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Mechanochemical Carboaluminothermic Reduction of WO_3 to produce Al_2O_3–WC nanocomposite

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The present study is about the synthesis of Al_2O_3–WC nano composite powders obtained through mechanochemical process. Generally, the mode of reaction inWO_3, Al and C mixture is MSR (mechanically induced self-propagating reaction). In order to elimination of undesirable W_2C, separation of reactions and conducting the heat with time intervals were used. Hence, at the initial stage WO_3 and Al powders milled in a high-energy ball mill for 1 h. Subsequently, 1 mol C is added to the milled powders and milled stepwise. Al_2O_3–WC Composite is obtained after 20h milling. To investigate morphological aspects of powder's surface, scanning electron microscopy (SEM) analysis is utilized. In addition, Powder samples were characterized by X-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX). Also the crystallite size of the produced nano composite was calculated according to Williamson–Hall method to about 31nm. .

1. Introduction[§]

Composites are the combination of two or more materials in which tailored properties are achieved by bringing the combined advantages of both reinforcement and matrix into full play, which gives us a rather high degree of freedom in material design. Ceramic–matrix composites have attracted the attention of researchers for many years because of their potential for structural applications. [1]

Among these can be pointed Al_2O_3 reinforced with nanosized particles such as TiC, WC, SiC, NbC. Tungsten carbide (WC) has potential applications due to its unusual properties, such, superior hardness, low friction coefficient, high oxidation resistance and good electrical conductivity, for use as wear-resistant parts, dies, or molds[2,3,4]. The high melting point with excellent abrasive and corrosion-resistance properties makes it most suitable substance for cutting tool industries [5]. In order to increase the tool life efforts are being made to synthesize nano-size WC powders [5]. These specifications of WC would be improved when the size of its particles or grains falls into the nano range[2].

The Older method of WC production is the controlled solid-state reaction between W and C

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that this method requires a very long time of heating at high temperatures and has two main disadvantages include high cost processing and large size (macro-sized) of particles. To eliminate these disadvantages, researchers used new materials such as tungsten salts and tungsten oxide, as well as new production routes such as Mechanical Alloying (MA) that is so simple, fast and low cost processing and can be performed at room temperature [2].

In fact, Mechanical Alloying (MA) is a solid-state powder processing techniques involving repeated welding, fracturing and welding of powder particles in a high-energy ball mill and has been used for preparing thermally stable metallic glasses and amorphous alloys, nanocrystalline and nanocomposite materials, and refractory hard materials[1]. The occurrence of reactions during milling depends on several factors, including thermodynamics, atomic and thermal diffusivity and the mechanical properties of the reactant powders and processing factors. The most important processing factors are the milling speed, ball-to-powder weight ratio and milling ball diameter. These parameters determine the rate of mechanical energy transference from milling media to the powder particles [6]. Many studies have been down about mechanochemical reactions and its mechanisms.

Some researchers [2,6,8] have synthesized Al2O3–WC mixture by mechanochemical route. They have reported that the reactions start with the highly exothermic reduction of WO_3 and subsequently reduced tungsten would react with carbon to produce WC. El-Eskandarany [6] obtained WC–32 at.%Al_2O_3 nanocomposite from WO3 , Al and graphite mixture after 100 h of milling. Also Eliria et al. [7] performed a similar study, but they obtained the undesirable W_2C instead of WC. Sakaki et al. [9] mentioned that carbon loss due to simultaneous reduction of WO_3 by carbon, which becomes activated at high temperatures, is the main reason for existence of W_2C phase in WO_3–C–Al system. Sakaki et al.[9] are presented different routes to elimination of W_2C formation. In the present study, synthesis of WC-Al_2O_3 nanocomposite at room temperature via mechanochemical carboaluminothermic reduction of WO_3 was investigated. For reaching a homogeneous nanocomposite in minimum milling time without undesirable W_2C, separation of reactions and conducting the heat with time intervals and optimized milling parameters were used

