



TUNGSTEN CARBIDE BASED CLADDING MATERIALS

A.P. ZHUDRA

E.O. Paton Electric Welding Institute, NASU

11 Bozhenko Str., 03680, Kiev, Ukraine. E-mail: office@paton.kiev.ua

The paper presents materials for cladding by composite alloys based on tungsten carbides. Brief description of the technology of producing special cladding hard alloys of type, macrocrystalline tungsten carbide, fused tungsten carbide WC + W₂C with crushed, surface-melted and spherical granules is given. Process schematic and unit for thermocentrifugal sputtering of refractory compound ingots with application of plasma arc as the heat source is described. Comparative data are given on hardness, chemical and stoichiometric compositions of tungsten carbide granules produced by different technologies. Macrostructures of composite layers, produced by the method of plasma-powder cladding, are shown. Schematic and macrostructure of a layer produced by the method of induction furnace impregnation is given. Commercial grades of powders of fused tungsten carbides in spherical granules and main grades of strip relit are presented. 22 Ref., 3 Tables, 8 Figures.

Keywords: tungsten carbides, relit, composite alloys, cladding, spherical granules, oxy-acetylene cladding, plasma cladding, thermocentrifugal sputtering, strip relit

High wear-resistance of deposited composite alloys with metallic matrix, strengthened by tungsten carbides, led to their wide acceptance for equipment protection from various kinds of intensive wear. This is related first of all to unique properties of reinforcing phase of such alloys, namely tungsten carbides. The most widely accepted by industry is tungsten monocarbide WC with 6.13 % C stoichiometry. It features high hardness of HV 2200, compressive strength of 5–7 GPa and modulus of elasticity of 700 GPa, while preserving its mechanical properties in a broad temperature range, is resistant to friction corrosion and is capable of forming a strong bond with metals [1, 2]. Tungsten carbide is much harder and performs much better under the conditions of wear and corrosion and high impact loads than martensite, ferric and chromium carbides. It is widely used in production of a number of steel grades, and in cladding in manufacture of flux-cored wires, strips and electrodes.

Moreover, WC monocarbide is the main component of sintered hard alloys of VK type, produced by powder metallurgy. Sulzer Metco WOKA, H.C. Starck, C&M Technologie, DURUM VERSCHLEISS-SCHUTZ (Germany), REED TOOL, KENMETAL (USA), Beijing Advanced Materials, BAM (China), Volgoburmash (Russia) and many other companies manufacture special metal-ceramic particles of VK-6 type of an oval shape (Figure 1, a) for drill tool strengthening [3, 4]. The process of manufactur-

ing such materials consists in long-time mixing of fine carbide particles with cobalt or nickel binder, preliminary low-temperature sintering under pressure, and then final sintering at the temperature of 1350–1600 °C in vacuum or hydrogen atmosphere. Here shrinkage and compaction at sintering practically eliminate porosity [5].

Tungsten carbide is sometimes mixed with other hard carbides to improve their properties. For instance, titanium carbide and tantalum or niobium carbides are sometimes used for improvement of chemical and thermal stability, as well as for preservation of high-temperature hardness.

Volume fraction and size of carbide particles can change, depending on requirements, and over the recent years a tendency of application of nanocrystalline carbide particles has been observed, which are effective for improvement of alloy wear resistance.

Many companies recommend crushed scrap of metal-ceramic alloys of VK or VN type for strengthening components for mining and metallurgical industry [3, 6]. Owing to their relatively high strength, such materials are particularly important in those cases, when application of particles of 1.5 mm and greater size is required.

Over the recent years, DURUM VERSCHLEISS-SCHUTZ, Sulzer Metco WOKA, BAM and other companies have been widely advertising the so-called macrocrystalline tungsten carbide. This is granulated powder (Figure 1, b) with predominantly up to 200 μm granule size, containing 6.13 % of total carbon, 0.03 % of free carbon and up to 0.15 % of impurities, mainly, iron [3, 4].

