

## Preparation of tungsten carbide from mixtures of natural wolframite and carbon-containing solid fuels with assistance of mechanical activation

L. Telmenbayar<sup>a</sup> and J. Temuujin<sup>b,\*</sup>

<sup>a</sup>School of Mechanical and Transportation Engineering, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia

<sup>b</sup>Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 51, Mongolia

Mechanically milled mixtures of wolframite and coke, coking coal or thermal coal have been characterized with DTA-TG, XRD and SEM techniques. Mixtures were milled with a planetary ball mill for 4 h and heated at 1000 °C or 1100 °C for 1 hr under argon gas. The mixtures with coke and coking coal contained WC and Fe<sub>3</sub>W<sub>3</sub>C whilst the mixture with thermal coal consisted of only Fe<sub>3</sub>W<sub>3</sub>C phase even after 1 hr calcination at 1100 °C. The amount of WC in the product from coke was higher than with coking coal. Thermal coal was not a suitable carbon source for forming WC by this route. Coke is considered the most preferable carbon source on preparation of WC in the carbothermic reduction of the wolframite.

**Key words:** Wolframite, Coke, Coking coal, Thermal coal, Milling, Thermal reaction, Tungsten carbide.

### Introduction

Tungsten carbide is an old and well known WC-based hard metal, which was invented in 1923. Since its invention, it has been widely used in geo-engineering as drill buttons and various wear resistant parts [1]. Tungsten cemented carbide is composite material built by hard refractory phase WC and soft binder phase Co. The combination of good wear resistance, high toughness and high hot hardness, makes tungsten carbide in most cases the first hand choice for tools for metal cutting operations [2]. Wolframite (FeWO<sub>4</sub>) is a principal source of tungsten (W) and tungsten carbide (WC). The material is produced using expensive powder metallurgical methods by reacting elemental tungsten with carbon at 1400–1600 °C in a hydrogen atmosphere [3]. In this conventional method, WC produced in results of high temperature processes at high cost. Obtaining WC directly from natural raw minerals at lowest possible temperature is big challenge. Although a few direct carbothermic reduction on WC is reported, though; it could be a method to simplify WC preparation procedures. For instance, Temuujin et al. have successfully prepared nano-sized WC from mechanically activated wolframite and activated carbon at 1100 °C [4]. Welham obtained WC from mechanically activated scheelite and graphite mixtures at 1000 °C [5]. Mechanical activation shows favorable effects on the preparation of WC from natural raw minerals [3–8].

The beneficial effects of mechanical activation were explained by shorter diffusion paths of the finely mixed particles and easier nucleation of WC from the reaction mixture. In a previous study, the thermal reactions of the mechanically activated natural wolframite and thermal coal stoichiometric mixtures under nitrogen and argon atmospheres showed a carbon deficiency when using a stoichiometric mixture [9]. A follow-up study using stoichiometric mixtures of wolframite and thermal coal and mixtures with excess 30% carbon showed that mixtures with excess thermal coal showed greater formation of the ternary carbide than a stoichiometric mixture, due to an increase in nucleation sites [10].

In this paper, the effects of mechanical activation and thermal reactions of wolframite with various solid fuels coke, coking coal and thermal coal on preparation of WC are examined. Preparation of WC directly from a mineral concentrate using a low cost carbon source would have a significant impact on production cost compared to the conventional process. Therefore, elucidation of the factors affecting WC formation using various low cost carbon sources is considered to be an important task.

### Experimental

Natural wolframite was purchased from a private company exploring the Buyant deposit, (Bayan-Ulgii province, western Mongolia). The chemical composition of wolframite was WO<sub>3</sub>: 68.76, Fe<sub>2</sub>O<sub>3</sub>: 25.86, MnO<sub>2</sub>: 0.54, CaO: 0.92 and SiO<sub>2</sub>: 3.99 wt%. The carbon sources were coke from the Darkhan metallurgical plant and coking coal and thermal coal from the coal washing plant of the Tavan-Tolgoi coal deposit (Ukhua

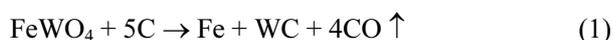
\*Corresponding author:  
Tel : +976-11-453334  
Fax: +976-11-453331  
E-mail: -jtemuujin@yahoo.com

