Investigation of adhesion and diffusion activity of Cu – Mn – Ni brazing filler metal with WC – 8Co cemented carbide

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In this work, the interaction between Cu – Mn – Ni brazing filler metal (BFM) melt and WC – 8Co cemented carbide is studied. In particular, the diffusion interaction in a binary system (BFM-cemented carbide substrate) and a ternary system (steel-BFM-cemented carbide substrate) is considered. An attempt has been made to control the interaction process by applying thin metal coatings (Ti, Cr, Al, Ni, Cu) by the magnetron sputtering method. For the CuMn24Ni9 filler metal temperature dependences of contact angles on cemented carbide are obtained. Their dependences on the coating material and the depth of interaction between BFM melt and cemented carbide substrate is also estimated. It was found that the thickness of the diffusion layer of brazing filler metal into the cemented carbide depends on the temperature and does not depend on the coating material and the amount of liquid interacting with the substrate. The depth of copper diffusion into the cemented carbide is 100 ± 5 μm for a heating temperature 1120 ^oC and 50 ± 8 μm for a temperature 960 ^oC. Without coating, the contact angle is 15. The minimum contact angle obtained on the Ni coating is 6. For Al, Cr and Ti coatings, to obtain a contact angle of less than 10, high temperatures are required, over 1200 ^oC. The evaluation of the failure mechanism of brazed samples with preliminary deposited metal coatings during shear testing has been carried out. Fracture of all brazed samples took place on the cemented carbide, except for those coated with Ti. Cracks in all samples originated in the region above the fillet, and then penetrated deep into the material.

Key words: high temperature brazing, brazed joints, cemented carbides, steels, microstructure, solid solution, mechanical properties, coatings.

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Introduction

Cemented carbide is a liquid-phase sintered composite consisting most often of tungsten carbide and a cobalt binder. In essence, cemented carbides are metal-ceramic composite materials. Such materials are widely used in the manufacture of highly loaded products where high wear resistance, hardness, and heat resistance are required: dies, cutters for metals and composite materials, cutting with high cutting speed, working parts of mining and drilling tools [1–2]. Due to the high content of tungsten, cemented carbides are expensive materials. Therefore, when designing products containing cemented carbide parts, the main principle is to minimize the use of cemented carbide. For this, products mostly consist of a steel body and a cemented carbide working part, which are joined together. Several methods are used to join cemented carbide with steel: a diffusion welding [3], a fusion welding [4–5], a brazing [6] and a TLP (Transient Liquid Phase) bonding. The most common process in the mass production of tools is brazing due to its technological characteristics, such as high production productivity.

Copper (Cu) and silver (Ag) based brazing filler metal`s (BFM) systems are mainly used because of their superior ductility and toughness. It is known that the adhesion of the BFM to the substrate is one of the factors determining mechanical properties of the brazed joint [7–8]. There are not so many works focused on wetting cemented carbides with melts [9–10]. Pure copper and silver do not wet well and spread over the cemented carbide in vacuum. Copper-based filler metals are alloyed with such elements as manganese (Mn), nickel (Ni) and cobalt (Co) to improve the wettability of the cemented carbide surface in vacuum, to increase the strength of the joint, as well as to ensure the hardening temperature of steel used as tool body material [3, 7]. At the same time, authors of [7] report that in the microstructure of the WC – Co/pure Cu/steel brazed joints, a diffusion zone is observed on the cemented carbide side of brazed seam with a thickness of 2–3 μm. In work [3], researchers note the presence of erosion activity of the filler metal in relation to cobalt binder of cemented carbide. Reasons and methods of influence on this phenomenon, as well as the degree of its influence on the mechanical properties are not specified.

Coatings are widely used to improve the mechanical properties of cemented carbide tools. Basically, the cemented carbide is coated to reduce friction during cutting, coatings in this case act as a thermal barrier and prevent overheating of the cutter [11–12]. Also coatings are used to increase the microhardness and wear resistance of cemented carbides [13–15]. In general, authors study either ceramic coatings, for example, titanium carbonitrides in various stoichiometric ratios, as indicated in works above. Also coatings are used to facilitate the brazing process by applying brazing filler metal thin film on cemented carbide [16]. The use of diffusion barriers to improve brazed joints is not discussed in the literature.

