

Synthesis, crystal structure, and density of $(W_{1-x}Al_x)C$

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Abstract

A new solid solution system of Al in WC, with the stoichiometry of $(W_{1-x}Al_x)C$ ($x = 0.10, 0.25, 0.50, 0.75, 0.86$), has been synthesized by a solid-state reaction between $W_{1-x}Al_x$ alloys and carbon at around 1673 K in vacuum. Environment scanning electron microscope, energy-dispersive analysis of X-ray, X-ray photoelectron spectroscopy, and inductively coupled plasma analyses are used to certify the formation of the products. The mechanism of the solid-state reaction is also discussed. $(W_{1-x}Al_x)C$ is identified to crystallize in the hexagonal space group $P6m2$ (No. 187) and belongs to the WC structure type. The atoms of W and Al occupy the same lattice site ($1a$ site) in the cell of $(W_{1-x}Al_x)C$. The cell parameters for each specimen in the phase of W–Al–C are quite close to that of WC, while their densities are far lower than that of WC.

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1. Introduction

Since Moissan published the first description of tungsten carbide, in 1896 [1], the alloys of tungsten and carbon have been studied repeatedly. Among these alloys, WC is best known for its exceptional hardness and superior wear resistance, and has a wide range of industrial application, especially in the tool cutting industry; around 95% of all cemented carbide cutting tools are tungsten carbide based [2].

But on the other hand, pure WC has many inevitable shortcomings, for instance, room temperature brittleness, high density and high operating costs. Therefore, in recent years, many studies have focused on how to avoid these defects and improve the physical and chemical properties of WC as well as to reduce its high operating costs. In this sense, the first approach is the partial substitution of WC by other non-oxide compounds such as Ti(C, N), Mo_2C , Cr_3C_2 , TiN, TiC, and VC [3–5], which results in the lower density while maintaining its hardness and wear resistance. The second alternative is to modify the binder component such as Co, Ni, Fe, etc. to improve the corrosion resistance and/or mechanical strength [6–9]. But no

work has been found on the solid solution of metals in WC until now.

Aluminum is more ductile and lighter than tungsten metal, so the solid solution of Al in WC is expected to enhance the bend strength of WC and reduce its density while retaining the high hardness and wear resistance of WC. In addition, aluminum is inexpensive compared to tungsten; thus, operating costs of ternary carbide Al–W–C are surely less than that of WC.

However, it is very difficult to synthesize the solid solution in the W–Al–C phase directly by W, Al, and C element powders because of the large differences of density and melting point between W and Al metal. In our previous paper [10], we have reported that $W_{1-x}Al_x$ ($x = 0–0.86$) alloys could be synthesized by mechanical alloying. Additionally, $W_{1-x}Al_x$ has the same body-centered cubic structure as W, and is stable at high temperatures up to 1400°C. So it is possible for $W_{1-x}Al_x$ ($x = 0–0.86$) to be carbonized at high temperature to prepare the solid solution $(W_{1-x}Al_x)C$ as the reaction between W and C to form WC.

In this paper, we describe a simple and economical technology for the synthesis of pure $(W_{1-x}Al_x)C$ solid solution powders by a solid-state reaction between $W_{1-x}Al_x$ and carbon at high temperature. Additionally, the reaction mechanism, the crystal structure and the density of the prepared materials are also discussed.

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2. Experiment

The precursors $W_{1-x}Al_x$ ($x = 0.10, 0.25, 0.50, 0.75, 0.86$) were prepared as follows [10]: firstly, the elemental powders of tungsten (-200 mesh, 99.8% purity) and aluminum (-200 mesh, 99.5% purity) were weighed out with the atomic ratio $W : Al = (1 - x) : x$. Secondly, the mixed powders were sealed (Al must be added step by step when $x > 0.50$) under an argon atmosphere into the steel vials with ball-to-powder weight ratios of 30:1–15:1. Finally, materials were ball milled for various times from 20 to 120 h (the larger the x value, the longer the reaction time) and then the pure $W_{1-x}Al_x$ alloys were obtained.

The prepared $W_{1-x}Al_x$ alloys ($< 0.1 \mu\text{m}$, 99% purity) and carbon ($< 34 \mu\text{m}$, 99% purity) were accurately weighed out such that the $W_{1-x}Al_x:C$ molar ratio was 1:1.02. The reason for the addition of a little excess carbon is that a little amount of carbon should be oxidized and lost at the elevated temperature in the following steps. About 25 g of each ball-milled mixture of the two materials was packed into a corundum crucible, and then these crucibles were placed into a resistance vacuum furnace connected to a continuously operating pump. The furnace was then heated up to 1673 K at a linear rate of 45 K/min. The reaction time for various compositions was different from 24 to 120 h. In addition, after the continuous reaction for 15–20 h, every specimen was repeatedly cooled and ball milled for 30 min in order to enhance the reaction speed.