**Table 1.** Chemical composition of the carbon sources and respective ashes.

Sample	C	N	H	Ash												
	%	%	%	%	Ash analysis, wt.%											
					Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	SrO	TiO <sub>2</sub>
Thermal coal	63.14	1.78	3.39	26.41	15.60	7.40	12.95	0.76	1.70	0.25	0.25	3.84	3.81	47.90	0.25	0.61
Coking coal	79.52	2.25	4.54	11.04	16.15	5.16	9.29	0.70	1.08	0.16	0.32	3.18	2.19	55.90	0.29	0.91
Coke	81.47	1.44	0.02	15.40	18.95	4.21	8.19	0.97	1.81	0.07	0.67	1.68	2.19	55.25	0.27	0.94

Khudag Mining). Quantitative chemical analysis of the solid fuels indicated that the content of the carbon (C), hydrogen (H) and nitrogen (N) and their ash content, respective chemical composition of the ashes are shown in Table 1.

All solid fuel samples were dried before use. Calculated amounts of the raw materials were weighed based on the reaction equilibrium shown below.



Mixtures were stoichiometrically prepared with excess 30 wt.% carbon.

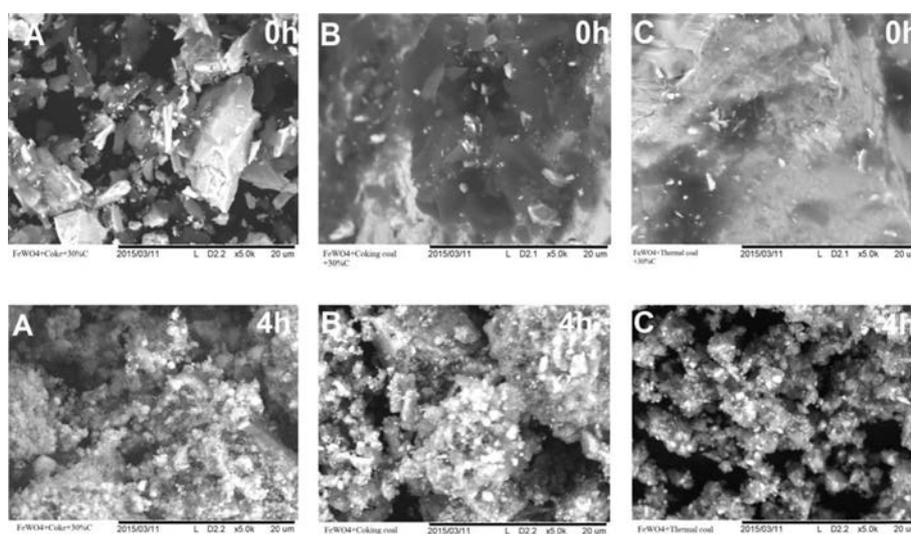
The three different carbon samples were mechanically milled with the wolframite in a planetary ball mill (Fritsch Pulverisette 5, Idar-Oberstein, Germany) for 4 hrs, using a ball to powder mass ratio of 50 : 1 at a rotation speed of 250 rpm. After milling, thermal analysis was carried out using DTA-TG (Hitachi, 8200) under a flowing argon atmosphere. The milled powders were also pressed into 1 cm diameter tablets using a uniaxial press under 20 MPa force. The tablets were then calcined for 1 hr at either 1000 °C or 1100 °C in a tube furnace under a flowing argon atmosphere. The furnace heating rate was kept constant at 10 °C/min. The constituent phases of milled mixtures and thermal reaction products were determined by XRD (Shimadzu MAXima-X XRD-7000), microstructure of the milled

samples was characterized by SEM (Hitachi S100). The argon gas flow rate for both DTA-TG measurements and tube furnace heating was 200 ml/min.

## Results and Discussion

Fig. 1 shows SEM micrographs of the unmilled and milled mixtures. The microstructure of the unmilled raw mixtures show the presence of the large particles of wolframite and coal as no size reduction was undertaken prior to mixing the powders. In the SEM micrograph of 4 hrs milled samples, particles are submicron in size and have a much narrower size distribution. Clearly it can be concluded that homogeneity was improved in the milled powders, especially the coke which also appeared to have the narrowest particle size distribution.

The XRD patterns of the 4 hrs milled three types of samples are shown in Fig. 2. The starting wolframite contained quartz as the main impurity. Intensities of the wolframite and quartz peaks reduced more after milling with coke than with either coking or thermal coal. XRD of the raw carbon sources (not shown) showed the typical lack of peaks for crystalline phases despite the ash content being 11-26%. In all milled samples the XRD peaks of wolframite broadened and weakened in comparison to the un-milled wolframite indicating crystallite size reduction and microstrain increase [9]. Based on the XRD patterns can be suggested that

**Fig. 1.** SEM images of the milled and unmilled mixtures (A) Mixtures with coke, (B) Mixtures with coking coal, (C) Mixtures with thermal coal.