Thus, analyzing modern trends in the study of cemented carbides, it can be concluded that the goal of researchers is either to improve the mechanical and abrasive properties of cemented carbides, or to study metallographic features of steel/cemented carbide brazed joints. At the same time, when studying the process of brazing cemented carbides with steel, the emphasis is placed on the interaction of the filler metal melt with steel, and the BFM-cemented carbide contact area is considered in passing.

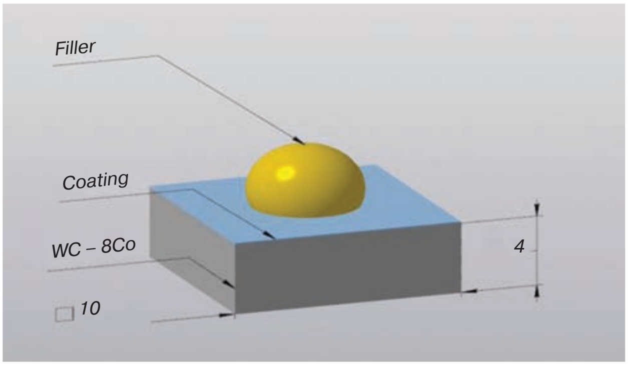


Fig. 1. Contact angle sample

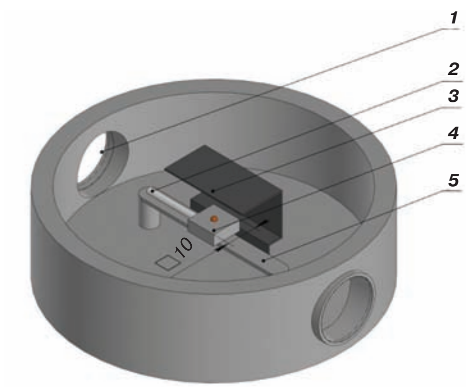


Fig. 2. Vega-M vacuum chamber scheme:
1 — optical input; *2* — S-type thermocouple; *3* — Ta-heater; *4* — sample; *5* — sample table

Table 1
Chemical composition of materials used in work

Alloy	Chemical composition, wt.%							
	C	Si	Mn	Ni	Cr	Cu	WC	Co
CuMn24Ni9	–	–	23.5	9	–	bal.	–	–
WC – 8Co	–	–	–	–	–	–	92	8
Steel	0.28–0.34	0.9–1.2	0.8–1.1	<0.3	0.8–1.1	<0.3	–	–

In this work, authors tried to focus on the study of the interaction zone between molten BFM and cemented carbide, focusing on the diffusion processes occurring with cobalt in a cemented carbide, and try to influence this process by applying thin metal coatings.

Materials and methods

In this work WC – 8Co cemented carbide and carbon steel were used as substrates. As a filler metal, an copper based alloy CuMn24Ni9 was chosen in the form of a powder with a particle size of 80–100 μm. Filler metal was applied to the substrates using an organic binder. The melting temperature range of BFM is 925–950 °C [17]. The chemical composition of materials used in work is presented in **Table 1**.

Ni, Cu, Ti, Cr, Al coatings were applied using vacuum magnetron sputtering. The thickness of the deposited metal layer was 0.2–0.4 μm. The samples were prepared in acetone ultrasonic bath before coating.

Two types of samples were used for metallographic research. The first type is binary sample (BFM — cemented carbide). The second one is ternary sample (steel substrate – BFM – cemented carbide).

The study of wetting and spreading of the filler metal on the surface of a cemented carbide was carried out in a vacuum chamber on a Vega-M furnace at 950–1120 °C without dwelling. The heating rate was 20 °C/min. The sample was photographed during heating, and then contact angles were determined by the sessile drop method. The sample is shown on **Fig. 1**.

