

Original Article

Persistence of the thin layers of transition metal carbides in contact with liquid NiBSi alloy

Mariusz Bober^{1*}, Jacek Senkara¹, Bogdan Wendler²

¹ Warsaw University of Technology, Dept. of Welding Engineering, Poland
jacek.senkara@pw.edu.pl (J.S.)

² Lodz University of Technology, Institute of Materials Science and Engineering, Poland
bogdan.wendler@p.lodz.pl (B.W.)

* Correspondence: mariusz.bober@pw.edu.pl (M.B.)

Received: 08.11.2020; Accepted: 23.12.2020

Abstract: The article presents the results of study on interaction between the liquid NiBSi alloy and solid, thin, micrometer-range layers of transition metal carbides of IVB - VIB groups of the periodic table. The reactive magnetron sputtering method was adopted to deposit of these layers on molybdenum substrates. Carbide layers are destroyed in contact with liquid alloy by dissolving, intensified by the penetration of the liquid along the coating – substrate interface. The strong interaction between liquid NiBSi and both the carbide ceramics and the refractory metal substrate was revealed. The effect intensity differs somewhat for both tested carbide groups: VIB (relatively fast) and IVB (less intense).

Keywords: transition metal carbides; NiBSi alloy; interfacial interaction

Introduction

In a number of joining/bonding processes and surface modification by welding methods, as well as in classic pyrometallurgy processes, we deal with contact of a liquid metallic phase with the surface of a solid body. Depending on the application, the materials should have the best possible wettability with liquid metals, or no such wettability. The first case is for bonded joints on a macro scale (e.g. soldered/brazed joints) or micro scale (e.g. joints between the reinforcing phase particles and the matrix in the abrasion-resistant hardfacing layers). In contrast, a deficit of wettability is necessary for such applications as backings/spacers, thermocouple sheaths, crucibles or refractory linings of melting furnaces, which should not be eroded by the action of liquid metal. While metals and alloys, i.e. materials with metallic bonds, are well wettable with liquid metals, creating low-energy interfaces, and ceramics with ionic (Al_2O_3 , MgO , ZrO_2 etc.) or covalent bonds (e.g. SiC , AlN , B_4C , Si_3N_4) are non-wettable without the addition of strong activators (Ti, Zr) [1], in the case of transition metal carbides of IVB - VIB groups of the periodic table, which are characterized by mixed bonds [2] – the situation is much more complex. Depending on the type of interaction with a metallic liquid (equilibrium system – adhesive, non-equilibrium – diffusive or reactive) they can create stable or less stable interfaces, which may be related to the dissolution of the solid in the liquid, penetration of the liquid into the substrate, diffusion in both directions or the formation of intermetallic phases [3].

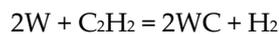
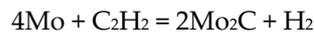
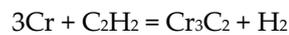
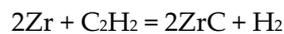
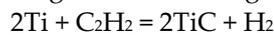
In this study, the behavior of thin layers of IVB (TiC, ZrC) and VIB (Cr_3C_2 , Mo_2C i WC) carbides in contact with a liquid NiBSi alloy was investigated. The attractive properties of these carbides have been well known for a long time: high hardness, high melting point and thermodynamic stability, finding a variety of applications [2]. Magnetron sputtering is a proper method of producing thin layers of materials at a reduced temperature. A broad characteristic of the structure and properties of the transition metal carbide layers obtained on various substrates can be found, for example, in a review work [15]. NiBSi alloy, due to its good resistance to corrosion and abrasive wear, as well as a relatively wide range of solidus-liquidus temperatures [16], is used in the processes of spraying, and plasma and laser surfacing as a powder, for the obtaining, among others, composite layers reinforced with hard particles, resistant to abrasion [21, 4-8]. Research on fabrication similar layers on the NiBSi matrix was also carried out using other methods: electron beam melting [17,18] and infiltration brazing [19]. An important achievement was also the adaptation of NiBSi alloy and its derivatives for high-temperature brazing [9,10, 20].

Research methodology, materials and devices used

Molybdenum was selected as the substrate material for the carbide layers. It is a metal with a high melting point (2883K), which eliminates the risk of partial melting during wettability tests, and low thermal expansion ($\lambda = 4,9 \cdot 10^{-6} \text{K}^{-1}$) [11], limiting the stress level at the substrate – carbide coating interface. The magnetron sputtering method was used for the coatings deposition.