The materials for various reaction times were examined by X-ray diffraction (XRD) using a Rigaku D/max-IIB X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The scan speed was $4^\circ/\text{min}$. The environment scanning electron microscope (ESEM, Philips XL30) and the energy-dispersive analysis of X-rays (EDAX) measurements were conducted to investigate the morphology and the quantitative material composition of the prepared powders. X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis were used to certify the formation of the products ($W_{1-x}Al_x$)C, where XPS was carried out on a VGES-CALAB MKII X-ray photoelectron spectrometer, while ICP-AES was performed on an Atomscan Advantage (Thermo Jarrell Ash Corporation).

Rietveld analysis was used to determine the structural state of the five specimens with increasing Al content. No evident violations of hexagonal symmetry were found on the XRD pattern of the specimens. Therefore, the refinement of the structure was carried out in the space group $P\bar{6}m2$. WC was taken as the starting model of the refinement, but W and Al atoms were constrained to occupy the $1a$ site alternatively. The site occupation factors (SOF), cell parameters, and densities were then refined.

The prepared ($W_{1-x}Al_x$)C powders were pressed into a column of 10 mm diameter and 5 mm high with a compaction pressure of 270 MPa, and then sintered under high temperature and high pressure, 1873 K and 4 GPa, respectively, for about 10 min, and then the density of the samples was determined by the Archimedes principle using distilled water.

3. Results and discussion

3.1. X-ray diffractometry

The powder XRD pattern of the one characteristic composition ($W_{0.5}Al_{0.5}$)C for various reaction times is presented in Fig. 1. The carbon powder to X-ray is very weak in our system, so only $W_{0.5}Al_{0.5}$ peaks are observed in the figure of the starting materials. As the reaction time increases, $W_{0.5}Al_{0.5}$ diffraction peaks continuously decrease, and a new phase is observed as the intermediate product, and this intermediate product is identified to adopt the hexagonal structure of W_2C type from its position of diffraction peaks. It is reported that during the process of the solid-state reaction between carbon and tungsten to form WC, W_2C is also observed as an intermediate compound [11]. Considering the component of the starting materials, the W_2C phase in our system is deduced as having the stoichiometry ($W_{0.5}Al_{0.5}$) $_2$ C. Further carbonization leads to the formation of a second new phase. This new phase is identified to be ($W_{0.5}Al_{0.5}$)C, which crystallizes in the WC structure type. With the passage of time $W_{0.5}Al_{0.5}$ peaks completely disappeared, and ($W_{0.5}Al_{0.5}$) $_2$ C became more and more faint, while the peak intensities corresponding to ($W_{0.5}Al_{0.5}$)C increased stably. After reaction for 73 h, only the ($W_{0.5}Al_{0.5}$)C peaks were observed and the pure solid solution ($W_{0.5}Al_{0.5}$)C has been obtained completely.

There was no aluminum carbide (Al_4C_3) formation during the whole reaction process, as evidenced by the absence of the Al_4C_3 peaks in the XRD patterns in Fig. 1. (The d -spacings of the three strongest peaks of Al_4C_3 were located at 2.38, 1.70, 2.90 [12], respectively, if Al_4C_3 crystallized in the hexagonal space group, or else were located at 2.81, 1.67, 2.24 [13] if it crystallized in the rhombohedral space group.) This means that the alloy $W_{0.5}Al_{0.5}$ does not decompose to W and Al under high temperature, but still retains its body-centered cubic structure to react with carbon to form the ($W_{0.5}Al_{0.5}$)C solid solution.

