

The Synthesis and Characterization of W- 1wt.% TiC Alloy Using a Chemical Method

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1. Introduction

The tungsten and its alloys have been used in many applications due to their excellent mechanical and thermal properties such as high melting point, high thermal conductivity, high strength at elevated temperatures, low sputtering yield in radiation environment and low tritium inventory [1-3]. Moreover, many researchers consider tungsten alloys as the most promising candidate for plasma facing components for future nuclear fusion reactors [4]. Nevertheless, the serious problems are discussed with tungsten such as low temperature embrittlement, high ductile-to-brittle transition temperature and low recrystallization temperature. It is known that the body centered cubic crystal structure of tungsten has almost no ductility [5,6]. Therefore, novel tungsten-based materials should be developed to overcome the problems stated above.

In the past few decades, many studies have demonstrated the dispersed second phase nano-particles in the tungsten matrix inhibit the grain growth and recrystallization, besides they improve the ductility and the irradiation resistance by hindering grain boundary sliding and stabilizing the microstructure [7]. La₂O₃, Y₂O₃, TiC or ZrC particles are usually considered as the second phase. However, some crucial issues should be solved such as the uniform distribution of these second phase particles and difficulty of the industrial mass production. By typical mechanical alloying and powder metallurgy, nano-particles tend to be agglomerated and concentrated at the grain boundaries due to the high surface energies introduced. Moreover, the milling process often produces detrimental phase by the wear of the milling equipment and media.

Xia et al. have firstly reported core-shell structured W/TiC using ammonium metatungstate ((NH₄)₆W₇O₂₄·XH₂O, AMT) and hydrochloric acid [7]. Nano-sized TiC particles are coated uniformly by

AMT precipitation formed by the addition of hydrochloric acid to the AMT solution. The core-shell structure particles were examined by TEM. In addition to this work, they have reported that use of Polyvinylpyrrolidone as dispersion agent to achieve better distribution. Also, L. Lou et al. have reported a use of ammonium paratungstate ((NH₄)₁₀H₂W₁₂O₄₂·XH₂O, APT) with oxalic acid to form core-shell structure instead of using AMT [2]. They have used spark plasma sintering as a consolidation method. The relative density achieved was 99.0%.

To achieve uniform distribution of TiC nano-particles, a wet chemical method is essential rather than typical mechanical alloying. Also, the use of the chemical method of alloying can be easily applied to the industry with cost-effective and environmental benefits.

Core-shell structure of W/TiC is a key technique in wet chemical method to achieve uniform distribution of TiC nano-particles. The confirmation of core-shell structure by transmission electron microscopy was subjected previously. On the other hand, rather than using only wet chemical method, core-shell structured W/TiC powder can be simply mixed with pure tungsten to achieve the uniform distribution of TiC nano-particles and to maintain mechanical properties. This combination method will benefit from the fabrication of alloys such as tungsten containing high entropy alloy.

In this study, nano-sized particles of W 10 wt.% TiC have been synthesized by a new method that is a combination of the wet chemical method and the 3D mixing method (more details about the method is discussed in the next section). For comparison purposes, two sample were prepared by two other different methods, these methods are the wet chemical method and the simple mixing method.

2. Experimental methods

2.1 Precursor synthesis, reduction, and sintering

Wet chemical method: 2.500g of oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) was dissolved in 600 ml of deionised water to form a clear solution, 0.050 g of TiC nano-sized particles (commercial powder, particle size about 50 nm, purity 99.9%, Alfa Aesar Korea) was added to the solution. The amount of TiC nano-powder was calculated by stoichiometry. The mixture was stirred for 30 minutes and the dispersion of TiC particles is supported by sonication to ensure that TiC particles are well distributed in the solution. 7.0280g of ammonium paratungstate (purity 99.9%, Alfa Aesar) was added to the solution. After stirring the solution for 2 hours, the W/TiC precursor was obtained by stirring and evaporating the mixture solution in phenyl methyl silicone oil bath at 165°C. The obtained powder was ground and then reduced by high purity hydrogen flow in a tube furnace at 800°C for 60 minutes. The resulting reduced powder was consolidated by Spark Plasma Sintering (SPS, Dr. Sintering SPS-515S, Japan). The powder was loaded in an electrically and thermally conductive graphite die with a diameter of approximately 13 mm at first and then under a uniaxial pressure of 50 MPa heated to 1800°C and hold for 3 minutes. For reference purposes in this paper, the sample that is prepared by this method is named as “WCM1”.

3D mixing: 0.100 g of TiC nano-sized particles and 9.000 g of tungsten powder (commercial powder, particle size <1.21 μm , Daegu Tek. Co) added into the plastic bottle and mixed in Turbula multi-directional mixer. Five millimeter diameter stainless steel balls were employed to break up agglomerates and mix the

powders. The mixed powder was sintered by Spark Plasma Sintering (SPS) at the same conditions used in the wet chemical method. The name of the sample prepared by this method is “3DM1”.