Macrocrystalline tungsten carbide is used predominantly for plasma-powder cladding in com-

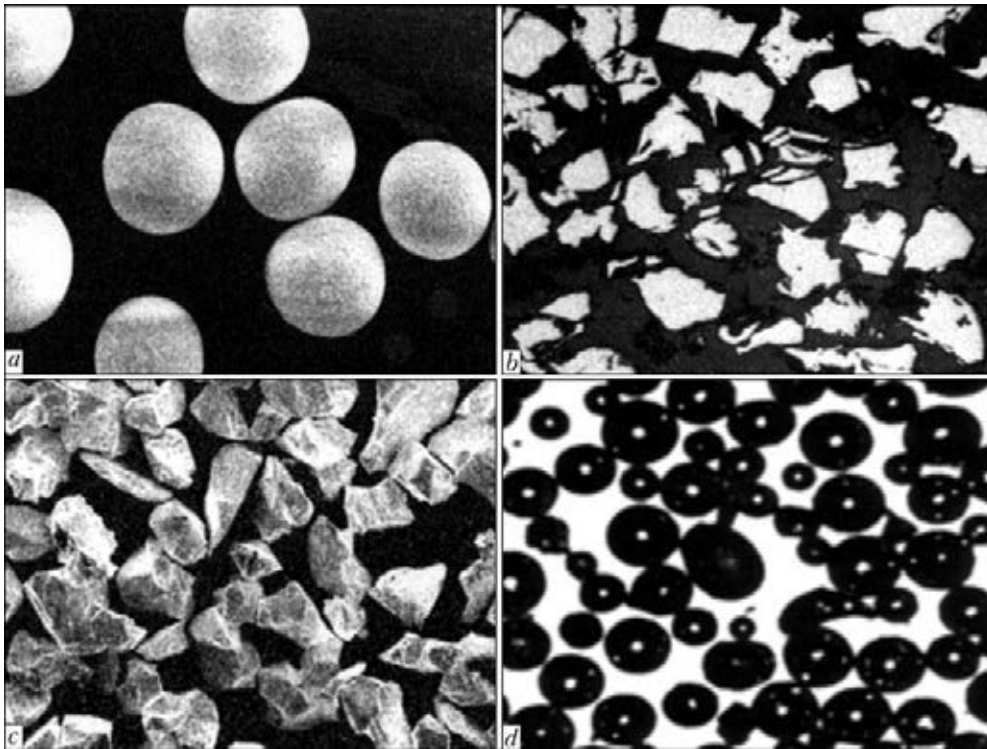


Figure 1. Cladding consumables from tungsten carbides produced by different methods: *a* – VK-6 alloy granules; *b* – macrocrystalline WC; *c* – crushed fused WC + W₂C; *d* – surface-melted WC + W₂C

bination with nickel-based matrix alloy. Its application is the most promising under abrasive conditions with small angles of incidence and low surface stresses. All the above-mentioned materials have become accepted to varying degrees in different industries.

Nowadays, however, fused tungsten carbide – relit (Figure 1, *c*) is the most widely accepted material as the reinforcing phase to produce highly wear-resistant composite layers. This is eutectic alloy of tungsten mono- and semicarbide WC + W₂C with 2735 °C melting temperature and microhardness from *HV* 1000 up to *HV* 2400, depending on manufacturer [1, 7].

Mostly cast tungsten carbide is used in the form of grit produced as a result of crushing of ingots, melted in Tamman resistance heating furnaces at 3100 °C. After sieving by fractions, the produced powder is used for plasma-powder induction or furnace cladding. For oxy-acetylene cladding so-called tubular-grain relit was used for a long time, and over the recent years strip relit has been used.

Alongside the high hardness and strength, fused tungsten carbide also has several disadvantages, related to the technology of producing it. A considerable part of grains features non-uniform composition, has characteristic casting defects, cracks and non-equiaxiality. In the long run this is negative for performance of deposited composite layers. In this connection, a continu-

ous search for the ways to improve this material is going on worldwide.