Fig. 2 shows the XRD pattern of several compositions after various reaction times. Only ($W_{1-x}Al_x$)C peaks can be seen in the figure, and no evidence of an obvious peak shift has been found by varying the aluminum content. One can come to the conclusion that solid solution powders of Al in WC were obtained,

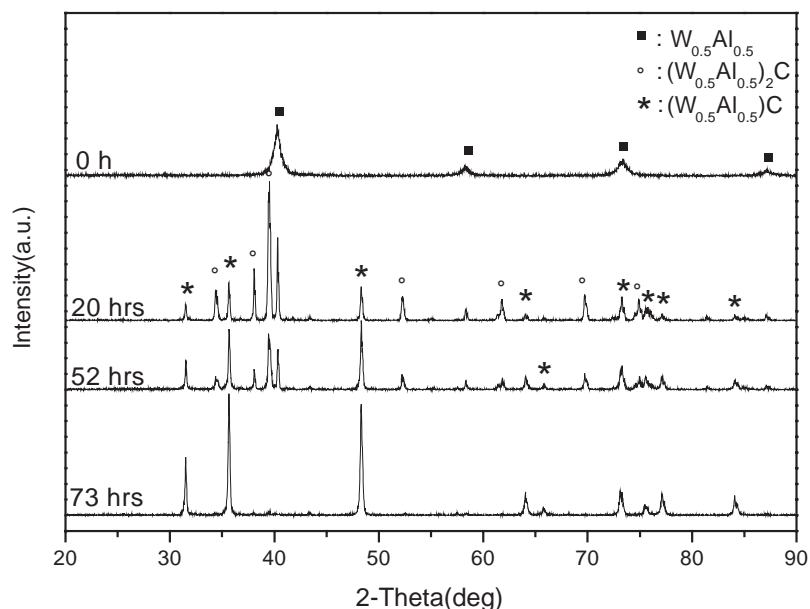


Fig. 1. XRD patterns of $(W_{0.5}Al_{0.5})C$ powders after various reaction times.

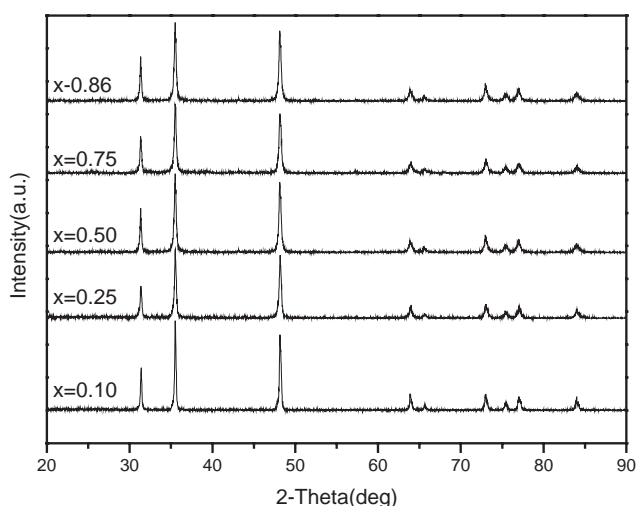


Fig. 2. XRD patterns of $(W_{1-x}Al_x)C$ as a function of Al content. Reaction time for $x = 0.10$ – 0.25 is 24 h, for $x = 0.50$ is 73 h, for $x = 0.75$ is 102 h, and for $x = 0.86$ is 120 h.

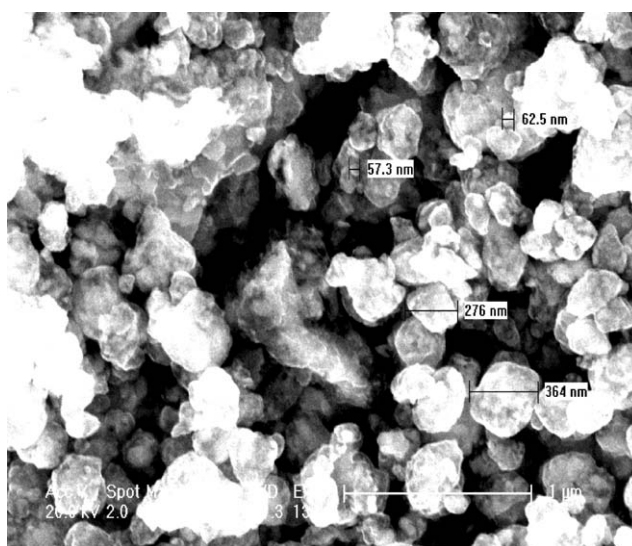


Fig. 3. ESEM micrograph of the $(W_{0.5}Al_{0.5})C$ powder.

and the solubility reaches an astonishing value of 86%. A longer reaction time is needed with increasing aluminum.