Fig. 2 shows a scheme of the working chamber for contact angles measuring equipment. Photographing was carried out through an optical input, the camera was placed on the same axis with the sample. The temperature was recorded with a S-type thermocouple. Thermocouple was brought to the end of the sample.

Brazing of samples for shear strength testing was carried out in a SNVE-1.3.1/16 vacuum furnace at 1020 °C with a 10 min dwelling. The design of samples was taken from works of other authors describing a shear testing of ceramic brazed joints [18–19]. The brazing gap was 150 μm.

Shear tests were carried out on a Quasar 50 testing machine in compression mode.

Both groups of samples: binary and ternary, were cut by spark cutting method with a cut line in the center of a cemented carbide. Cut samples were prepared for metallographic research on diamond grinding wheels of various sizes. A polishing was carried out with a diamond monocrystalline emulsion.

Metallographic studies of the structure of the interaction zone and the distribution of elements were carried out on a TESCAN VEGA SBH3 scanning electron microscope (SEM) with an Oxford Instruments Advanced AZtecEnergy attachment for EDS (Energy-dispersive *X*-ray spectroscopy).

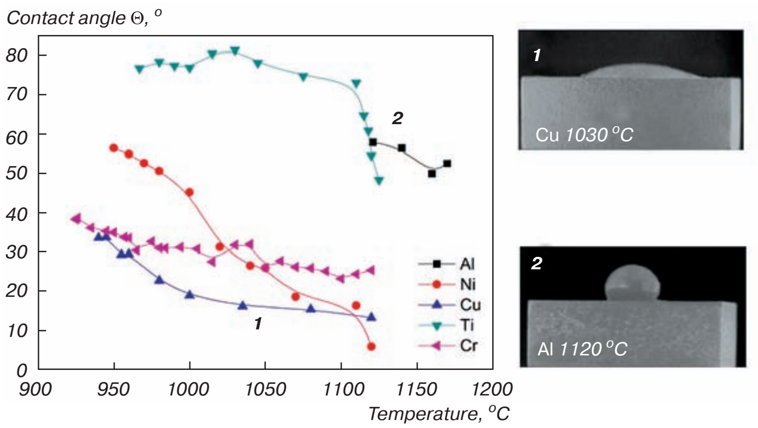


Fig. 3. Temperature dependence of the contact angle for coated samples

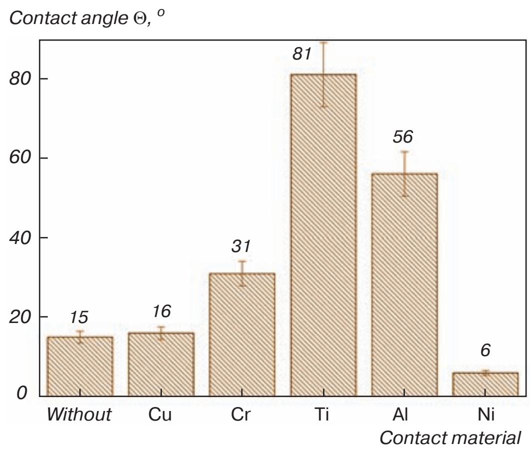


Fig. 4. Contact angle at 1020 °C

Results and discussion

Investigation of contact angles

Influence of temperature on the contact angle were shown on **Fig. 3.** Typical images of droplets for two temperatures are indicated by numbers.

Dependwences have a decreasing character with a smooth reaching a plateau for copper, chromium and aluminum. Titanium and nickel are characterized by a decreasing dependence with a sharp change in the contact angle at the critical temperature of 1120 °C.

It was found that the filler metal melt tends to the minimum contact angle with Ni, Cu coatings, and also without coating (**Fig. 4**). This occurs because Ni and Cu are includes in BFM chemical composition and reduce the surface energy of the liquid-solid interface, facilitating wetting and spreading of the filler metal melt. The minimum contact angle obtained on the Ni coating is 6. Without coating, the contact angle is 15. For Al, Cr and Ti coatings, high temperatures are needed to obtain a contact angle of less than 10, over 1200 °C.