Considering intense development of plasma-powder cladding processes over the recent decade, an important factor is spherical shape of powder particles, which ensures maximum looseness and stable operation of metering devices, respectively. At some time, US and Canadian specialists [8–11] developed an induction-plasma technology of producing spherical particles of fused tungsten carbide. It consists in surface melting of earlier prepared crushed grains during their passage through induction plasma column. As a result, particles of a spherical shape with preserved chemical composition are produced (Figure 1, *d*). To avoid losses due to particle overheating and their subsequent evaporation, thorough optimization of melting and spheroidization processes is required that involves development of expensive computer programs. Other disadvantages of this technology include higher power cost, need for preliminary crushing of ingots, large amount of wastes (non-spherical particles) of up to 30 % and size limitation predominantly to 200 μm that significantly narrows the area of its application.

PWI developed and has successfully implemented on production scale technology of thermocentrifugal sputtering of ingots of fused tungsten carbide, which allows producing powder with spherical particles of 50 μm to 1000 μm size

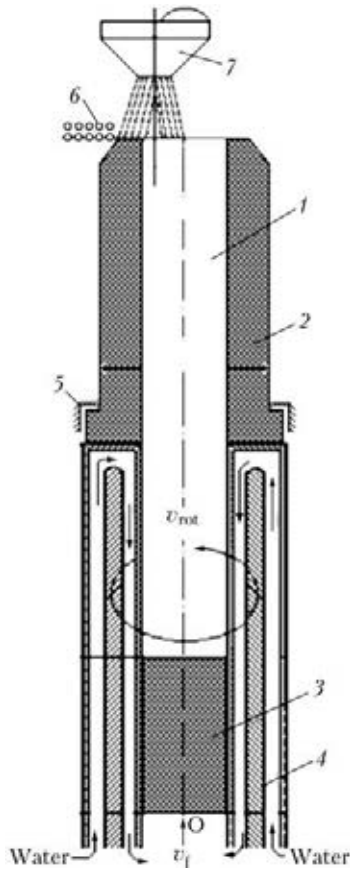


Figure 2. Schematic of thermocentrifugal sputtering of refractory compounds using plasma arc as the heat source; 1 – sputtered rod; 2 – graphite bushing; 3 – graphite pusher; 4 – water-cooled shaft; 5 – component of graphite bushing connection with the shaft; 6 – liquid metal drop; 7 – direct-action plasmatron

[12, 13]. Schematic of the process of thermocentrifugal sputtering is shown in Figure 2. With this method, the edge of quickly rotating blank is surface-melted in a vacuum chamber filled with inert gas, and the formed melt under the impact of centrifugal forces comes off the ingot periphery and is spheroidized in flight. Owing to repeated remelting, alloy composition is homogenized, content of

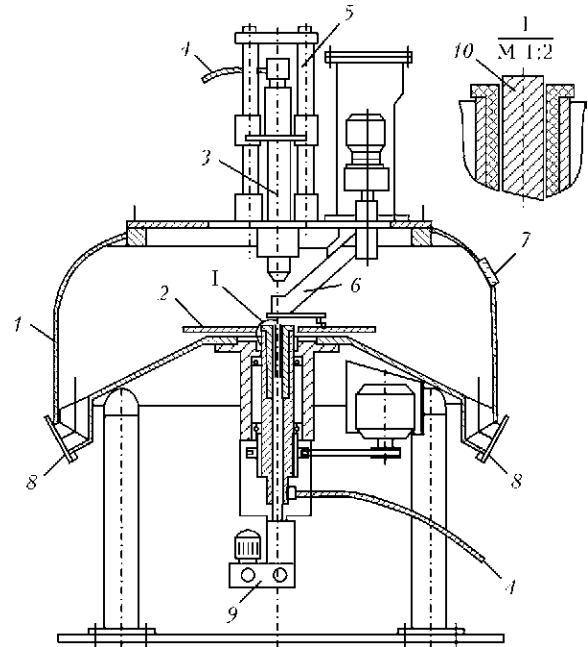


Figure 3. Schematic of unit for ingot sputtering: 1 – chamber case; 2 – spindle component; 3 – plasmatron; 4 – current contact jaw; 5 – plasmatron adjustment mechanism; 6 – rod loading mechanism; 7 – viewing window; 8 – finished product collectors; 9 – rod feed mechanism; 10 – sputtered rod

free carbon and foreign matter is reduced. Figure 3 shows the schematic of the unit to produce spherical granules of tungsten carbide by the method of thermocentrifugal sputtering [12].