Based on the information obtained from Figs. 1 and 2, it may be possible to establish the reaction process of $(W_{1-x}Al_x)C$. The reaction between $W_{0.5}Al_{0.5}$ and C is similar to the process of W reacting with carbon to form WC [11]. At the beginning of the reaction, some small $(W_{1-x}Al_x)_2C$ clusters are formed at the interfaces of $W_{1-x}Al_x$ and carbon under the force of high temperature. The distribution of the clusters is uniform and these clusters act as nucleation sites. With the passage of time, the nucleation reacts with carbon and grows up step by step, eventually leading to the formation of

$(W_{1-x}Al_x)C$ completely. On the whole, the essence of the solid reaction between $W_{1-x}Al_x$ and C is that carbon atoms diffuse into the lattice of $W_{1-x}Al_x$ and form the intermediate phase $(W_{1-x}Al_x)_2C$, and then the residual carbon atoms go on diffusing into the lattice of the intermediate phase and finally form the product $(W_{1-x}Al_x)C$. The high temperature, doubtless, provides the reaction kinetics for these continuous solid reactions. Firmly, the reaction process consist of the following two steps:

- (1) $2W_{1-x}Al_x + C = (W_{1-x}Al_x)_2C$,
- (2) $(W_{1-x}Al_x)_2C + 2C = 2(W_{1-x}Al_x)C$.

3.2. ESEM-EDAX, XPS, and ICP results

Fig. 3 shows the micrograph of $(W_{0.5}Al_{0.5})C$ powder after the solid-state reaction for 73 h. It can be seen that the particles have aspherical shape, and that the sizes are

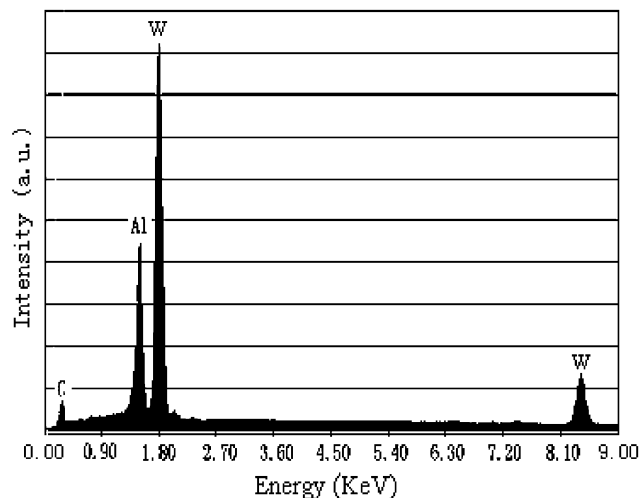


Fig. 4. EDAX spectrum of the $(W_{0.5}Al_{0.5})C$ powder.

Table 1
EDAX semi-quantitative analysis for $(W_{0.5}Al_{0.5})C$

Element	Weight ratio (%)	Atomic ratio (%)
W	78.82	25.47
Al	11.02	24.28
C	10.16	50.25

Table 2
ICP results for $(W_{0.5}Al_{0.5})C$

Element	Content (mg/g)	Atomic ratio (%)
W	794.5	51.6
Al	109.4	48.4

mostly less than $1\ \mu\text{m}$. The EDAX spectrum of the $(W_{0.5}Al_{0.5})C$ powder is shown in Fig. 4 and the result for semi-quantitative analysis is presented in Table 1. It shows that the atomic ratio W:Al:C in $(W_{0.5}Al_{0.5})C$ is about 0.5:0.5:1, which is in good agreement with the atomic ratio deduced from the starting materials.

To further obtain the exact contents of Al and W in the product, the result of ICP for $(W_{0.5}Al_{0.5})C$ powder is given in Table 2. It can be seen clearly that the atomic ratio W:Al in $(W_{0.5}Al_{0.5})C$ is nearly 0.5:0.5, which is quite consistent with the results analyzed by EDAX.

Fig. 5 shows the XPS result of the $(W_{0.5}Al_{0.5})C$ powder. The peak of $Al2p$ is centered at 73.4 eV that is different from Al (72.8 eV) [14] or Al_2O_3 (74.3–74.7 eV) [14], which shows that Al atoms may displace the positions of tungsten and are mostly coordinated with other C atoms. The $W4f_{7/2}$ spectrum of the sample has a binding energy of 31.4 eV, which is close to the corresponding $W4f_{7/2}$ value in WC (31.5 eV) [14].

Based on all the analyses, it can be concluded that Al is stable in the hexagonal structure at room temperature, and the ratio of metal to carbon agrees well with the starting materials.