Thus, coatings such as Ti and Cr greatly reduce the adhesion of the melt to the substrate in temperature ranges of brazing by Cu – Mn – Ni filler metals, while Ni and Cu increase adhesion by facilitating the interaction of liquid and solid.

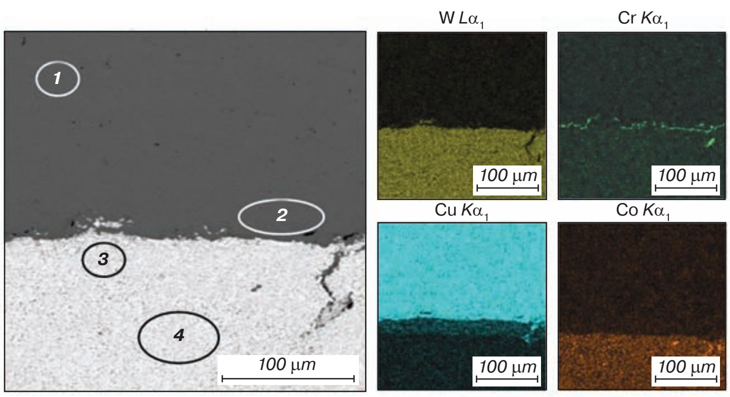
Metallographic research

Metallographic studies were carried out both on samples of the binary system (filler metal – substrate) and on samples of the ternary system (steel – filler metal – cemented carbide substrate). In the real process of brazing, the number of surfaces of the base metal in contact with melt is greater, and the volume of liquid metal in the brazed seam is less than during wetting tests. This study shows the effect of the amount of liquid on the diffusion behavior of the melt, its interaction with the substrate and the coating material. The depth of diffusion interaction was estimated from the depth of penetration of copper into the cemented carbide with an excess of the liquid phase and a deficiency.

Metallographic studies of binary system samples (filler metal-cemented carbide substrate)

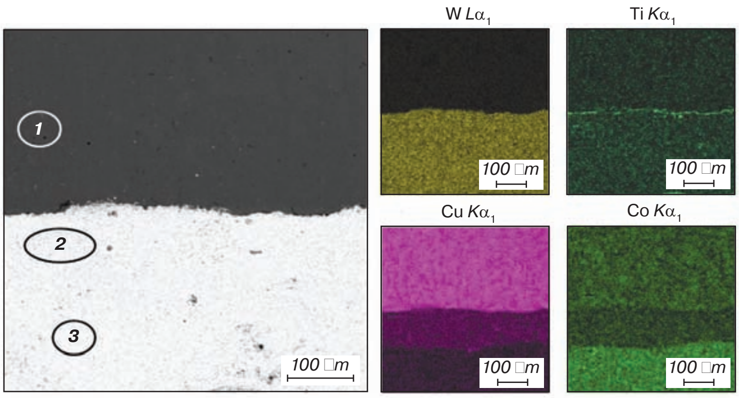
Initially, all samples were coated with a continuous film of magnetron sputtered metal. However, during metallographic studies of samples, it was revealed that during the thermal process, all coatings, with the exception of Ti and Cr, dissolved in the BFM melt (**Figs. 5, 6**).

In general, the microstructure of brazed joints can be divided into 2 zones. Area 1– filler metal (Spectrum 1, Fig. 5 and Spectrum 1, Fig. 6). This zone consists of a solid solution based on copper. The content of cobalt, which dissolved from cemented carbide binder, and manganese, which evaporated in vacuum due to the low pressure of saturated vapor, changes depending on the heating temperature [20]. Area 2 — diffusion zone (Spectrum 3, Fig. 5 and Spectrum 2, Fig. 6). According to the EDS, the chemical composition here is fundamentally different



Area №	Chemical composition, wt.%							
	C	Cr	Mn	Fe	Co	Ni	Cu	W
1	4.68	0.11	21.18	1.09	1.06	10.24	61.22	0.44
2	6.12	1.49	20.59	1.26	1.45	9.8	58.38	0.9
3	7.04	0.01	2.27	0	0.1	0.97	6.66	82.86
4	7.9	0.07	0	0.03	7.59	0	0.37	84.05