2. Experimental Procedure

Powders used in this study are commercial powders (MERK CO. Germany) of WO_3 (<50μm, >99%), graphite (<1μm, >99.9%), Aluminum (>10μm, >99%). High energy ball milling was performed using a planetary milling machine (RETSCH PM 400). For each run of experiments, required amounts of the reactant powders were mixed by hand and transferred to the milling pots. Both vial (250ml) and milling balls were made of hardened steel. Balls with 20mm and 7mm of diameters were used in the mechanical alloying experiments. The material to ball mass ratio was set at 1:25 and the milling speed of 400 rpm was applied. Milling operation was performed under argon gas atmosphere at room temperature. In First stage, a stochiometric mixture of WO3–2Al powder was milled to completion of the aluminothermic reaction (Eq. (1)).

$$WO_3 + 2Al = W + Al_2O_3 \quad (1)$$

The milling process was interrupted for 1 h to cooling the product. After cooling, 1mol of C is added to the milled mixture at a glove box under argon gas atmosphere. The ball mill has been stopped after 15 min working and again started after 15 min. Eq. (2) reveals the reaction of carbide formation:

$$W + Al_2O_3 + C = WC + Al_2O_3 \quad (2)$$

During each stage, samples were taken to study the phase evolution and the completeness of the reaction using X-ray diffraction instrument (Expert Philips diffractometer) with Cu–K_α radiation(λ=1.5404A°). The morphology of the mechanically alloyed powders and the distribution of elements were examined by a VEGA TESCAN scanning electron microscope (SEM) and Moxtek EDS, respectively. Williamson–Hall method (Eq. (3)) was used to calculate the crystallite size:

$$b\cos\theta = 0.9\lambda/d + 2\eta\sin\theta \quad 3$$

where θ is a diffraction angle, η is lattice strain, d is average of crystallite size, λ is a X-ray wavelength and B is the XRD peak broadening calculated from the full width at half maximum (FWHM) of the most intense peaks.

3. Results and Discussion

In order to understand the formation mechanism of the reaction processes, the thermodynamic calculation on reactions has been applied. Thermodynamic values of ΔG°, ΔH° and Tad for the concerning reactions were calculated and presented in table1. Generally, the changes of the Gibbs free energy (ΔG) and the reaction heat (ΔH), is used to judge the spontaneous direction of a process and determine the endothermic and exothermic type of reactions. Although there is a difference between ΔG° and ΔH with ΔG and ΔH, ΔG°, ΔH could presumably be used to explain the behavior of the system. The adiabatic temperature (Tad) is used to characterize the degree of self-heating. It is defined as the maximum temperature which could be attained as a result of the reactions heat [10].

Mechanically induced self-sustaining (MSR) and gradual reaction are two kinds of formation mechanism Of WC–Al_2O_3 by high-energy ball milling at different milling conditions[9].

MSR is a self-propagating process that can be ignited after a certain mechanical activation time. After ignition, the reaction propagates thermally, similar to an SHS process [10].

The large negative free energy and considerable released heat of exothermic reaction are resulted a self-propagation in MSR process. It is clear, the temperature of the reactant in MSR reaction could be considerably increased by the released reaction heat. Hence, a high value of adiabatic temperature is expected. Merzhanov has stated that if the value of Tad for a reaction is higher than 1800 K, the reaction wave propagates by itself [9]. The calculated thermodynamic parameters and the type of reactions is summarized in table1.

XRD patterns of the un-milled and 1hour milled WO_3–2Al mixtures are presented in Fig.1. it is clear that after 1h milling new peaks correlated to metallic W and Al_2O_3 crystals have been appeared and the starting materials peaks disappeared. It is indicated that the reduction of WO_3 with Al was completed Rapid changes of XRD patterns reveal that the mode of reactions occurring in the WO_3–2Al mixtures is MSR reaction[9]

that confirm with summarized prediction in table1. XRD patterns of a previously milled sample with 1mol carbon addition, milled again for various periods of times are shown in Fig.2.

It is shown that intensities of W, Al_2O_3 and C peaks decrease gradually with the increase of milling time and diffraction peaks of initial carbides (W_xC) appeared. Formation of W_xC instead of WC is due to the shortage of graphite caused by heterogeneity of the milled powder [8].

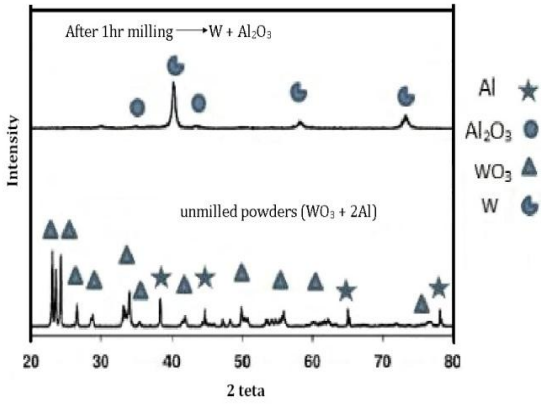

Fig.1: XRD patterns for unmilled and 1hour milled WO_3–2Al mixtures.

