U.P.B. Sci. Bull., Series B, Vol. 87, Iss. 4, 2025 ISSN 1454-2331

THEORETICAL AND PRACTICAL ASPECTS REGARDING THE OBTAINING OF GRANULES WITH A METASTABLE STRUCTURE BASED ON TUNGSTEN CARBIDES, INTENDED FOR THE PRODUCTION OF RELIT-TYPE ELECTRODES

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Experimental research has shown that by ultra-rapid cooling of the W-C alloy melt containing carbon within the limits of 3.8-4.11 % mass, granules with a structure outside thermodynamic equilibrium can be obtained that contain new, metastable phases, formed by a non-diffusion mechanism of the martensitic type, alongside which there may be separations of the tungsten-poor α-WC type phase that do not worsen the operating characteristics of the product (granule), provided that they precipitate at the boundary of the α' (β-WC)-α' martensite phase crystals. The microhardness of the product resulting from the rapid solidification of the melt (W-C), intended for the manufacture of the granulated material, used in the execution of RELIT-type electrodes, frequently reaches values of the order of 3000 HV0.1, reaching local values of approximately 3800 HV0.1.

Keywords: granules; W-C alloys; metastable structures; martensitic transformation; highly wear-resistant refractory coatings

1. Introduction

The development of the production of wear-resistant materials has brought to the forefront a series of innovations that have finally materialized through the emergence of new materials capable of exceptional performance in this field. Among these, it is worth mentioning the RELIT type composite materials (WC-W_2C alloy with eutectic composition: 78-80% mass W_2C and 20-22% mass WC), formed by hard tungsten carbides embedded in an iron-based metallic matrix, with

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a high carbon content, materials that have gained wide use in the manufacture of products that are highly stressed by abrasive wear, such as mining and oil drilling tools etc [1-5]. The technology of deposition by welding with the oxyacetylene flame of these materials required the manufacture of electrodes made of a steel pipe with a composition of max. 0.15%C, max. 0.65%Mn, max. 0.3%Si, max. 0.025%S, max. 0.025%P, iron difference up to 100 %, internal diameter of 4-5 mm and lengths of the order of 400-700 mm, into which granulated carbide particles were introduced, sorted by granulometry, with dimensions, depending on the destination, in the range of values 16-2500 µm [1]. By deposition with the oxyacetylene flame, the steel pipe material melts, and through diffusion it is enriched in carbon (taken from carbides), up to a content that makes the appearance of ledeburite possible. In this way, the tool intended for abrasive wear will have a layer made up of a hypoeutectic white cast iron on the outside and carbide grains inside. The relatively low hardness of tungsten monocarbide (HV0.1=1600-1800) and the tensile strength (below 300 daN/mm^2), respectively bending strength in the case of tungsten-rich carbide W_2C (below 500 daN/mm^2), make it impossible to use any of the two possible tungsten carbides alone, in their pure state. The solution of using a material whose phase composition corresponds to the simultaneous presence of both tungsten carbides was consequently adopted. The W-C system (Fig. 1) has been analyzed so far especially in connection with tungsten monocarbide, the carbide used for the production of sintered hard alloys intended for the production of cutting inserts by specific powder metallurgy methods, used for high-speed cutting operations. In the specialized literature, studies related to the formation of structures of materials based on double carbides obtained by granulating melts, directly, or by grinding the product obtained by solidifying the melt, are relatively rare, which is why the objective of this work is the analysis of the phase transformations that occur during the rapid cooling of tungsten and carbon melts with carbon contents within the limits of 3.1-4.1% mass.

2. Theoretical aspects regarding equilibrium in the W-C system: phases and phase transformations in the solid state

The W-C phase equilibrium diagram and the particularities of the main reactions that occur during slow cooling of alloys in this system are presented in Fig. 1, respectively Table 1.

The transformations of interest included in Table 1 are in agreement with [6], with corrections made within the stability range of tungsten carbide W_2C.

Regarding the equilibrium phases in the W-C system, it comprises two, namely WC and W_2C, each of which has several structural modifications, stable in certain temperature and concentration ranges (Fig. 1).