Fig. 5. The central region of a spreading drop on chrome coated sample heated to 960 °C



Area №	Chemical composition, wt.%							
	C	Ti	Mn	Fe	Co	Ni	Cu	W
1	3.91	0	12.92	1.5	4.24	12.26	64.64	0.52
2	8.04	0.08	1.33	0.12	0.56	0.89	6.97	82.01
3	7.96	0.04	0.02	0.11	6.41	0.02	0.11	85.34

Fig. 6. The central region of a spreading drop on titanium coated sample heated to 1120 °C

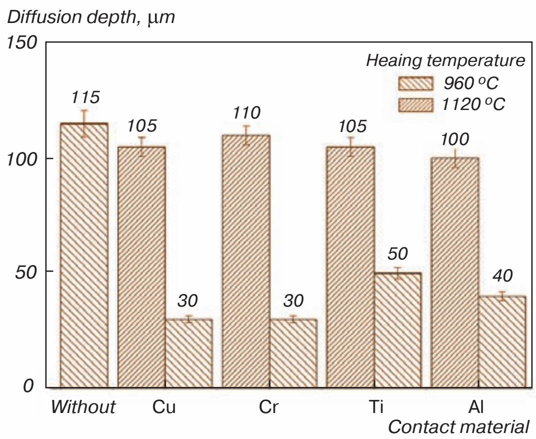


Fig. 7. The effect of coating material and heating temperature on diffusion interaction depth on binary samples

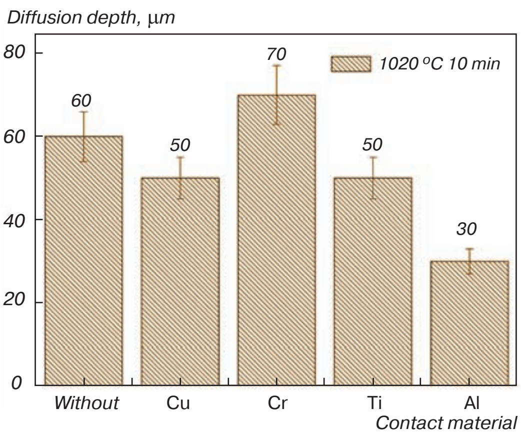


Fig. 8. The effect of coating material on diffusion interaction depth on samples brazed at 1020 °C for 10 min

from the initial one and there is an almost complete replacement of the hard alloy binder with BFM components. Spectrum 4 on Fig. 5 and Spectrum 3 on Fig. 6 correspond in chemical composition to the cemented carbide WC – 8Co.

Fig. 7 illustrates the effect of heating temperature and coating material on the diffusion behavior of the melt. Microstructure of the contact zone cemented carbide – filler metal for binary samples (with a large amount of melt) showed significant diffusion of BFM elements into cemented carbide and, at the same time, diffusion of Co from cemented carbide into fillers melt. The effect of the thin-film coating on the amount of the diffusion interaction was not detected for high heating temperature (1120 °C). Cr and Cu reduce diffusion activity of BFM at low temperature (960 °C) compared with Ti. If compare data from Fig. 2 and Fig. 7 it could be concluded that contact angle can't be an indicator of melts diffusion activity. These phenomena may occur because the melt can break through coating and interact with cemented carbide. And the contact angle was not changed while this happens. In all cases, diffusion of cobalt from the cemented carbide into the fillers melt was observed (Fig. 7). In this case, the minimum concentration of cobalt was observed in the near-surface zone of 100 μm for a temperature of 1120 °C and 40 μm for a temperature of 960 °C. Further into the depth of cemented carbide, the concentration of cobalt increased to normal values (Spectrum 2, 3 on Fig. 6). The cobalt concentration also increased in the volume of the filler metals droplet. It has been found that even melt-insoluble coatings do not function as a diffusion barrier. On average, filler metal dissolves 4 times more cobalt when the temperature changes from 960 to 1120 °C.