Table1:
Results of thermodynamic calculations for reactions and prediction of reaction type

reaction	ΔG°_{298} [kJ/mol]	ΔH°_{298} [kJ/mol]	T_{ad} [K]	reaction type
General Reaction:	-837.86*	-872.832*	3870*	MSR
WO_3+C+ **2**Al→ Al_2O_3+WC	Large negative value	highly exothermic	higher than 1800K	
Aluminothermic Reaction:	-811.064*	-832.791*	3880*	MSR
WO_3 +2Al → W + Al_2O_3	Large negative value	highly exothermic	higher than 1800K	
Carbothermic Reaction:	-26.795*	-40.01*	580*	Gradual
W + Al_2O_3+ C → WC + Al_2O_3	small negative value	not highly exothermic	smaller than 1800 K	

* data are estimated with thermodynamics relation. Refer to metallurgical thermodynamics references for more information.

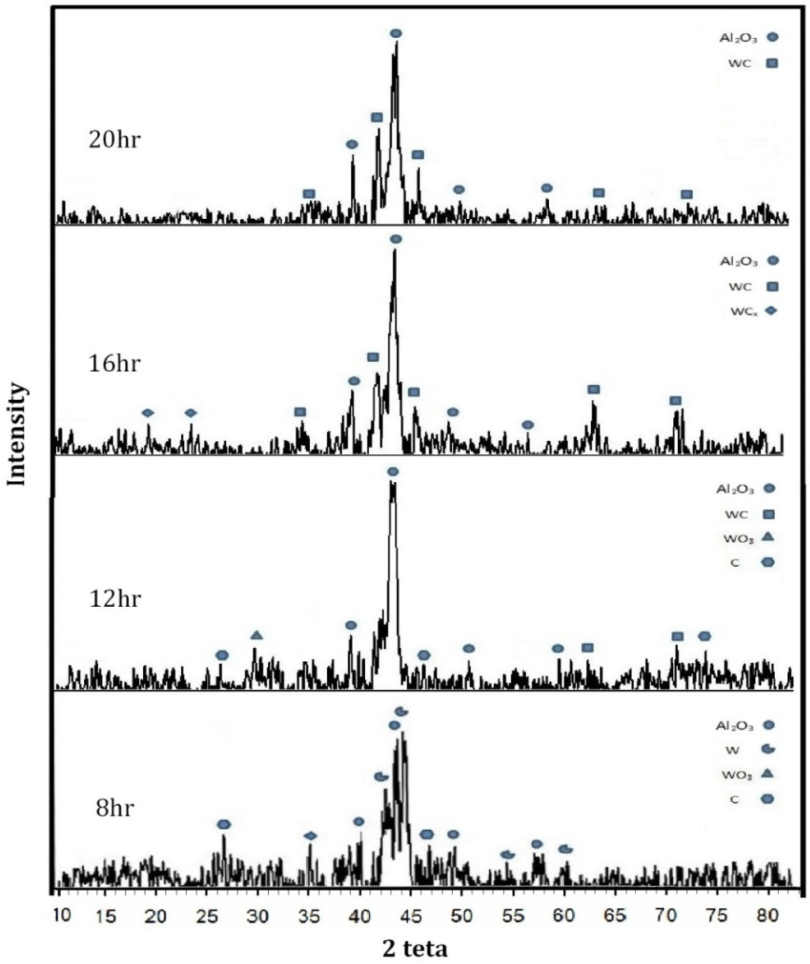

Fig.2: XRD patterns of Al_2O_3-W-C samples after different times of milling.

The peaks of WC can be observed after milling for 12h, coexisting with some peaks of the unreacted W and C and W_xC. No phase of the starting reactant materials (W and C) being detected after 16h. The peaks of W_xC have disappeared completely after 20h and intensity of WC peaks have increased. On the other hand, the carbide formation reaction has been promoted and a homogeneous WC-Al_2O_3 composite formed successfully after 20h. The important results at this route is capability of producing WC with the elimination of W_2C phase[9].