Coatings produced by PVD methods are connected to the substrate by adhesive forces, which requires appropriate surface preparation. 18x18 mm molybdenum plates were cut from a 1 mm thick sheet, and then mechanically ground, and polished. The average value of the roughness parameter R_a measured on five samples was $0.07 \mu\text{m}$. The final stage of the preparation of the substrates was washing with acetone in an ultrasonic cleaner.

The process of deposition of coatings from 5 different carbides: titanium, zirconium, chromium, molybdenum and tungsten was carried out using a device with a reaction chamber equipped with four flat, circular magnetrons. Molybdenum substrates were hung on a special thread attached to the turntable at an appropriate distance from the targets and parallel to their surface. A mixture of gases was used: neutral (argon) and reactive – acetylene. As a result of sputtering the appropriate cathode material (titanium, zirconium, chromium, molybdenum and tungsten) and interaction with a reactive gas, carbide layers were formed on the molybdenum substrates, according to the following reactions:



The obtained coatings were identified by means of the X-ray diffraction phase analysis (XRD) method using a diffractometer equipped with a high-resolution semiconductor detector Si[Li] and Cu, Mo, Cr, Fe, Co lamps. An optical metallographic microscope with digital image recording was used to determine the continuity of the coating, its thickness and initial structure characteristic.

The nickel alloy was made from pure components in a vacuum induction furnace for melting and casting. The chemical composition of the melt was determined by the atomic absorption spectrometry (AAS) method. To test the interaction of NiBSi alloy with carbide layers, a device designed and manufactured at the Department of Welding Engineering of the Warsaw University of Technology was used (Fig. 1). The description of the device was presented previously in [12].

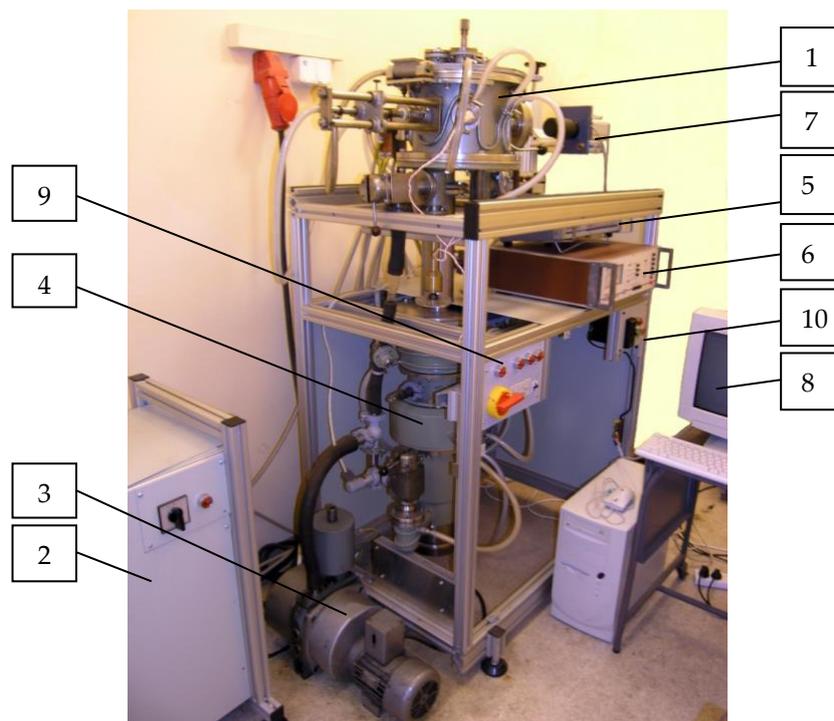


Fig. 1. Stand for the solid phase-liquid metal phenomena investigation: 1 – working chamber, 2 – transformer, 3 – vacuum rotary pump, 4 – diffusion pump, 5 – resistance vacuum gauge, 6 – ionization vacuum gauge, 7 – camera, 8 – control computer, 9 – control panel, 10 – regulator

Before starting the experiment, the samples were washed in acetone in an ultrasonic washer, and then the plates with a carbide layer and a Ni alloy sample were placed on a carefully leveled measuring table in the chamber of the device. All NiBSi samples had the same shape and the same volume (cylinder $\varnothing 3 \times 3$ mm). The tests were carried out under an argon atmosphere of 99.999% purity. The working chamber of the device was pumped down to a pressure of 10^{-1} hPa, and then filled with argon. This treatment was repeated twice to thoroughly remove any residual air. Then a constant argon flow of 0.5 L/min was established. The samples were heated from ambient temperature to 900 °C at a rate of 100 °C/min, then the heating rate was reduced to 20 °C/min. The process was discontinued after reaching the temperature at which the surface of the liquid droplet spreading on the substrate stabilized. Two tests were carried out for each Ni alloy – carbide substrate system.

