

BEHAVIOR OF TUNGSTEN CARBIDE IN WATER STABILIZED PLASMA

V. Brožek, J. Matějčíček, K. Neufuss

Abstract

Tungsten carbide powder was processed by water stabilized plasma, generated by IPP's WSP® plasma torch, which can reach exit temperatures up to 28000 K. Oxidation of the molten carbide was prevented by a nitrogen protective atmosphere, during deposition onto substrates placed immediately above the liquid nitrogen level. Analysis of both deposits and solidified free-flight particles determined the W:W₂C:WC ratios and their mechanical properties, especially in dependence on the feedstock particle size.

Keywords: *water stabilized plasma, tungsten carbide, tungsten hemicarbide, plasma spray deposition, decarburization*

INTRODUCTION

Tungsten carbide WC is an important and irreplaceable material in applications like high speed cutting or high pressure forming. Its main disadvantages are complex phase behavior, decomposition to W₂C at high temperatures, etc. Thus, tungsten carbide parts can be produced only by sintering with (mostly cobalt-based) binders; in this way, however, many unique properties of WC are not utilized efficiently [1].

During spheroidization or thermal spraying of tungsten carbide powders, the particles are heated above 2776°C, at which irreversible decomposition occurs. When the resulting melt cools down below 2710°C, it decomposes to a WC + W₂C solid mixture, with further decarburization to a W + W₂C mixture [2]. Decarburization takes place mostly during the initial heating phase, by a carbon diffusion toward the surface of the molten particles and by a reaction with the plasma and the ambient atmosphere. During the flight in the plasma jet, many complex kinetic, chemical and aerodynamic processes take place, ending with a rapid quenching. Dwell time of the molten WC particle depends on many factors, e.g., particle size, weight, injection location and velocity and carrier gas or other transport medium. It is very difficult experimentally to cover all the "degrees of freedom". Therefore, we concentrated on a systematic investigation of the behavior of chemically reactive particles in a plasma jet. The first experiments were performed in water stabilized plasma, generated by Czech plasma torch WSP® PAL 160.

EXPERIMENTAL

Tungsten carbide, produced by Sylvania Tungsten s.r.o. Bruntál and sieved to +32 µm – 63 µm (Fig.1), and 63-100 µm in a single case, was used for plasma spraying.

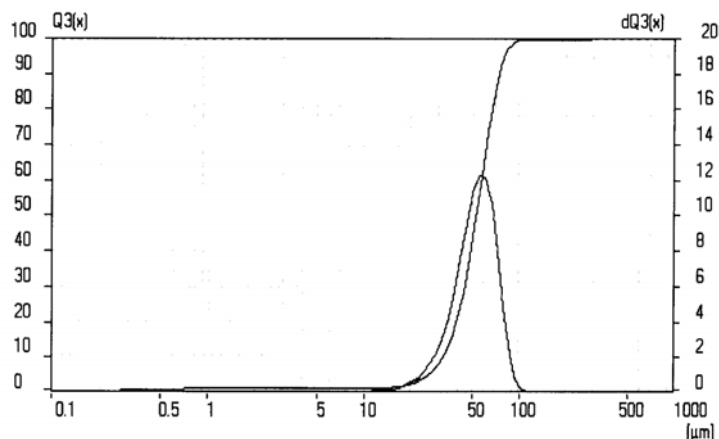


Fig.1. Particle size distribution of the WC feedstock.

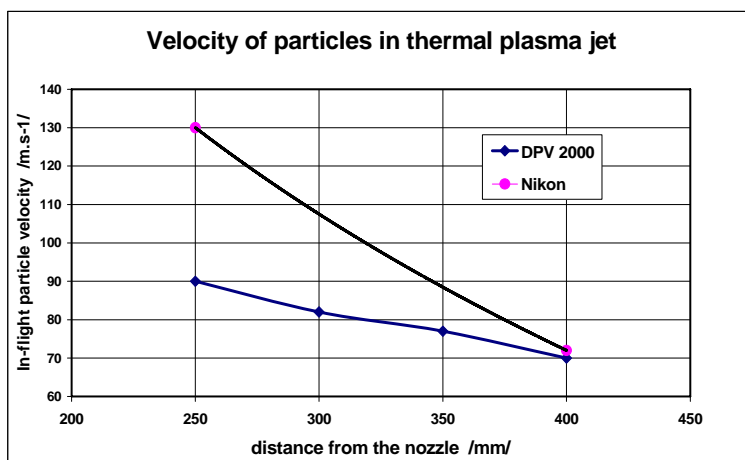


Fig.2. Velocity of the particles in thermal plasma jet.