Metallographic studies of the ternary system (steel-filler metal-cemented carbide substrate)

Then brazing occurs there is a smaller amount of melt in the contact area with cemented carbide substrate due to the fact that a strictly defined amount of liquid can move into the brazing gap. This amount of liquid is much smaller in volume than in a drop. In addition, the diffusion activity of the filler is spent on both: dissolution of steel body and dissolution of cobalt from cemented carbide. **Fig. 8** shows a diagram of diffusion depth`s dependence of BFM elements on the coating material brazed at 1020 °C for 10 min.

Fig. 8 shows, that in ternary system only Al decrease diffusion activity of the melt. However, comparing the data from Figs. 7 and 8, it can be concluded that with a decrease in the volume of the melt in the brazed joint, its diffusion activity will not decrease for 150 μm brazing gap. For 1020 °C the amount of diffusion interaction is between 960 °C and 1120 °C. It can be concluded that amount of liquid BFM in 150 μm brazing gap is enough to dissolute Co from cemented carbide. Only Al decrease depth of diffusion interaction for this temperature, while have more than 60 contact angle.

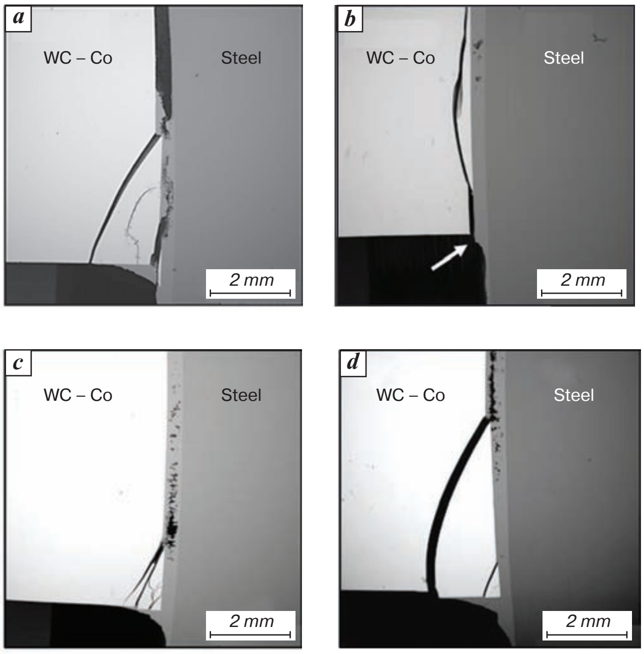


Fig. 9. SEM images of brazed samples after shear test:
a — without coating; *b* — Ti; *c* – Cr; *d* – Cu

Table 2
Shear test results

Coating	Shear strength, MPa
Without coating	224 ± 22
Cu	390 ± 40
Ti	296 ± 29
Cr	237 ± 24

Mechanical testing of brazed joints

Brazed joints, like others, for example, welded or bolted, are stress concentrators in the construction. Service conditions of most brazed joints are shear stresses. Therefore, in this work, the influence of the microstructure of the contact cemented carbide/filler metal region on the shear strength of the joint and the nature of its failure depending on the metal of the coating was evaluated.

Fig. 9 shows SEM images of tested samples. Obtained data of the ultimate strength in shear tests gave irrelevant values. Test results are shown in **Table 2**. These values are associated with a feature of the shear test method. Fig. 9 *a*, *d* illustrates the trace from the equipment then in the fillet part of brazed joints. The tooling pressed on the fillet, changing the stress distribution pattern in the brazed seam during testing.

In this regard, a more interesting result is the nature of the sample failure. As noted in [21], when joining steel with cemented carbide at the filler metal/cemented carbide interface, metal carbides other than WC can be formed. The nature of the destruction of the sample with a titanium coating (Fig. 9, *b*) indicates that Ti_xC_y carbide was most likely formed in the near-boundary region. This is evidenced by the "peeling" of the BFM from WC – Co, which is not typical for other sample from this series. Cracks in all samples originated in the region above the fillet and then penetrated deep into the material. Fracture of all brazed samples took place on cemented carbide, except for those coated with Ti.