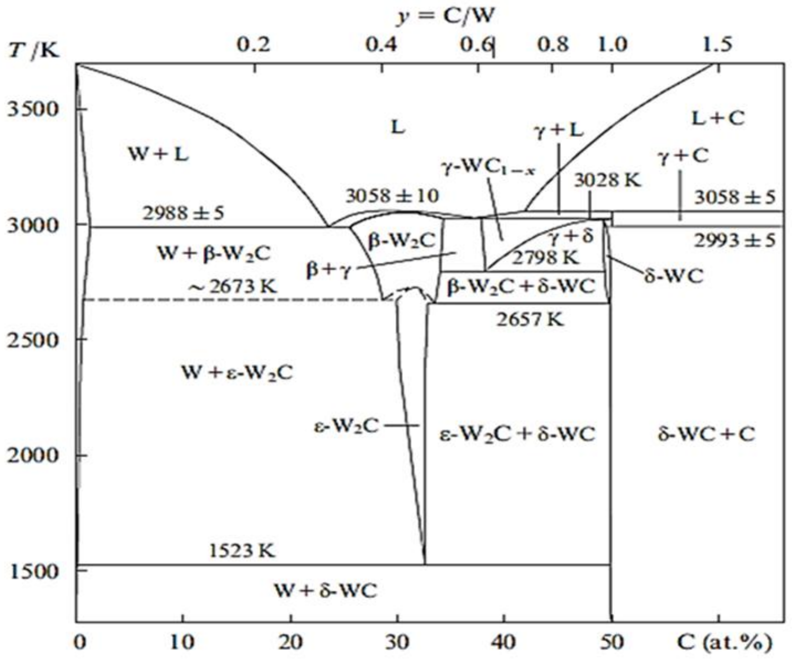

Fig.1 W-C phase equilibrium diagram [6]

Table 1

Transformations of interest in the phase diagram of the W-C system at temperatures above 1300 K [6]

Reaction	Composition of phases involved in the reaction (at. % of C)			T [K]	Reaction type
L ↔ W	0	0	-	3755 ± 5	melting
L ↔ β-W_2C	~30.6	~30.6	-	3058 ± 10	congruent melting
L + C ↔ γ-WC_{1-x}	~42.0	100	50	3058 ± 5	peritectics
L ↔ W + β-W_2C	~23.5	~1.2	~25.5	2988 ± 5	eutectics
L ↔ β-W_2C + γ-WC_{1-x}	~37.0	~34.3	~37.8	3028 ± 5	eutectics
γ-WC_{1-x} ↔ δ-WC	~49.3	~49.3	7	3008 ± 5	polymorphic transformation
γ-WC_{1-x} ↔ δ-WC + C	50	~49.8	100	2993 ± 5	eutectoid decomposition
γ-WC_{1-x} ↔ β-W_2C + δ-WC	~38.2	~34.0	~49.5	2798 ± 5	eutectoid decomposition
β-W_2C ↔ W + ε-W_2C	~28.6	~0.7	~29.7	2673 ± 10	eutectoid decomposition
β-W_2C ↔ ε-W_2C	~31.6	~31.6	-	2728 ± 10	disorder-order transformation
β-W_2C ↔ ε-W_2C + δ-WC	~33.5	~32.8	~49.8	2657 ± 10	eutectoid decomposition
ε-W_2C ↔ W + δ-WC	~32.6	0	50	1523 ± 5	eutectoid decomposition

The specialized literature reports four possible modifications for the lower tungsten carbide W_2C - three of these are β''-W_2C stable at low temperature, β'-W_2C at intermediate temperatures and β-W_2C at high temperatures, found in other sources [7-9] with other notations, respectively α, β and γ-W_2C. However, the structures of these modifications have been proposed based on limited experimental data [10, 11]. The structure of another modification designated as ε-W_2C [12] has been revealed by neutron diffraction studies. Tungsten-rich tungsten carbide (W_2C) is in reality a solid solution based on W_2C carbide, which melts congruently at 2795 °C [6]. It has the ability to dissolve small amounts of carbon (within the range of 2.34-3.16 % by mass).

In all W_2C modifications, the tungsten atoms form a hexagonal close-packed metallic sublattice, in which half of the octahedral interstitials are occupied by carbon atoms. These atoms are randomly distributed at high temperatures and are ordered at low temperatures. The possibility of forming several structural modifications of W_2C carbide is associated with the different types of distribution of carbon atoms [10].

The higher carbon content carbide, WC, with hexagonal structure is designated as δ-WC (α-WC [12] or simply WC [8, 9]); to these are added the tungsten carbides of α-WC_{1-x} [8, 9] or simply WC_{1-x} type. For the first time, tungsten carbide with cubic structure and a lattice parameter of 0.416 nm was synthesized by its deposition from the carbonyl vapor state of $W(CO)_6$ and described as a cubic modification of W_2C carbide [13].