The WSP® generator, operating on the Gerdien arc principle, produces at 160 kW power plasma with temperatures 25 – 28000 K and velocities up to 900 m/s at the nozzle exit (Table 1). In-flight particle trajectories of WC feedstock were observed optically - by a TV Nikon camera at 1/1,000 s and 1/2000 s exposure times - and also by the DPV 2000 sensor (Tecnar Automation, Canada) using the time-of-flight method. Their velocities were determined at 250 mm and 400 mm from the nozzle exit (Fig.2).

Tab.1. Technical parameters of tungsten carbide deposition by WSP®.

Arc current	[A]	500	Plasma medium mass flow	[g/s]	0.285
Arc voltage	[V]	278	Axial density	[g/m ³]	0.98
Power	[kW]	139	Axial temperature	[K]	26000
Useful power	[kW]	93	Feed rate	[kg/h]	45

Free-flight particles were captured directly into liquid nitrogen; deposits were produced on steel substrates placed immediately above the level, surrounded by an atmosphere of evaporating nitrogen. The free flight particles were sieved into different fractions and the composition of both types of samples was analyzed by X-ray diffraction. E-modulus of the deposits was determined from the load-depth curves during indentation on a Shimadzu Murasakino (Kyoto, Japan) instrument. Carbon content was determined by chemical elemental analysis after combustion of samples in an O_2 atmosphere at $1100^\circ C$. Thus the formed carbon dioxide was detected by TCD in an Elementar Vario III (Hanau, Germany) device.

RESULTS AND DISCUSSION

During melting and the subsequent cooling, tungsten carbide decomposes into W_2C and free carbon, which can diffuse towards the melting surface. Superheated carbon and also tungsten can evaporate in the plasma jet or react chemically with the plasma forming media. The molten particles can also react with the surrounding atmosphere upon leaving the plasma. To prevent the often undesirable oxidation, spraying can be performed in a hermetically closed chamber, gas shrouding of the jet can be applied, or the products are captured in water or liquid nitrogen. Efficient enclosure of the WSP® is technically difficult; shrouding by argon, helium or acetylene proved to be inefficient for the spraying of tungsten carbide. Therefore, during our experiments, we focused on capturing the free-flight particles in liquid nitrogen; also, the substrates for obtaining deposits were placed immediately above an open Dewar vessel (see Fig.3).

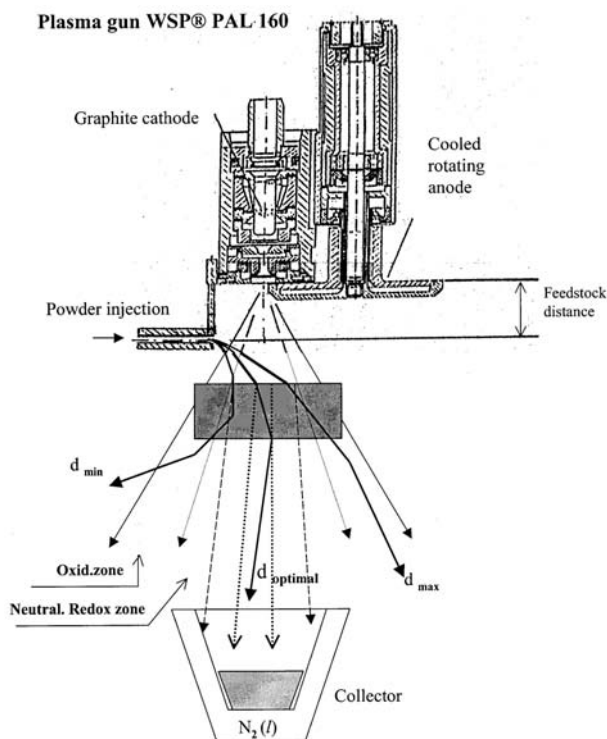


Fig.3a. Schematic of the plasma spraying setup, showing particle trajectories in the plasma jet.