3.3. Structure refinement

The profile fit for X-ray data of the characteristic composition $(W_{0.5}Al_{0.5})C$ is presented in Fig. 6. The entire refinement proceeds smoothly to give the final atomic data, cell, and space group information in Table 3. The indexing result of the characteristic composition $(W_{0.5}Al_{0.5})C$ is presented in Table 4. $(W_{1-x}Al_x)C$ has been identified to crystallize in the hexagonal space group $P6m2$ as WC. Generation of the expected coordinates of W, Al, and C atoms gave reasonably good agreement with the observed data. Namely, atom Al has the same atomic coordinates (1a site) as atom W in the cell of $(W_{1-x}Al_x)C$; therefore,

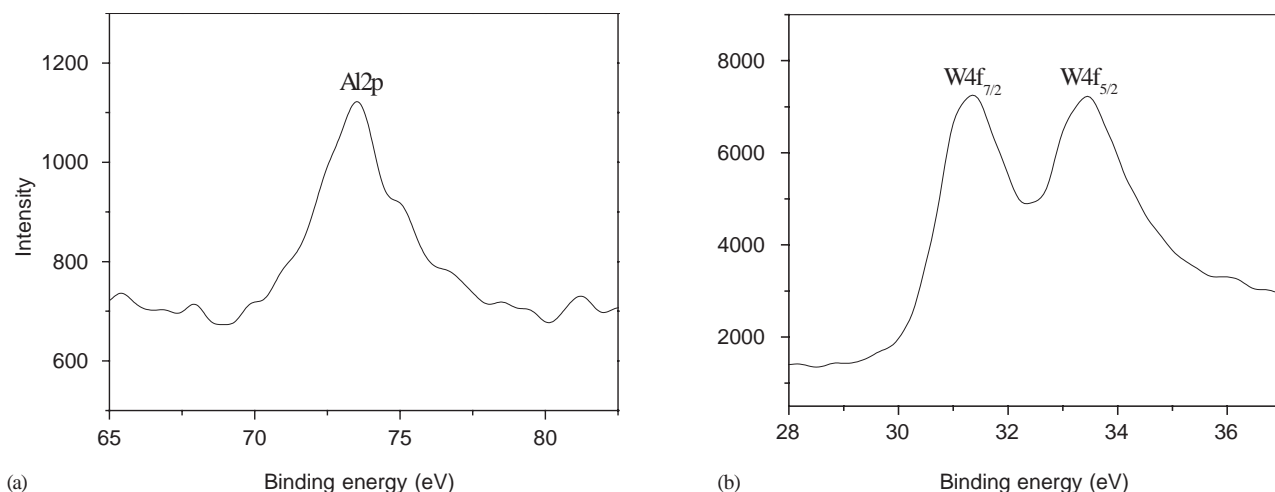


Fig. 5. (a and b) XPS results for $(W_{0.5}Al_{0.5})C$.

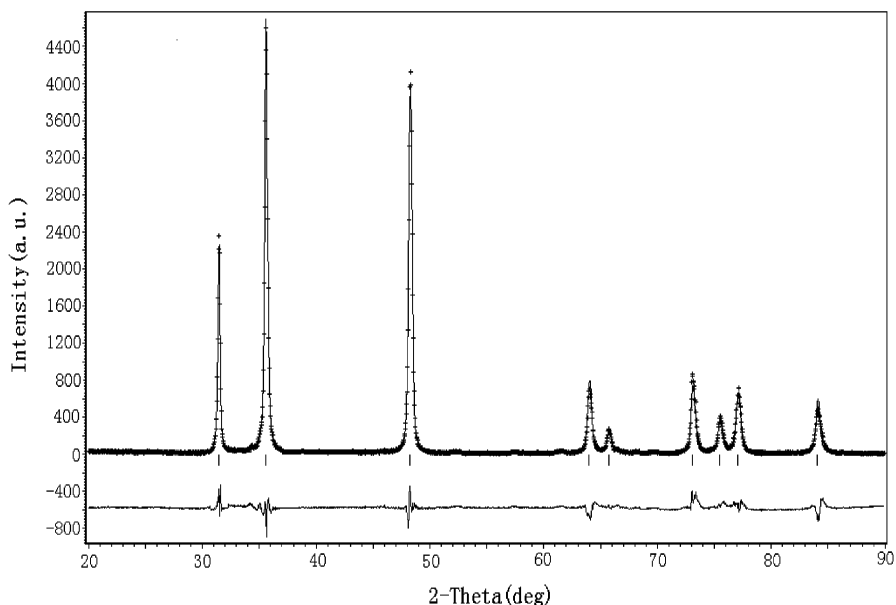


Fig. 6. Final profile from the powder X-ray data refinement of $(W_{0.5}Al_{0.5})C$. The observed data are crosses, the calculated pattern a solid line, and the lower line is the difference plot. The middle tick represents $(W_{0.5}Al_{0.5})C$ phase.