Conclusions

The work investigated the adhesion of the CuMn24Ni9 filler metal to the WC – 8Co cemented carbide depending on the temperature and material of coatings (Ti, Cr, Al, Cu, Ni) applied by magnetron sputtering. The depth of diffusion interaction was measured and the effect of coatings on failure mechanisms for the joint zone was estimated. Following conclusions were made:

1. It has been established that temperature dependences of contact angles are decreasing with a smooth reaching a plateau for Ni and Cu. Without coating, the contact angle is 15. The minimum contact angle obtained on the Ni coating is 6. For Al, Cr and Ti coatings, to obtain a contact angle of less than 10, high temperatures are required, over 1200 °C.

2. It was found that the thickness of the diffusion layer of brazing filler metal into the cemented carbide depends on the temperature. In compare with binary samples with high amount of melt, melt in 150 μm brazing gap is enough to dissolute Co from cemented carbide substrate. The depth of copper diffusion into the cemented carbide is 100 ± 5 μm for a heating temperature 1120 °C and 50 ± 8 μm for a temperature 960 °C. At the same depth, the boundary zone of cemented carbide is depleted in Co and is replaced by filler metal components.

3. The shear test method used in this work is not suitable for the numerical determination of shear strength of brazed joints. Shear ultimate strength values from 220 to 390 MPa, so this testing method poorly suited for obtaining numerical values of steel\cemented carbide brazed joints shear strength. Fracture of all brazed samples took place on the cemented carbide, except for those coated with Ti. Cracks in all samples originated in the region above the fillet, and then penetrated deep into the material.

4. To improve mechanical properties, it is impractical to apply metal coatings to the cemented carbide. However, it is advisable to use coatings of metals that includes in filler metals chemical composition to improve the technological properties of the process by increasing the adhesion of BFM to cemented carbide.

Results of research can be useful for factories engaged in the production of tools mining and drilling tools. Data obtained in this work can be used for the correct design of brazed joints and the selection of optimal brazed modes.

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References

1. Yousfi M. A., Weidow J., Nordgren A., Falk L. K. L., Andr n H.-O. Deformation Mechanisms in a WC – Co Based Ce-

mented Carbide During Creep. *International Journal of Refractory Metals and Hard Materials*. 2015. Vol. 49. pp. 81–87.

2. Soleimanpour A. M., Abachi P., Simchi A. Microstructure and Mechanical Properties of WC – 10Co Cemented Carbide Containing VC or (Ta, Nb)C and Fracture Toughness Evaluation Using Different Models. *International Journal of Refractory Metals and Hard Materials*. 2012. Vol. 31. pp. 141–146.

3. Barrena M. I., G mez de Salazar J. M., Matesanz L. Interfacial Microstructure and Mechanical Strength of WC–Co/90MnCrV8 Cold Work Tool Steel Diffusion Bonded Joint with Cu/Ni Electroplated Interlayer. *Materials & Design*. 2010. Vol. 31, Iss. 7. pp. 3389–3394.

4. Chen G., Shu X., Liu J., Zhang Bo, Zhang B., Feng J. Investigation on Microstructure of Electron Beam Welded WC–Co/40Cr Joints. *Vacuum*. 2018. Vol. 149. pp. 96–100.

5. Cheniti B., Miroud D., Badji R., Allou D., Csan di T., Fides M., Hvizdo P. Effect of Brazing Current on Microstructure and Mechanical Behavior of WC–Co/AISI 1020 Steel TIG Brazed Joint. *International Journal of Refractory Metals and Hard Materials*. 2017. Vol. 64. pp. 210–218.

6. Zhang X., Liu G., Tao J., Guo Y., Wang J., Qiao G. Brazing of WC–8Co Cemented Carbide to Steel Using Cu–Ni–Al Alloys as Filler Metal: Microstructures and Joint Mechanical Behavior. *Journal of Materials Science & Technology*. 2018. Vol. 34, Iss. 7. pp. 1180–1188.

