than the others with regard to corrosion potential.
- Corrosion behavior of the composites is influenced from milling time, porosities in the bulk structure and grain size.

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NOTICE

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REFERENCES

1. Tugrul, A.B., Demir, E., Yilmaz, O., Sonmez, S., Ovecoglu, M.L., and Buyuk, B., (2016). An investigation on the mass attenuation

coefficients of W-VC-C and W-VC-TiC-C composites for gamma radioisotopes. Acta Phys Pol A. 129(4):724-7.
2. Coşkun, S., Genç, A., and Öveçoğlu, M.L., (2013). Synthesis of W-3 wt% Mn-2 wt% VC composites by high energy milling and sintering, Metals and Materials Int. 533-41.
3. Miao, S., Xie, Z.M., Zhang, T., Wang, X.P, Fang, Q.F, and Liu, C.S., (2016). Mechanical properties and thermal stability of rolled W-0.5 wt% TiC alloys. Mat Sci Eng a-Struct. 671:87-95.
4. Veleva, L., Schaeublin, R., Battabyal, M., Plociski, T., and Baluc, N., (2015). Investigation of microstructure and mechanical properties of W–Y and W–Y_2O_3 materials fabricated by powder metallurgy method. International Journal of Refractory Metals and Hard Materials 50:210-6.
5. Choi, K. and Hwang, N.M., (2000). Effect of VC addition on microstructural evolution of WC–Co alloy: mechanism of grain growth inhibition. Powder Metallurgy 43(2):168-72.
6. Luyckx, S., Osborne, C., and Cornish, L., (2013). Whitefield D. Fine grained WC–VC–Co hardmetal. Powder metallurgy.
7. Lin, C., Kny, E., Yuan, G., and Djuricic, B., (2004). Microstructure and properties of ultrafine WC–0.6VC–10Co hardmetals densified by pressure-assisted critical liquid phase sintering. Journal of Alloys and Compounds. 383(1–2):98-102.
8. Suryanarayana, C. and Al-Aqeeli, N., (2013). Mechanically alloyed nanocomposites. Progress in Materials Science. 58(4):383-502.
9. Jiang, Y., Yang, J.F., Xie, Z.M., Gao, R., and Fang, Q.F., (2014). Corrosion resistance of W-Cr-C coatings fabricated by spark plasma sintering method. Surf Coat Tech. 254:202-6.
10. Jiang, Y., Yang, J.F., and Fang, Q.F., (2015). Effect of chromium content on microstructure and corrosion behavior of W-Cr-C coatings prepared on tungsten substrate. Front Mater Sci. 9(1):77-84.
11. Park, S.A., Kim, J.G., and Yoon, J.B., (2014). Effect of W, Mo, and Ti on the Corrosion Behavior of low-alloy steel in sulfuric acid. Corrosion. 70(2):196-205.
12. Ren, F.Z., Zhu, W.W., Chu, K.J., and Zhao, C.C., (2016). Tribological and corrosion behaviors of bulk Cu-W nanocomposites fabricated by mechanical alloying and warm pressing. Journal of Alloys and Compounds. 676:164-72.
13. Liu, X.Y., Xiang, Z., Niu, J.C., Xia, K.D., Yang, Y., and Yan, B., (2015). The corrosion behaviors of amorphous, nanocrystalline and crystalline Ni-W alloys coating. Int J Electrochem Sc. 10(11):9042-8.
14. Kuznetsov, V.V., Pavlov, L.N., Vinokurov, E.G., Filatova, E.A., and Kudryavtsev, V.N., (2015). Corrosion resistance of Cr-C-W alloys produced by electrodeposition. J Solid State Electr. 19(9):2545-53.
15. Habibi, M., Javadi, S., and Ghoranneviss, M., (2014). Investigation on the structural properties and corrosion inhibition of W coatings on stainless steel AISI 304 using PF device. Surf Coat Tech. 254:112-20.