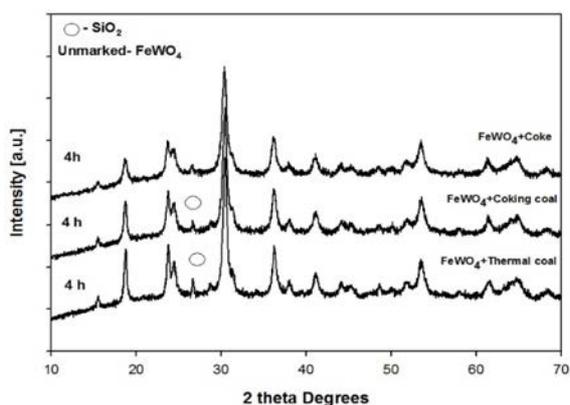


Fig. 2. XRD patterns of the samples after milling for 4 hrs.

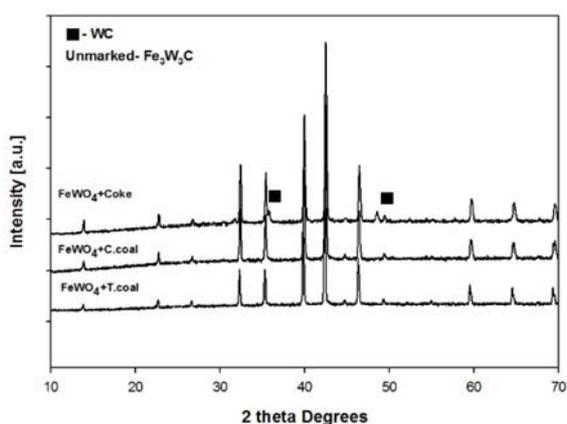


Fig. 3. XRD patterns of the three types of the mixtures calcined at 1000 °C.

preliminary pyrolyzed rigid structure coke shows beneficial influence in amorphization behavior of the wolframite. The reason of weaker influence of coals on the amorphization of the wolframite likely to be related with the softness of the coal samples which reduce the milling impact by sticking on the surface of milling body.

Figs. 3 and 4 show the XRD patterns of the samples after heating for 1hr at 1000 °C and 1100 °C respectively. In the samples heated at 1000 °C, the ternary carbide  $\text{Fe}_3\text{W}_3\text{C}$  was observed in the mixtures with coking coal and thermal coal. There was a minor amount of WC observed in the mixture with coke. These data suggest that the ternary carbide is the main product formed at this heating temperature. In the mixtures heated at 1100 °C, thermal coal contained only  $\text{Fe}_3\text{W}_3\text{C}$ , coking coal contained  $\text{Fe}_3\text{W}_3\text{C}$  with a small amount of WC whilst abundant WC was observed with coke.

In other words, in the mechanically activated various mixture the reaction ability of the carbon containing solid fuels varies with following order coke > coking coal > thermal coal.

Fig. 4 also indicates that in coke containing mixture appears a peak resembling to FeSi (PDF 086-0794) was formed. Since, the iron content in the coke was the lowest among 3 carbon sources, it is unlikely iron from the coke participated in formation of FeSi. More

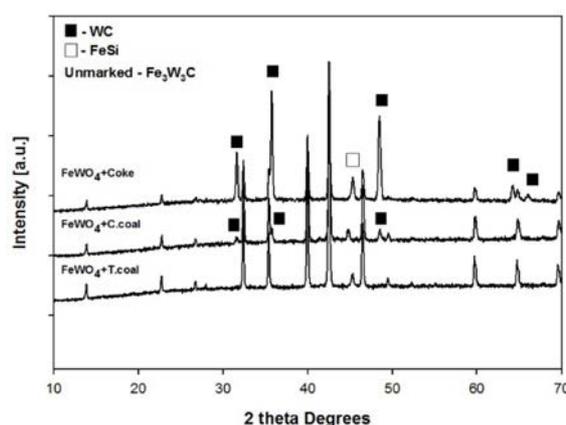


Fig. 4. XRD patterns of the three types of the mixtures calcined at 1100 °C.