3. Materials and Methods

Obtaining W-C granules with metastable structures (outside thermodynamic equilibrium) was possible by ultra-rapid cooling of melts of a mixture of tungsten and carbon black powders (between 3.8 and 4.11% mass); subsequently, the granules thus obtained were introduced into a carbon steel sheath (0.15%C), thus generating electrodes used to obtain very high hardness layers on the surface of certain categories of parts subjected to stresses resulting in intensive wear. The formation of granules with a metastable structure based on tungsten carbide intended for the production of RELIT type electrodes was carried out following this technology: after advanced homogenization (in ball mills made of sintered WC-Co hard alloys) of the mixture of tungsten powders with carbon black powder in a proportion of 3.8-4.11% mass, the mixture was melted in a graphite-enclosed furnace, with an installed power of 130 kVA (104 kW; T_{max} = 3000 °C) in an argon environment, a furnace produced by the MRF-USA company, equipped with graphite heating and thermal shielding elements. The furnace was modified so that once the melting temperature was reached, the melt could be released from its lower part, and the molten jet of the melt could be disintegrated with concentrated jets of argon gas, the resulting fragments falling into a (double-walled) pool with strongly recirculated water. Note: The movement of the fragments from the pulverization/disintegration pool into the water in the pool is also carried out in a neutral argon environment.

The tungsten powder used in the research, KW08, was purchased from Kennametal – USA, has a purity greater than 99.95 %, the proportion of oxygen contained is below 0.35%, the Scott density between 25 and 45 g/in^3 (1.56 – 2.74 g/cm^3) and an average diameter within the limits of 0.6-1.0μm.

The carbon black powder used in the research was purchased from Alfa Chemical Co Ltd-China, with an ash content below 0.1%, moisture below 0.5% and volatile substances below 1.5%.

The verifications of the obtained results aimed at the complex characterization of the granules resulting from the ultra-rapid cooling of the melts of the powdered mixtures of tungsten and carbon black (3.8-4.11% mass). Thus, the evaluation of the microstructure and distribution of tungsten on the section of the granules obtained by ultra-rapid cooling was carried out - using a Neophot microscope, respectively a Jeol microprobe and the microhardness was determined using a Vickers microhardness tester Leitz Miniload.

4. Results and discussions

Metallographic investigations (Fig. 2 and Fig. 3), carried out on samples of the eutectic $WC-W_2C$ alloy rapidly cooled from the molten state, have highlighted a predominantly acicular and not lamellar appearance, the form in which the eutectoid (ε-W_2C – δ-WC) should be presented.

The situation is due to the fact that, given the very high cooling rate of the melt and the solid solution δ-WC, the transformation that must ensure on the one hand very high hardnesses, and on the other hand their uniformity throughout the product volume, is not the eutectoid transformation, which should occur at a temperature of 2798K, $\gamma\text{-}WC_{1-x} \rightarrow \beta\text{-}W_2C + \delta\text{-}WC$, but the martensitic transformation $\gamma\text{-}WC_{1-x} \rightarrow \delta'\text{-}WC$ (diffusion-free transformation) [14]. The "diffusion-free" character of the γ-WC_{1-x} solid solution transformation becomes evident if we refer to the values of the diffusion coefficient of carbon in the γ-WC_{1-x} solid solution (table 2) and compare these values with those corresponding to the martensitic transformation in steels.

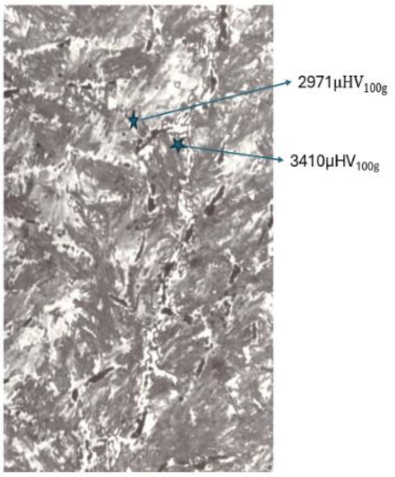

Fig. 2. Microstructure of WC-W_2C alloy with eutectic composition (RELIT), after ultrafast cooling from the liquid state, 500x; Murakami etching reagent