Fig.3b. Photo of the actual spraying run.

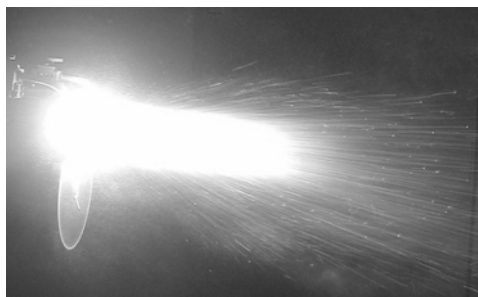


Fig.3c. Detail of the actual spraying run.

X-ray analysis of particles and deposits

Photos of spheroidized particles and plasma sprayed deposit are shown in Fig.4 and Fig.5. Diffractograms of free-flight particles in Fig.6 show a mixture of W and W_2C . Fig.6a shows dominant reflections of elemental tungsten; from the intensity of the remaining lines, a content of 2-5 % W_2C could be estimated. The diffractogram in Fig.6c shows the phase composition of a surface deposit. Its W: W_2C :WC ratio was estimated as 30:50:20. A cross-section of this deposit is shown in Fig.5. More accurate composition results from the bonded carbon analysis and density measurements are in Table 2.

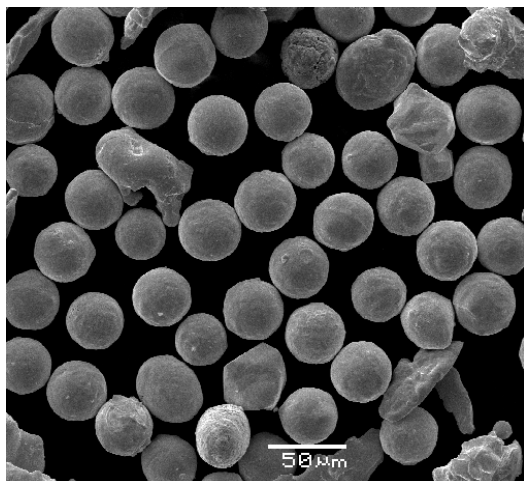


Fig.4. Photo of spheroidized particles.

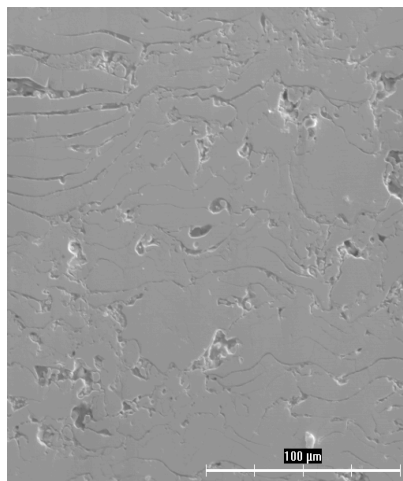
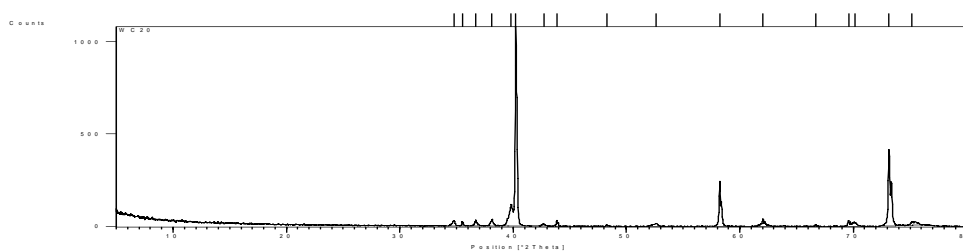