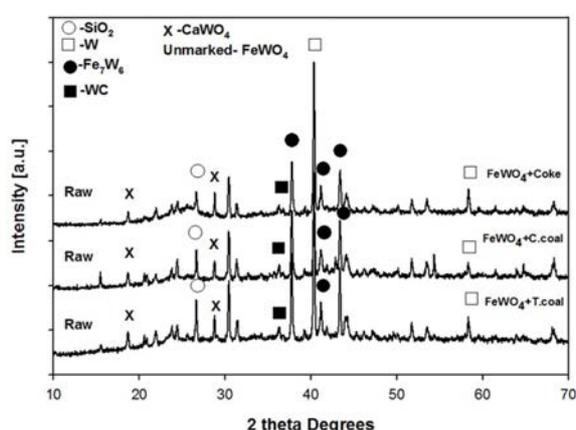


Fig. 5. XRD patterns of the un-milled mixtures calcined at 1100 °C.

plausible explanation is related on the abrasion of the milling medium and its interaction with the silica and carbothermic reduction during the heating. In the coke containing mixture still ternary carbide  $\text{Fe}_3\text{W}_3\text{C}$  is observed though, the content is lower than in other 2 mixtures.

In order to show the influence of mechanical activation on the carbothermic reduction, the raw (non-milled) mixtures were pressed into tablet and calcined at 1100 °C. The XRD pattern of the raw mixtures calcined at 1100 °C is shown in Fig. 5. The raw mixtures consisted of the unreacted  $\text{FeWO}_4$ , W,  $\text{Fe}_7\text{W}_6$ ,  $\text{SiO}_2$  and small amount of  $\text{CaWO}_4$ . Interestingly in the all mixtures was also formed a little amount of WC, though, it was not observed in the 4 h milled thermal coal containing sample that was calcined at the same temperature (Fig. 4).

XRD patterns (Fig. 5) indicate that in the non-milled thermal coal containing mixture were formed W and  $\text{Fe}_7\text{W}_6$  with unreacted traces of wolframite and  $\text{CaWO}_4$ . From the previous research, in the stoichiometric mixture were formed  $\text{Fe}_7\text{W}_6$  and W, which was explained in terms of carbon deficiency and occurrence of the following reaction [9]:

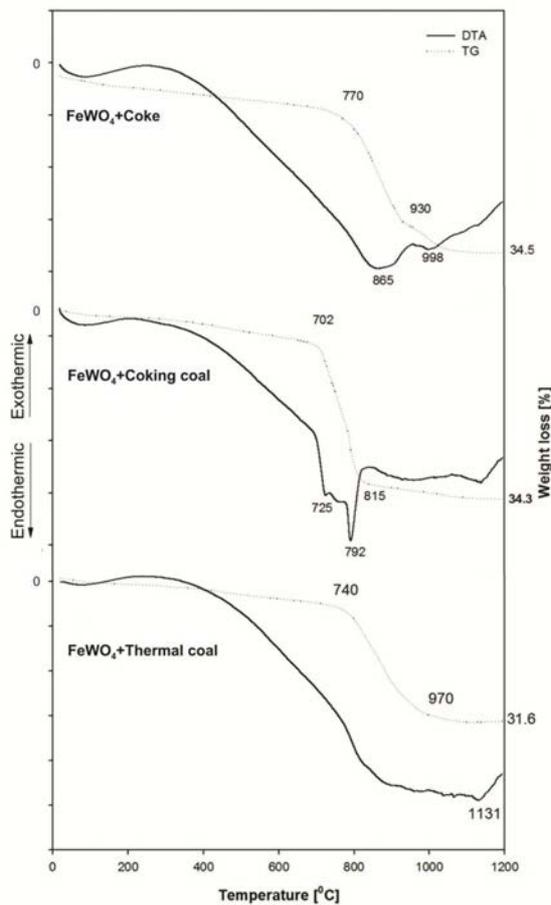
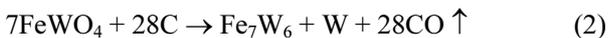


Fig. 6. DTA-TG traces of the milled sample with 3 different carbon sources.



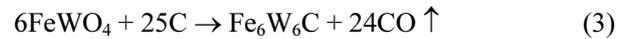
In the present case the carbon content was 30 wt.% higher than required by stoichiometric equation (1). Therefore, the presence of the  $\text{Fe}_7\text{W}_6$ , W and raw wolframite may be an indication of local carbon deficiency caused by inhomogeneity of non-milled starting mixture. Another explanation is the longer diffusion paths caused by the inhomogeneity will result in thermodynamically unstable phases forming due to slower achievement of equilibrium leaving intermediate phases.

Fig. 6 shows DTA-TG traces of the milled three types of mixtures.