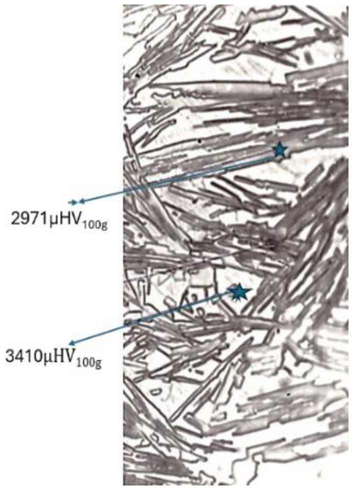

Fig. 3. Microstructure of WC-W_2C alloy with eutectic composition (RELIT), after ultrafast cooling from liquid state, 1000x; Murakami etching reagent

Table 2

Carbon diffusion parameters in the W-C system [3]

No	Temperature range in which the parameters were determined, °C	The phase in which diffusion occurs	Diffusion parameters D_0,cm^2/s	Diffusion parameters Q, J/mol
1.	1100-1600	δ-WC, ε-W_2C	$8.91\cdot10^{-2}$	223630
2.	1500-1880	δ-WC, ε-W_2C	$3.45\cdot10^{-3}$	158000
3.	1600-1700	δ-WC, ε-W_2C	$1.56\cdot10^{-3}$	434720
4.	1700-2050	δ-WC, ε-W_2C	$3\cdot10^{-3}$	523000
5.	1800-2800	Solid solution (β-W_2C)	$9.22\cdot10^{-3}$	168454

Martensitic transformation is possible in steels only if cooling avoids diffusion transformation in the pearlitic bend zone, located in the case of unalloyed steels in the temperature range 550-600 °C. The diffusion coefficient of carbon in austenite undercooled to this temperature range can be calculated with the Wells-Mehl relation [15]:

$$D_C^{\gamma} = D_0 \cdot e^{-\frac{Q}{RT}} = 0.07 \cdot e^{-\frac{133760}{8.31\cdot(600+273)}} = 6.88 \cdot 10^{-10} cm^2/s \qquad (1)$$

where: D_0 – pre-exponential factor (cm^2/s), Q – activation heat of diffusion (J/mol), R – is the ideal gas constant (R = 8.314 J/mol·K), T – absolute temperature (K).

Considering in the case of the tungsten carbide mixture ε-W_2C + δ-WC a undercooling achieved up to approximately 1523 K, the minimum temperature up to which the solid solution based on ε-W_2C carbide is stable, the carbon diffusion coefficient has the value:

$$D_C^{\varepsilon-W_2C+\delta-WC} = D_0 \cdot e^{-\frac{Q}{RT}} = 8.91 \cdot 10^{-2} \cdot e^{-\frac{223630}{8.31 \cdot (1250+273)}} \tag{2}$$
$$= 18.9 \cdot 10^{-10} cm^2/s$$

Based on the assumptions adopted, values of the diffusion coefficient of carbon in undercooled austenite were obtained, in order to martensitic transformation in unalloyed steels of the same order of magnitude as that corresponding to the diffusion of carbon in the mixture of tungsten carbides ε-W_2C + δ-WC. Analyzing the mechanism of the transformation, it can be concluded that the structures that ensure the mechanical characteristics imposed on the grains of the eutectic mixture of WC-W_2C carbides, obtained by ultra-rapid cooling of their melts, are the result of a diffusion-free transformation, of the martensitic type. In support of the hypothesis of diffusion-free transformation of the mixture of solid solutions based on ε-W_2C and δ-WC carbides (the range in which the solid solution based on this compound is stable is relatively narrow, 3028 K to 2657 K) are also the results of investigations using the electron microprobe (Fig. 4 and Fig. 5).