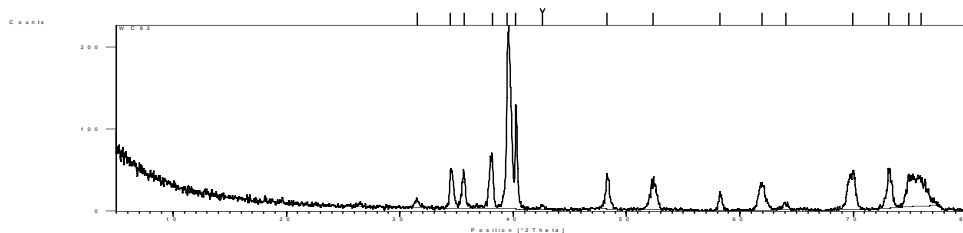
Fig.5. Cross-section of plasma sprayed deposit.



Diffractogram of <20 μm free flight particles

Peak List	
89-3659	
65-3896	
41-1230	
73-0471	

Peak list with powder diffraction standards 89-3659 = W, 65-3896 = W_2C ,
41-1230 = WO_3 , 73-0471 = WC



Diffractogram of a deposit surface

Fig.6. X-ray diffraction patterns and identification of the phases present in the samples.

Figure 6a Diffractogram of $-20\ \mu\text{m}$ free flight particles, fig.6b Peak list with powder diffraction standards 89-3659 = W, 65-3896 = W_2C , 41-1230 = WO_3 , 73-0471 = WC, Fig.6c Diffractogram of a deposit surface.

Tab.2. Analysis of bonded carbon and density in dependence on the final size of free-flight particles.

	WC feedstock 32 – 63 μm	Diameter of free-flight particles				
		+ 63 μm	63-40 μm	40-20 μm	- 20 μm	- 5 μm
C [wt. %]	6.13	3.60	3.09	0.31	0.27	0.0
Density [g/cm ³]	15.596	16.068	16.849	17.794	18.335	18.505

An analysis of the spheroidized tungsten carbide powder showed marked changes in chemical and phase composition, especially in dependence on particle size. In sub-micron (or, as they are fashionably called [a la mode], nanometric) particles, the bonded carbon content is reduced to nearly zero and increases with particle diameter. Nanometric particles consist of almost pure tungsten, while larger ones consist of a homogeneous $\text{W}+\text{W}_2\text{C}$ mixture. From this conclusions can be drawn about the tungsten carbide decomposition and carbon transport in molten carbide under extreme conditions of plasma melting and deposition onto solid substrates. The results are interesting in that they show the creation of “auto-shrouding”. The tungsten and tungsten carbide particles flying in the plasma are surrounded by a protective CO atmosphere, in a fashion similar to burning the cover plates of a space shuttle. The presence of atomic and ionized hydrogen from a plasma forming medium, characterized by a high H_β spectral intensity, can have a positive effect as well. A suitable choice of the WC feedstock size allows one to control the final composition of the deposit or the spheroidized powder. An important parameter in this regard is the dwell time of the particle in the variable temperature field of the plasma. The in-flight particle velocity depends on the powder size, carrier gas flow and injector angle. From the measured velocity (70 m/s or more – Fig.2), the dwell time was determined to be 5-6 ms. From the tabulated values of thermal conductivity of W and WC (W_2C data were not available), diffusion and reactive diffusion coefficients in the W-C system can be estimated. Considering that W has practically the highest activation energy of spontaneous diffusion, 506 kJ/mol, it is clear that the diffusion of carbon, likely to have lower activation energy, will be the controlling phenomenon in the decarburization of tungsten carbide in the plasma. Diffusion and reactive diffusion coefficients of carbon are known for a majority of transition metals whose carbides are industrially important. Data for the W-C system were not available; however, it is known that reactive diffusion coefficients are at least an order of magnitude higher than the diffusion coefficient of carbon in IV.A and V.A group metals. With increasing activation energy, the diffusion mobility of carbon atoms in the metal lattice decreases. Its estimate for W in the 3000-3500 K range is $9 \times 10^{-4}\ \text{m}^2\text{s}^{-1}$ [7]. If the dwell time is $5 \times 10^{-3}\ \text{s}$, then the mean diffusion distance $x=(2Dt)^{1/2}$ will be 3 mm. Experimental results indicate a much lower value of D though, or a higher temperature of the smaller free flight particles.