W_2C which is a hexagonal-close-packed (hcp) tungsten rich phase was formed in high temperatures or in presence of carbon deficiency at low temperatures, thermodynamically [11]. Since the aluminothermic reaction has been separated from carbothermic reaction, its released heat has been lost during the cooling period and no carbon deficiency due to carbothermic reduction of WO_3, is expected[9]. In addition, rise of the temperature would decrease the thermodynamic stability of WC and increased tendency of W_2C formation. Thus regular time intervals to control temperature. Increasing due to the milling balls impact, can be effective to elimination of W_2C phase[2,9].

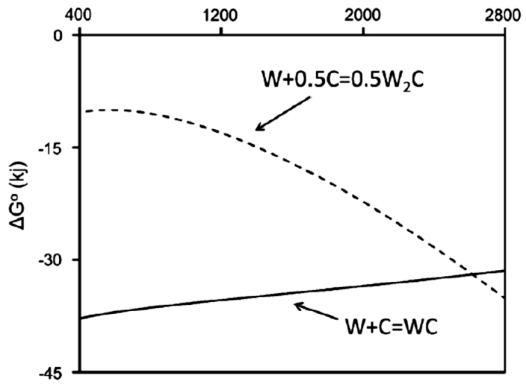

Fig. 3: Comparison between thermodynamic stability of WC and W_2C over a wide range of temperature[2].

The mean crystalline size of WC phases and the amount of internal stress were determined by Williamson–Hall method. The size of the crystals and the mean strain of the WC phase after 16h and 20h of milling time are presented in Table2. These values can be inferred from a graph similar to Fig.4As it is observable, crystallite size is in nanoscale and decrease with increasing the milling time.

SEM micrographs using secondary electrons (SE) of 16 and 20 h milled samples are shown in Fig.5 (a-b) and Fig.6 (a-b), respectively.

Fig.5(a) shows the powders milled and large agglomerates are clear in the powder mixture. These agglomerates consist of fine particles that are cold welded together due to the very hard plastic deformation. Higher magnification figure indicates that the product contains nano-size particles (Fig.5(b)). EDS analysis revealed that this nanoparticles contain W and C elements (table 3). Hence, they are WC particles that dispersed inside the Al_2O_3 agglomerates.

With increasing the milling time to 20h, the agglomerate sizes increased (Fig.6(a)) but the particles became finer and more homogeneous in their sizes and distributions (Fig.6(b)). It is clear that during milling, heavy deformation is induced into the particles. This is manifested by the presence of a variety of crystal defects, such as dislocations, vacancies, stacking faults, and increased number of grain boundaries [12]. Rise in boundaries density and nucleation of new carbide phase can be due to decreasing the crystallites size and improving its distribution [6,8,2].

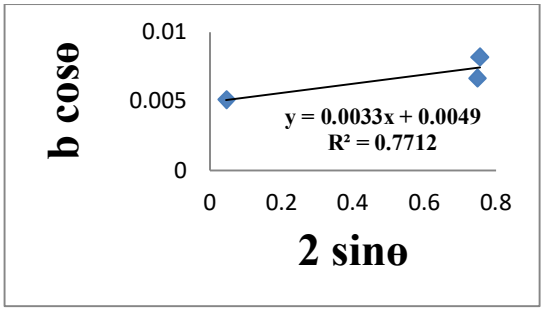

Fig. 4: Williamson–Hall equation curve for determination of mean crystalline size and strain in sample with 16h of milling time .

Table 2: Crystallite size and lattice strain of samples with 16h and 20h of milling time

Milling time (h)	Mean crystallite size (nm)	lattice strain η (%)	0.9 λ/d
16	46	0.49	0.0033
20	31	0.61	0.0045

Table 3: weight presence of elements are measured with EDX.