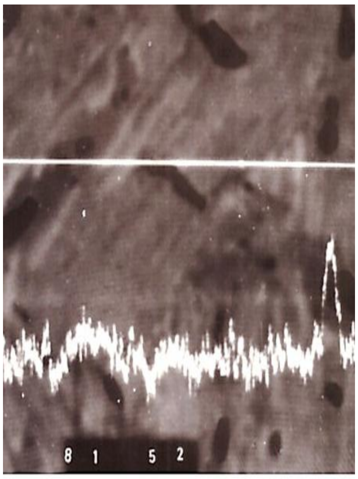

Fig.4. Composition image and tungsten distribution profile in the granule with eutectic composition 78-80 % wt W_2C and 20-22 % wt WC (1200x)

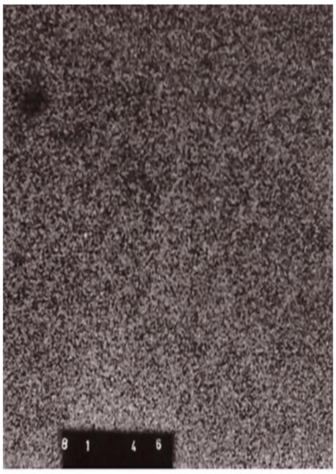

Fig.5. X-ray image of the distribution of tungsten in the granule with eutectic composition 78-80 % wt W_2C and 20-22 % wt WC (300x)

The tungsten distribution profile (Fig. 4) on the RELIT grain section is relatively uniform, the more abrupt variations in the composition being due to the crossing of phases richer in this element, phases of the W_2C type, whose presence is relatively difficult to explain. The uniform distribution of tungsten in the analyzed sections is also confirmed by the X-ray images (Fig. 5) made on the samples studied. The solid solution supersaturated in carbon δ’-WC, represents a metastable phase, with a martensitic morphology. A more careful metallographic analysis of the grains with eutectic composition WC-W_2C cooled ultra-rapidly from the liquid phase, highlights the presence of a lighter colored phase (Fig. 6), locally with a Widmanstätten structure, separated in the form of a discontinuous network at the boundaries of the former β-WC solid solution crystals. The nature of this phase could be identified by analysis using the electron microprobe (Fig. 4), the result being evidence of the fact that it represents a phase richer in tungsten (compared to the background, characterized by a martensitic δ’-WC type structure), the phase being of the W_2C type. The peaks presented by the tungsten distribution profile on the section of the analyzed sample are poorly highlighted, because the differences in tungsten concentration in the three phases δ'-WC-phase with the martensitic structure, β-WC and W_2C, respectively, are quite small: 92.6 % W in the δ'-WC phase, 96.5%W in the W_2C phase and 94%W in tungsten monocarbide (β-WC), respectively.

The presence of the W_2C phase in the mass with the martensitic structure can be explained / justified only by the existence of some local, random segregations of tungsten.

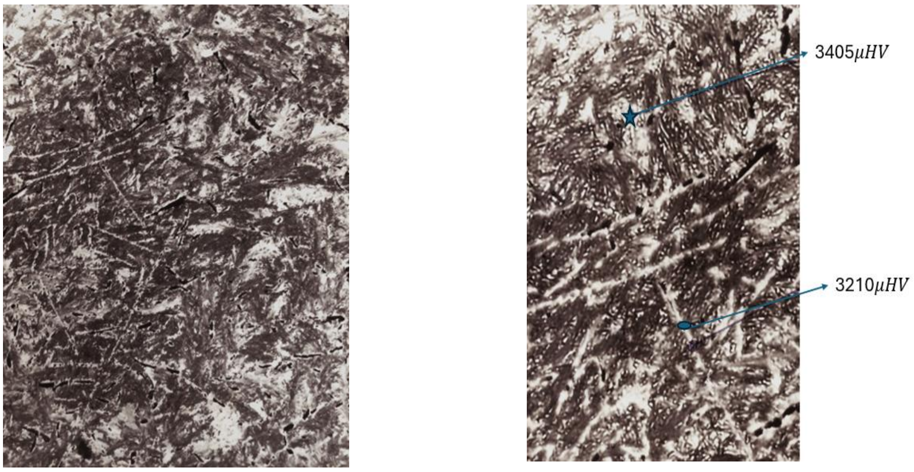

Fig. 6. Microstructure of WC-W_2C alloy with eutectic composition (RELIT) after ultrafast cooling from the liquid state, Murakami etching reagent. Left – 500x, right – detail of the micrograph on the right, 1000x

As it can be seen from the figures 2, 3 and 6, the microhardness values HV0.1 are within a range between 2971 and 3410.

5. Conclusions

1. From the analysis of the experimental results, it emerged that, by ultra-rapid cooling of melts with eutectic composition, a new, metastable phase, δ'-WC, with a martensitic structure ($\gamma\text{-WC}_{1-x} \rightarrow \delta'\text{-WC}$ – transformation without diffusion) can be obtained. The presence of such a phase ensures the best use properties of the material obtained by ultra-rapid cooling of the tungsten and carbon melt with a carbon content within the limits of 3.8-4.1% mass.