From a starting WC powder of a 63-100 μm size, processed by water stabilized plasma, all three phases are present, i.e., WC, W_2C and W. Products from the $<40\ \mu\text{m}$ particles contain only two phases, W and W_2C , and a minute amount of carbon (under 0.27%). The W_2C content, determined by a quantitative X-ray analysis, corresponds with the analytically determined bonded carbon content. Therefore, all carbon from the thermal

decomposition of WC diffused to the surface and reacted with the ambient atmosphere. The density of the products is higher than that of pure W_2C , 17.2 g/cm^3 . Particles produced smaller than $5 \text{ }\mu\text{m}$ are practically composed of pure tungsten (carbon and ditungstencarbide content were below the detection limit). Still, the density of these particles reaches 18.5 g/cm^3 only, pure tungsten density being 19.3 g/cm^3 . On a metallographic cross-section of the particles, closed micropores were observed. These were possibly formed by a mixture of hydrogen from the plasma in high turbulence regions.

Mechanical properties of the deposits are influenced by the W: W_2C ratio. Microhardness is homogeneous in the entire sample volume. Its values for samples with 3.09% bonded C were HV 14.89-16.22 GPa; for the fine-grain products with a carbon content less than 0.27 % they decrease to HV 13.6 GPa – this corresponds approximately to the arithmetic average of the individual components' hardnesses. E-modulus reaches values 340-360 GPa and decreases to 233 GPa for the fine-grained structure. Figure 7 shows an example of the measurement of the Young modulus for the sample containing 3 phases – W, W_2C and unreacted WC- whose ratio from X-ray analysis is about 30:50:20 % (see diffractogram in Fig.6c).

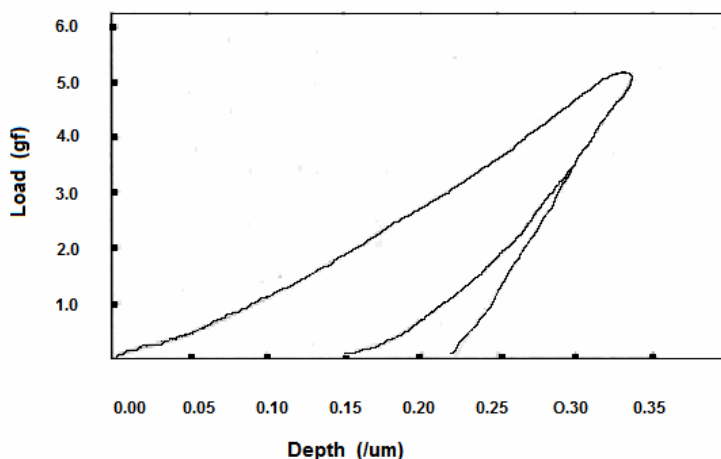


Fig.7. Example of a load-depth curve for the determination of Young's modulus and microhardness (Shimadzu Murasakino instrument).

CONCLUSIONS

By plasma spraying WC using water stabilized plasma, spheroidized particles or thick deposits could be produced. Spheroidal particles smaller than $23 \text{ }\mu\text{m}$ consist of only two phases: W and W_2C . The W_2C content decreases and the W content increases with the decreasing diameter of the free flight particles. The deposits were composed of a homogeneous W + W_2C mixture and residual WC; their ratio depends on the size of the starting WC powder. Carbon freed from the monocarbide decomposition to ditungsten carbide and tungsten contributes to the formation of a protective CO atmosphere.

The auto-shrouding effect of WC can also be applied to improve the plasma spray deposition of pure tungsten. Recent experiments show that tungsten particles readily oxidize and the oxide forms a cloud that hinders further heating and melting of the particles. With a suitable admixture of WC powder, this problem can be suppressed. As the

carbon from the carbide oxidizes, ambient oxygen is consumed and its access to tungsten is reduced. Improved tungsten melting was observed; the deposits contained less oxide than those from pure tungsten, and only minute amounts of W_2C [6].

Acknowledgment

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