	W	C	Al	O	Cr	Fe	Mn
16h milled	31.27	6.35	6.48	13.24	1.02	40.74	0.90
20h milled	29.48	6.22	6.85	13.46	1.14	41.91	0.95

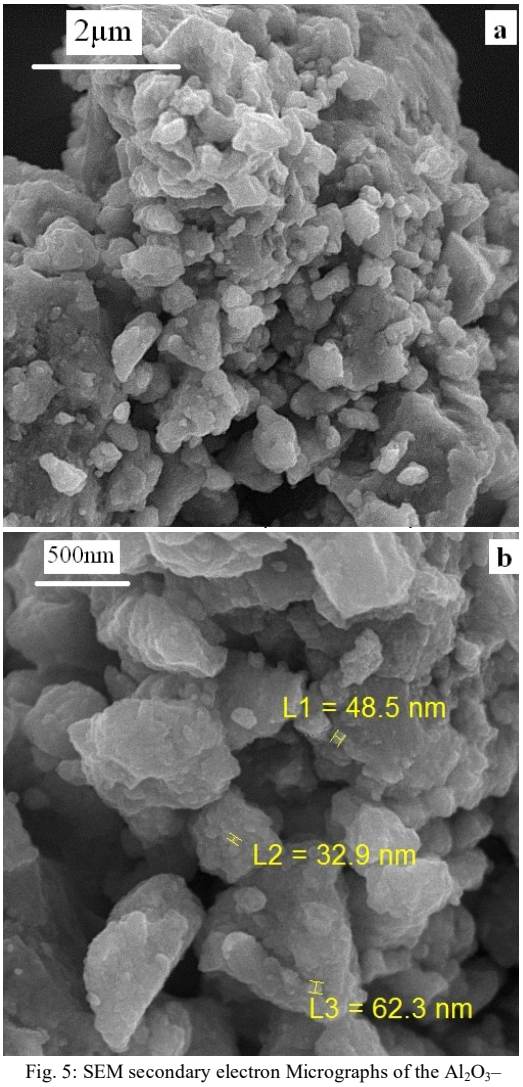

Fig. 5: SEM secondary electron Micrographs of the Al_2O_3–W-C powders milled 16h.

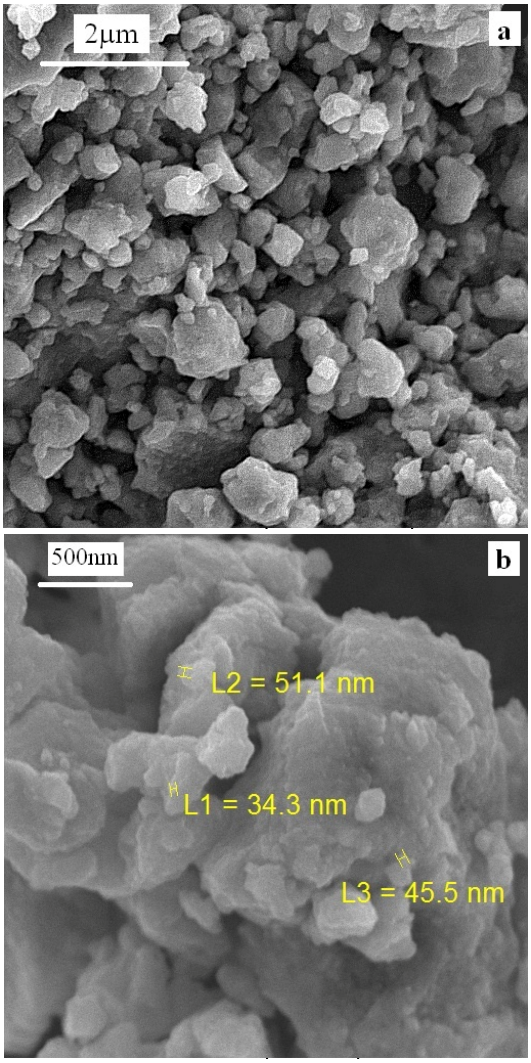

Fig. 6: SEM secondary electron Micrographs of the Al_2O_3–W-C powders milled 20h.

4. Conclusion

Al_2O_3–WC nano composite powders were obtained through a high-energy reactive milling of a mixture of elemental Al, WO_3, and C powders. In order to elimination of W_2C phase, process temperature is controlled by a stepwise milling method. A summary of findings of this work is presented as follows:

- Al_2O_3–WC nano composite powders with good distribution of carbide phase were produced after 20h of milling.
- The results showed that the types of reactions happened in the WO_3–2Al mixtures (aluminothermic reaction) are MSR and in the Al_2O_3-W-C (carbothermic reaction) are gradual.
- According to the Williamson–Hall method, the crystallite size of the Al_2O_3–WC powders was in the nanometer scale that confirms the SEM results.

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