2. Separations of tungsten-rich carbide of the W_2C type are random and at least theoretically should not exist if the manufacturing technology of the RELIT type of alloy is rigorously followed, meaning the correct dosage of the powder mixture components, the choice of thermal and temporal parameters of the melting operation, the spraying conditions etc.

REFERENCES

[1] *A. P. Zhudra*, Tungsten carbide based cladding materials, The Paton Welding Journal, No. **06,** 2014, pp. 66-71;

[2] *H. Okamoto,* CW (Carbon-Tungsten), Journal of Phase Equilibria and Diffusion, vol. **29**, Iss. 6, 2008, pp. 543-544, DOI: 10.1007/s11669-008-9396-7;

[3] *G. V. Samsonov, I. M. Vinitkii*, Tugoplavkie Soedinenia – Spravocinik (Refractory Compounds - Handbook) - Moskva, Metallurghia, 1976;

[4] *I. Yu. Trosnikova, P. I. Loboda*, Influence of Obtaining Conditions on Microstructure, Phase Composition and Properties of Eutectic Alloy of WC-W_2C System, Journal of Superhard Materials, vol. **41**, 2019, pp. 49-52;

[5] *N. Nayak, T. Dash, D. Debasish, B. B. Palei, T. K. Rout, S. Bajpai, B. B. Nayak*, A novel WC–W_2C composite synthesis by arc plasma melt cast technique: microstructural and mechanical studies, SN Appl. Sci., vol. **3,** 2021;

[6] *A. S. Kurlov, A. I. Gusev,* Phase equilibria in the W – C system and tungsten carbides, Russian Chemical Reviews, vol. **75**, Iss. 7, 2006, pp. 617-636, DOI: 10.1070/RC2006v075n07ABEH003606;

[7] *H Holleck*, Binäre und Ternäre Carbid- und Nitridsysteme der Übergangsmetalle - Materialkundlich-technische Reihe, 6 (Binary and Ternary Carbide and Nitride Systems of Transition Metals - Materials Science and Technology Series, 6), Gebrüder Bornträger Verlag, Stuttgart, 1984;

[8] *E. Rudy, S. Windisch*, Evidence for Zeta Fe_2N-Type Sublattice Order in W_2C at Intermediate Temperatures, J.Am.Ceram.Soc., vol. **50**, Iss.5, 1967, pp. 272-273;

[9] *E. Rudy, J. R. Hoffman*, Phasengleichgewichte im Bereich der kubischen Karbidphase im System Wolfram-Kohlenstoff (Phase equilibria in the cubic carbide phase in the tungsten-carbon system), Planseeber. Pulvermetall., vol. **15, Iss.** 3, 1967, pp. 174-178;

[10] *V. Z. Kublii, T. Y. Velikanova,* (2004) Structural studies of materials-ordering in the carbide W_2C and phase equilibria in the tungsten-carbon system in the region of its existence, Powd. Metall. Met. Ceram., vol. **43,** 2004, pp. 630–644;

[11] *E. Rudy,* Experimental phase equilibria of selected binary, ternary, and higher order systems, Part V: The Phase Diagram W-B-C, Technical report AFML-TR-69-117, Wright-Patterson Air Force Base. Ohio, USA, 1970;

[12] *K. Yvone, H. Nowotny, F. Benesovsky,* Zur Kristallstruktur von W_2C (On the crystal structure of W2C), Monatshefte für Chemie, vol. **99**, 1968, pp. 726-729, DOI: 10.1007/BF00901228

[13] *J. J. Lander, L. H. Germer*, Coating with molybdenum, tungsten and chromium by thermal decomposition of their carbonyls, Trans. Metall. Soc. AIME, **175**, 1949, pp. 648-692;

[14] *I. Yu. Trosnikova, P. I. Loboda, O. P. Karasevska, O. I. Bilyi*, Effect of the Cooling Rate During Melt Solidification on the Structure and Properties of WC–W_2C, Powder Metallurgy and Metal Ceramics, vol. **52**, 2014, pp. 674-679;

[15] *C. Wells, W. Batz, R. Mehl*, Diffusion coefficient of carbon in austenite, JOM - Journal of the Minerals, Metals and Materials Society, vol. **2**, 1950, pp. 553–560. doi:10.1007/BF03399032.