Produced granules have perfect spherical shape, stable stoichiometric composition, fine globular structure and, as a result, hardness higher than $HV\ 3000$ and high strength. The technology ensures producing specified grain-size composition of powder particles in a narrow range of dimensions and presence of wastes (non-spherical component) in the range of 5–8%. Appearance and macrostructure of spherical granules of tungsten carbide are shown in Figure 4.

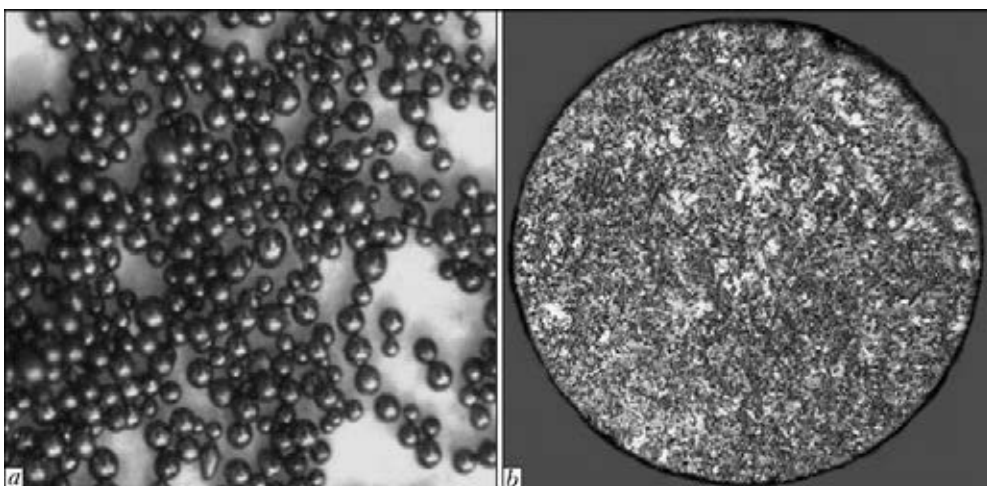


Figure 4. Appearance (a) and macrostructure (b) of spherical granules of tungsten carbide



Table 1. Composition and properties of tungsten carbide with spherical and crushed granules

Chemical composition (wt.%) and characteristics	Spherical	Crushed
Tungsten	94.5–95.5	94.3 (min)
Total carbon	3.8	0.1–3.8
Free carbon	0.02–0.05	0.1 (max)
Iron	0.1–0.3	0.5 (max)
Impurities (Cr, V, Nb, etc.)	0.5–0.8	1.2 (max)
Hardness <i>HV</i>	2800–3100	2000–2200
Microstructure	High-quality, acicular, globular	Acicular
Yield, 50 g/s	7.2–8.0	10.5–12.0
Density, g/cm ³	10.0–10.8	7.6–8.4
Wettability	Excellent	Excellent

Table 2. Phase composition and hardness of tungsten carbide produced by different technologies

Kind of particles	C, %	Phase	Phase content, wt.%	<i>HV</i>
Crushed	3.9	WC	36.20	1800–2300
		W ₂ C	63.80	
Macrocrystalline	6.0	WC	95.42	1900–2150
		W ₂ C	4.08	
Spherical (surface melting)	3.9	WC	31.12	1900–2800
		W ₂ C	57.20	
Spherical (sputtering)	4.0	WC	22.66	2600–3300
		W ₂ C	77.34	

Table 1 gives the composition and properties of fused tungsten carbide with spherical and crushed granules.

Investigations revealed that unique hardness and increased strength characteristics of spherical tungsten carbide granules are largely dependent on stoichiometric composition of WC + W₂C eutectic alloy. Maintaining it in the range of 78–82 % W₂C–18–22 % WC in combination with fine-grained macrostructure, which forms as a result of high solidification rates, ensures granule microhardness above *HV* 3000.

Table 2 gives the data on phase composition and hardness of tungsten carbide granules, pro-

duced by different technologies, which are indicative of the advantages of material manufactured by thermocentrifugal sputtering [14].