7. Zhang X. Z., Liu G. W., Tao J. N., Shao H. C., Fu H., Pan T. Z., Qiao G. J. Vacuum Brazing of WC–8Co Cemented Carbides to Carbon Steel Using Pure Cu and Ag–28Cu as Filler Metal. *Journal of Materials Engineering and Performance*. 2016. Vol. 26, Iss. 2. pp. 488–494.

8. Amelzadeh M., Mirsalehi S. E. Influence of Braze Type on Microstructure and Mechanical Behavior of WC–Co/Steel Dissimilar Joints. *Journal of Manufacturing Processes*. 2018. Vol. 36. pp. 450–458.

9. Mousavi S. A. A. A., Sherafati P., Hoseinion M. M. Investigation on Wettability and Metallurgical and Mechanical Properties of Cemented Carbide and Steel Brazed Joint. *Advanced Materials Research*. 2012. Vol. 45. pp. 759–764.

10. Amelzadeh M., Mirsalehi S. E. Dissimilar Vacuum Brazing of Cemented Carbide to Steel Using Double-Layer Filler Metals. *Journal of Manufacturing Processes*. 2019. Vol. 47. pp. 1–9.

11. M'Saoubi R., Ruppi S. Wear and Thermal Behaviour of CVD α-Al_2O_3 and MTCVD Ti(C,N) Coatings During Machining. *CIRP Annals*. 2009. Vol. 58, Iss. 1. pp. 57–60.

12. Jingjie Zhang, Zhanqiang Liu, Chonghai Xu, Jin Du, Guosheng Su, Peirong Zhang, Xiangfei Meng. Modeling and Prediction of Cutting Temperature in the Machining of H13 Hard Steel of Multi-layer Coated Cutting Tools. *The International Journal of Advanced Manufacturing Technology*. 2021. Vol. 115, Iss. 11-12. pp. 3731–3739.

13. von Fieandt L., Johansson K., Larsson T., Boman M., Lindahl E. On the Growth, Orientation and Hardness of Chemical Vapor Deposited Ti(C,N). *Thin Solid Films*. 2018. Vol. 645. pp. 19–26.

14. von Fieandt L., Larsson T., Boman M., Lindahl E. Texture Formation in Chemical Vapor Deposition of Ti(C,N). *Journal of Crystal Growth*. 2019. Vol. 508. pp. 90–95.

15. Ruppi S. Advances in Chemically Vapour Deposited Wear Resistant Coatings. *Le Journal de Physique IV*. 2001. Vol. 11, Iss. PR3. pp. 847–859.

16. Zhu L., Luo L., Luo J., Wu Y., Li J. Effect of Electroless Plating Ni–Cu–P Layer on Brazability of Cemented Carbide to Steel. *Surface and Coatings Technology*. 2012. Vol. 206, Iss. 8-9. pp. 2521–2524.

17. Petrunin I. E. (Ed.). Handbook of Brazing (3^{rd} ed., rev. and exp.). Moscow: Mashinostroenie, 2003. 480 p.

18. Jiang C., Chen H., Zhao X., Qiu S., Han D., Gou G. Microstructure and Mechanical Properties of Brazing Bonded WC–15Co/35CrMo Joint Using AgNi/CuZn/AgNi Composite Interlayers. *International Journal of Refractory Metals and Hard Materials*. 2018. Vol. 70. pp. 1–8.

19. Santos S. I., Balzaretti N. M., Jornada J. A. H. Adhesion between CVD diamond and WC–Co Induced by High-Pressure and High-Temperature. *Diamond and Related Materials*. 2006. Vol. 15. pp. 1457–1461.

20. Kemmitt R. D. W. Manganese. In: *The Chemistry of Manganese, Technetium and Rhenium*. Pergamon, 1973. pp. 771–876.

21. Lee W. B., Kwon B. D., Jung S. B. Effects of Cr_3C_2 on the Microstructure and Mechanical Properties of the Brazed Joints Between WC–Co and Carbon Steel. *International Journal of Refractory Metals and Hard Materials*. 2006. Vol. 24, Iss. 3. pp. 215–221. NFM