Table 3
Final refinement results of $W_{1-x}Al_xC$

Stoichiometry	$(W_{0.90}Al_{0.10})C$	$(W_{0.75}Al_{0.25})C$	$(W_{0.50}Al_{0.50})C$	$(W_{0.25}Al_{0.75})C$	$(W_{0.14}Al_{0.86})C$
SOF					
W1a (0,0,0)	0.9020	0.7504	0.5117	0.2634	0.1478
Al1a (0,0,0)	0.0980	0.2496	0.4883	0.7366	0.8522
C1f (2/3, 1/3, 1/2)	1.0	1.0	1.0	1.0	1.0
a (Å)	2.9071	2.9051	2.9065	2.9066	2.9060
c (Å)	2.8371	2.8364	2.8397	2.8413	2.8410
Vol (Å ³)	20.765	20.731	20.775	20.788	20.777
Density (g/cm ³)	14.434	12.541	9.528	6.412	4.967
Space group	<i>P6m2</i>	<i>P6m2</i>	<i>P6m2</i>	<i>P6m2</i>	<i>P6m2</i>
Z	1	1	1	1	1
R_{wp}	8.30	7.52	7.91	8.53	9.12
S	1.45	1.05	1.23	1.26	1.31

Table 4
Indexing result of $(W_{0.5}Al_{0.5})C$

No.	<i>I</i>	$d_{(exp)}$ (nm)	$d_{(cal)}$ (nm)	(<i>hkl</i>)
1	51.4	0.2843	0.2840	(001)
2	100.0	0.2520	0.2517	(100)
3	95.6	0.1884	0.1884	(101)
4	17.0	0.1454	0.1453	(110)
5	6.0	0.1420	0.1420	(002)
6	22.0	0.1294	0.1294	(111)
7	9.9	0.1259	0.1258	(200)
8	16.9	0.1236	0.1237	(102)
9	11.0	0.1150	0.1150	(201)

it can be concluded that Al substitutes the lattice site of W when it dissolves into WC. The SOF for various compositions show a close match to their formulation $(W_{1-x}Al_x)C$, which were deduced from the starting

materials. The cell parameters for every composition are very close to that of WC, and no evidence has been found that the cell volume is enlarged with the increased aluminum content, which is quite consonant with the result of Fig. 2 in which no obvious peak shift has been observed with the increase of aluminum content. This is possibly because the atomic radius of Al is modified to be very close to that of W in the cell of $(W_{1-x}Al_x)C$.

3.4. Density

Table 5 shows the experimental densities of the several compositions. The results show a close match to the theoretical densities as shown in Table 3. It also shows that all these prepared compounds are lighter than pure WC (15.63 g/cm³) [15]. The measured density is more consistent with a substitutional solid solution

Table 5
Experimental densities of $W_{1-x}Al_xC$

Stoichiometry	$(W_{0.90}Al_{0.10})C$	$(W_{0.75}Al_{0.25})C$	$(W_{0.50}Al_{0.50})C$	$(W_{0.25}Al_{0.75})C$	$(W_{0.14}Al_{0.86})C$
Density (g/cm^3)	14.145	12.353	9.376	6.271	4.763

than an interstitial solid solution [16], so the values of the density decrease remarkably with increasing concentration of Al.

4. Summary

In our present work, the first example of solid solution of other metals in WC with the stoichiometry $(W_{1-x}Al_x)C$ ($x = 0.10, 0.25, 0.50, 0.75, 0.86$), has been synthesized by carbonation of the precursors $W_{1-x}Al_x$ at about 1673 K for nearly 24–120 h. $(W_{1-x}Al_x)C$ belongs to the WC structure type and crystallizes in the hexagonal space group $P6m2$. Al atoms were identified to substitute the lattice site of W comparable to the cell of WC. The cell parameters of the prepared solid solutions were close to that of WC, while their densities were much lower. Considering the lower operating costs and the simple technology, the new solid solutions are expected to be the new cemented carbides with lower density and may have the potential to replace the standard materials for cutting tools, and wear parts, and so on.

Acknowledgments

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