Moreover, spherical granules are much less susceptible to the process of dissolution in steel matrix at deposition of composite layers. This is an extremely important aspect, as at penetration of tungsten carbides into a liquid matrix melt tungsten and carbon diffusion takes place with subsequent formation of complex ferric-tungsten carbides, which lead to essential embrittlement of the matrix [15–17].

As was noted earlier, in addition to high hardness and strength, tungsten carbide powder in

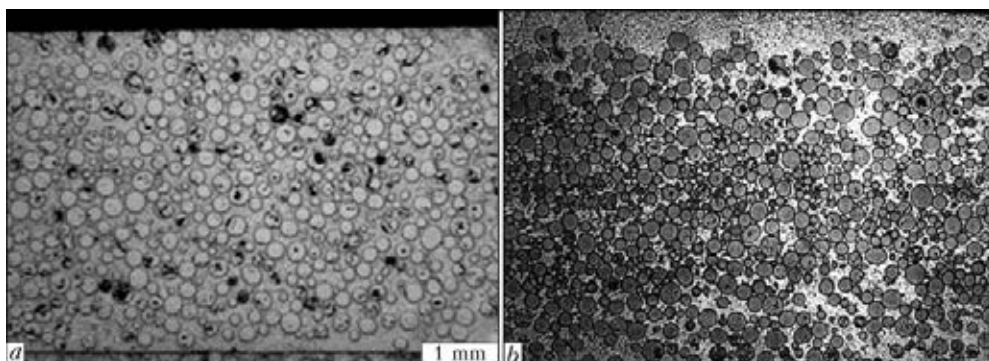


Figure 5. Macrostructure of composite layer deposited by plasma-powder method: *a* – C-Fe-V-Cr matrix + 50 % WC + W₂C; *b* – Ni-Cr-Si-B matrix + 50 % WC + W₂C

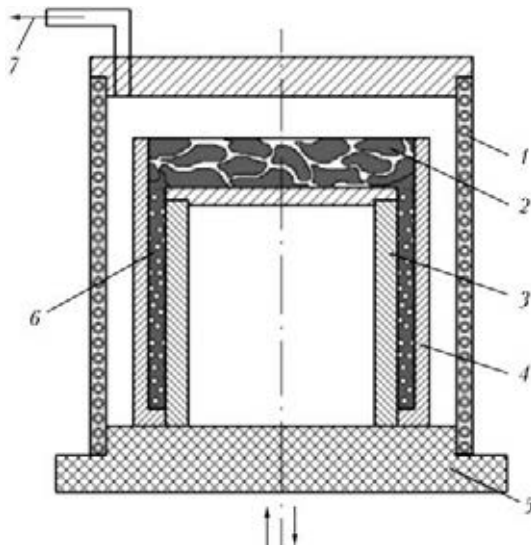


Figure 6. Schematic of induction furnace cladding (impregnation method): 1 – inductor; 2 – material for binding composite alloy (German silver); 3 – part for cladding; 4 – technological shell; 5 – furnace hearth; 6 – deposited composite alloy; 7 – pumping down system

spherical granules also has high flowability that predetermined its broad application in plasma-powder and laser cladding [18, 19]. These processes ensure feeding of matrix and reinforcing powder into the weld pool so as to minimize the thermal impact on tungsten carbide particles and, thus, prevent their dissolution. Reinforcing phase concentration in the deposited layer higher than 50 % is achieved here.

Figure 5 shows macrostructures of composite alloys on nickel and iron base reinforced by spherical granules of tungsten carbide.

In addition to traditional cladding methods, it is widely applied in powder metallurgy, when manufacturing composite layers by the method of impregnation of pre-compacted granules of

tungsten carbide powder by matrix melt. Figure 6 shows a schematic of induction furnace cladding by impregnation method. Composite alloys produced by such a technology, feature unique wear resistance owing to a high concentration of reinforcing phase in the alloy. This process has become widely accepted in manufacture of slide bearings of submersible drive oil pump units and other components of drilling equipment. Figure 7 shows the appearance of a bushing and macrostructure of the deposited layer, produced by impregnation in induction vacuum furnace.