Wet chemical method + 3D mixing: the same procedure of wet chemical method was hired here, but the difference here is the amount of TiC that was 0.500 g, instead of 0.0500 g (10 times more), was used to synthesize W 10 wt.% (instead of 1 wt.%) TiC precursor. To obtain the W 1 wt.% TiC, 10% of the TiC precursor was mixed with pure tungsten powder for 3 hours so that the resulting powder W 1 wt.% TiC to match the previously discussed methods. The last step here is sintering, and it is exactly the same as the previous two methods with the same conditions, too. Finally, the resulting sample of this method is called “W3D1”.

2.2 Characterization

The crystal phases of each sintered samples were identified using X-ray diffraction (XRD) and the microstructures were characterized using Field-emission scanning electron microscopy (FE-SEM). Energy dispersive X-ray spectrometry (EDS) installed on SEM was used for the elemental analysis. The density of the sintered sample was measured by Archimedes principle. Vickers microhardness was measured with polished samples under 200 g loads and a dwell time of 20 s at room temperature.

3. Results

The microstructures of each fabrication method by FE-SEM were presented in Fig. 1 with the same magnifications for the comparison.

All three samples show full density up to 99 %. Vickers microhardness data shows 560

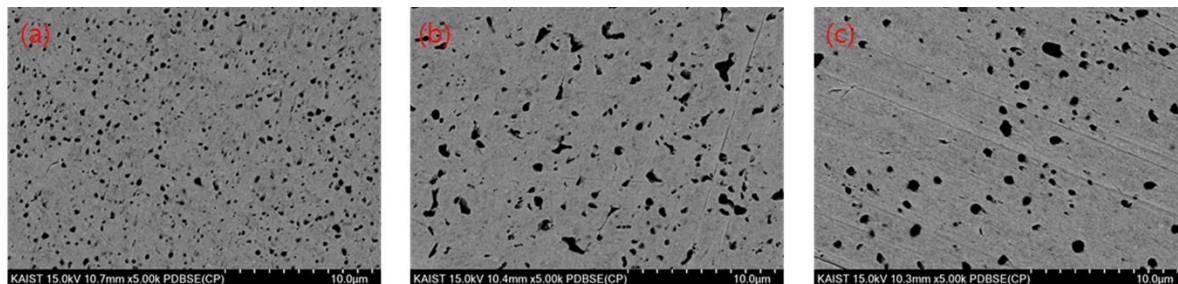


Fig. 1. FE-SEM image of SPS sintered samples of (a) Wet chemical method (WCM1) (b) 3D mixing (3DM1) and (c) wet chemical + 3D mixing (W3D1)

HV for 3DM1 and W3D1 samples and 701 HV for WCM1 sample. 3DM1 and W3D1 samples showed agglomeration of TiC particles with the particle size of few microns, while the distribution of nano-sized TiC particles was achieved with WCM1 sample.

4. Conclusion

Three samples of W – 1.0 wt.% TiC composites with the different fabrication methods were successfully developed. The combined method of the wet chemical method and 3D mixing showed small amount of agglomeration of TiC particles, however, the TiC particle sizes were smaller than 3DM1 sample. Since the WCM1 showed the better mechanical property, microhardness, the main future plan is to achieve the same or improved mechanical property of W3D1.

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Reference

- [1] P. Zhao, S. Wang, S.B. Guo, Y.X. Chen, Y.H. Ling, J.T. Li, Bonding W and W–Cu composite with an amorphous W–Fe coated copper foil through hot pressing method, *Mater. Des.* 42 (2012) 21–24.
- [2] X.Y. Tan, L.M. Luo, Z.L. Lu, G.N. Luo, X. Zan, J.G. Cheng, Y.C. Wu, Development of tungsten as plasma-facing materials by doping tantalum carbide nanoparticles, *Powder Technol.* 269 (2015) 437–442.
- [3] H. Kurishita, S. Kobayashi, K. Nakai, H. Arakawa, S. Matsuo, T. Takida, K. Takebe, M. Kawai, Current status of ultra-fine grained W–TiC development for use in irradiation environments, *Phys. Scr.* T128 (2007) 76–80.
- [4] J.W. Davisa, V.R. Barabashb, A. Makhankovc, L. Plochld, K.T. Slattery, Assessment of tungsten for use in the ITER plasma facing components, *J. Nucl. Mater* 258 (1998) 308-312.
- [5] H. Kurishita, S. Matsuo, H. Arakawa, T. Sakamoto, S. Kobayashi, K. Nakai, T. Takida, M. Kato, M. Kawai, N. Yoshida, Development of recrystallized W–1.1% TiC with enhanced room-temperature ductility and radiation performance, *J. Nucl. Mater.* 398 (2010) 87–92.
- [6] N. Farid, S.S. Harilal, O. ElAtwani, H. Ding, A. Hassanein, Experimental simulation of materials degradation of plasma facing components using lasers, *Nucl. Fusion* 54 (2014) 012002 (7 pp).
- [7] M. Xia, Q.Z. Yan, L. Xu, L.X. Zhu, H.Y. Guo, C.C. Ge, Synthesis of TiC/W core-shell nanoparticles by precipitate coating process, *J. Nucl. Mater.* 430 (2012) 216–220.