The sample with coke exhibited a 34.5% weight loss in the temperature range between 770 °C and 930 °C. There is an endothermic peak observed at 865 °C, which coincides with start of a rapid weight loss. At 998 °C also occurred another endothermic peak which likely to associated with the weight loss starting from 930 °C.

With coking coal the sample exhibited a 34.3% weight loss in the temperature range between 702 °C and 815 °C. There are sharp endothermic peaks at 725 °C and 792 °C. Also an endothermic peak was observed at 1130 °C. The sample with thermal coal exhibits weight loss of 31.6% in the temperature range

between 740 °C and 970 °C. As for coking coal an endothermic peak was also observed at 1131 °C, this was not associated with any weight loss suggesting a phase change was occurring. Previous results have indicated that the carbothermic reduction of wolframite occurs according to following reactions [3, 4]:



The weight loss occurring at 700-1000 °C is related to equation (3). From the previous research ternary carbide  $\text{Fe}_6\text{W}_6\text{C}$  is an initial intermediate product for the WC synthesis which accompanied weight loss. However, the steep weight loss from the mechanically activated mixtures of the chemically pure active carbon and graphite with the wolframite occurred at 900°C i.e. at a higher temperature than that of at the present case [3, 4].

The sharp endothermic peaks in the coking coal containing mixture (b) seem to be not related to the carbothermic reaction path, because the reaction products were identical with the thermal coal containing mixture (c). In the milled sample (Fig. 4), only  $\text{Fe}_3\text{W}_3\text{C}$  was produced without other impurity phases. In this sample, (3) and (4) reactions could be occurred. However, Welham observed  $\text{Fe}_3\text{W}_3\text{C}$  appearance in the mechanically milled and calcined mixture of scheelite with graphite and magnesium in preference to WC [11]. It suggests that  $\text{Fe}_3\text{W}_3\text{C}$  is more stable compound than WC and there may exist an alternative reaction path to form WC. Clearly, the source of the carbon is important in determining the final products of reaction (5). The coals used for the present experiment shows 11-26 wt.% ash contents.

There is some chemical interaction probability of inorganic constituents of the coal with the wolframite by formation of low or poor crystalline carbides, during heating. Mechanical activation of coking and thermal coals with wolframite doesn't show a substantial favorable effect on the WC formation. In these coal samples, pyrolysis will start at lower temperature than the carbothermic reduction. Release of gaseous components from the ultimately bound mixture of the coals and wolframite will cause increase the diffusion path between the newly pyrolyzed carbon and wolframite and it may be a reason of high reactivity of the coke over the coking and thermal coals.

## Conclusions

Mechanical activation of wolframite and coke mixture was the most effective way for the preparation of tungsten carbide (WC) among the 3 different carbon sources trialed. The WC was formed via intermediate ternary carbide phases. A mixture with thermal coal consisted of only ternary carbide  $\text{Fe}_3\text{W}_3\text{C}$  at 1100 °C

whist coking coal also contained some WC. It can be suggested that volatile component containing carbon sources are not suitable for the carbothermic formation of the WC from a mechanically milled mixture.

### Acknowledgements

J.T. wishes to thank the A von Humboldt Foundation for awarding the Georg Forster award which provided funding to undertake part of this work.

### References

1. X. Ren, H. Miao, Z. Peng, J. Refractory Met. Hard Mater. 39 (2013) 61-77.
2. J. Weidow, S. Norgren, H-O. Andren, J. Refractory Met. Hard Mater. 27 (2009) 817-822.
3. J. Temuujin, M. Senna, Ts. Jadambaa, D. Byambasuren, J. Metastable Nanocryst Mater. 24-25 (2005) 581-584.
4. J. Temuujin, M. Senna, Ts. Jadambaa, D. Byambasuren, J. Am. Ceram. Soc. 88 (2005) 983-985.
5. N.J. Welham, Inst. Chem. Eng. J. 46 (2000) 68-71.
6. H. Lin, B. Tao, J. Xiong, J. Ceram. Inter.39 (2013) 2877-2881.
7. B.S. Terry, D.C. Azubike, Trans. Inst. Mineral Metal. [C] (1990) 167-174.
8. N.J. Welham, Mater. Sci. Eng. A 248 (1998) 230-237.
9. J. Temuujin, L. Telmenbayar, J. Thermal Anal. Calor. 121 (2015) 597-601.
10. L. Telmenbayar, J. Temuujin, Proceedings of the Int. Conf. on Sustainable Materials Sci. and Tech., Paris, 15-17 July 2015.
11. N.J. Welham, J. Mater. Res. 14 (2009) 619-627.