Commercial production of tungsten carbide in spherical granules by thermocentrifugal sputtering method was organized in Ukraine at the end of the previous century. Unique equipment was developed, technology of sputtering and screening of the produced material by particle size and removal of non-spherical component was developed. Volume of annual manufacture of the material is within 25–30 t. It is successfully exported to leading companies of European countries, USA and Russia. Particle-size distribution of cast tungsten carbides is within 0.04–2.50 mm and it has the designation of PKVS (i.e. fused spherical tungsten carbide) [20].

A large fraction of fused tungsten carbides, both with crushed and with spherical granules, is used in cladding of drilling tools. Strip relit has become widely accepted for these purposes

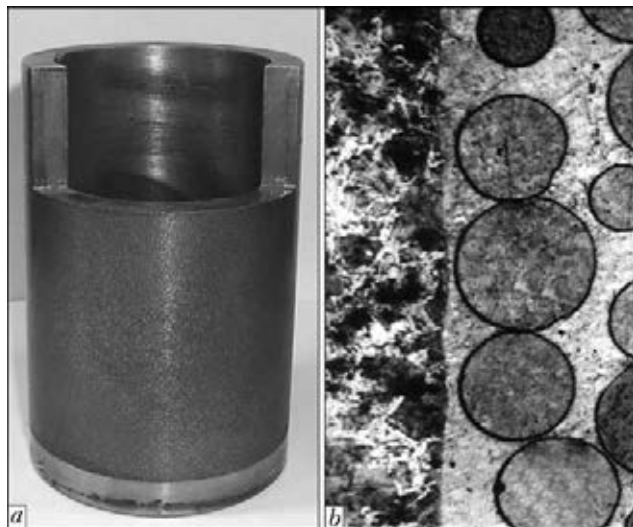


Figure 7. Appearance of bushing (a), and macrostructure of deposited layer produced by impregnation in induction vacuum furnace (b)

Table 3. Main strip relit grades

Grade	Size of particles of main relit fraction, mm	Dimensions, mm		Marking (colour)
		B = 0.5	H = 0.3	
LZ-4-6 LS-4-6	0.28–0.45	6	3	White
LZ-6-7 LS-6-7	0.45–0.63	7	3	Yellow
LS-8-7	0.63–0.80	7	3	Orange
LZ-11-7 LS-11-7	0.63–1.10	7	3	Green
LSZ-6/4-7	0.45–0.63-S 0.28–0.45-Z	7	3	Red
LSZ-8/4-7	0.63–0.80-S 0.28–0.45-Z	7	3	Brown
LSZ-8/6-7	0.63–1.10-S 0.45–0.63-Z	7	3	Blue
LSZ-11/4-7	0.63–0.80-S 0.28–0.45-Z	7	3	Light blue
LSZ-11/6-7	0.63–0.80-S 0.45–0.63-Z	7	–	Violet

Note. Overlap of not less than 1 mm; length of 670 ± 5 mm; S – spherical; Z – granular (crushed) tungsten carbide.



Figure 8. Section (1 – shell; 2 – WC + W₂C; 3 – charge) (a), and appearance of strip relit in rods (b) and bundle (c)

in Ukraine and CIS countries. This material is a strip, inside which relit granules with a complex of de-oxidizing alloying and fluxing components are packed [16, 21]. Depending on requirements to deposited layer, the composition of this material can include crushed or spherical tungsten carbide grains or their mixture. The material is manufactured in the form of rods for gas cladding or continuous strip electrode in case of its application as filler material in mechanized plasma cladding. Appearance of strip relit in the form of rods or in a bundle is shown in Figure 8, and Table 3 gives commercial grades of strip relit rods [22].

Cones and blades of drill bits, connecting elements of drill strings, calibrators and a number of other types of drilling tools are clad by strip relit. Moreover, it has become applied in strengthening components of crushing equipment, road-construction machinery and various kinds of screws. In metallurgical industry strip relit is used for cladding valves, cones and bowls of blast furnaces, thus ensuring the maximum interrepair cycle.

Note that unique properties of fused tungsten carbides are by far not exhausted. Work on its improvement by alloy doping with elements of transition metal group already at the initial research stage allowed producing granules with hardness exceeding HV 3000. Results of this work will be presented in subsequent publications.

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