After the process was completed, the droplet's spreading area on individual substrates was measured using a stand equipped with a stereoscopic microscope and a program for the analysis of metallographic images, and microstructure studies were carried out. The carbide – Ni alloy interface was examined on specimens in a plane perpendicular to the substrate's surface and passing through the center of the Ni alloy droplet. Scanning electron microscopy (SEM) and Electron Probe X-Ray Microanalysis (EPMA) were used.

Research results and discussion

Initial samples: carbide substrates and Ni alloy

X-ray images of the deposited carbide layers showed a highly fine-crystalline and even amorphous structure of the resulting coatings, as evidenced by the specific, wide shape of the peaks. Therefore, all samples with applied layers were subjected to 1 hour annealing in a vacuum furnace at a temperature of 800 °C and a pressure of 10^{-3} Pa, obtaining coatings with a clear crystal structure. Their phase analysis showed that the obtained layers were TiC, ZrC, Cr₃C₂, Mo₂C and WC_{1-x}. Figures 2 a, c show, for example, the diffraction patterns of the ZrC carbide layers before and after the annealing process.

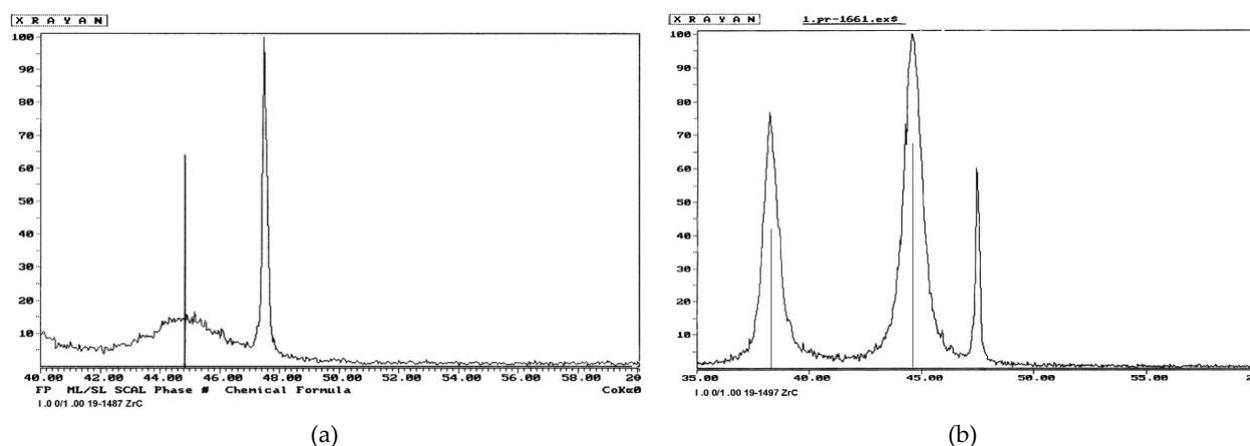


Fig. 2. An example of XRD pattern ZrC layer on a molybdenum substrate: a) directly after magnetron sputtering; b) after sputtering and annealing

The surfaces of the applied carbide coatings were subjected to roughness measurements. The average roughness value measured on five samples was 0.09 μm , with a spread of $0.07 \div 0.11$ μm . This proves that the surface topography of the obtained layers reproduces the surfaces of molybdenum substrates with a slight increase in roughness.

Figure 3 shows pictures of the microstructure of the deposited coatings. All obtained coatings are continuous, of constant thickness and adhesively bonded to the molybdenum substrate along the entire length.

No defects were observed in the coatings themselves and in the interface between the carbide coating and the molybdenum substrate. Using the metallographic image analysis program, the thickness of the applied layers was measured, the results are presented in Table I in the form of the arithmetic mean of five measurement points. The thickness of the coatings of individual carbides is different and ranges from 1.3 μm for WC to 7.8 μm for Mo₂C. Table II presents the results of determination of the chemical composition

by the atomic absorption spectrometry (AAS) method of NiBSi alloy melted in a vacuum furnace. It corresponds to the composition of the commercially available material in powder form.

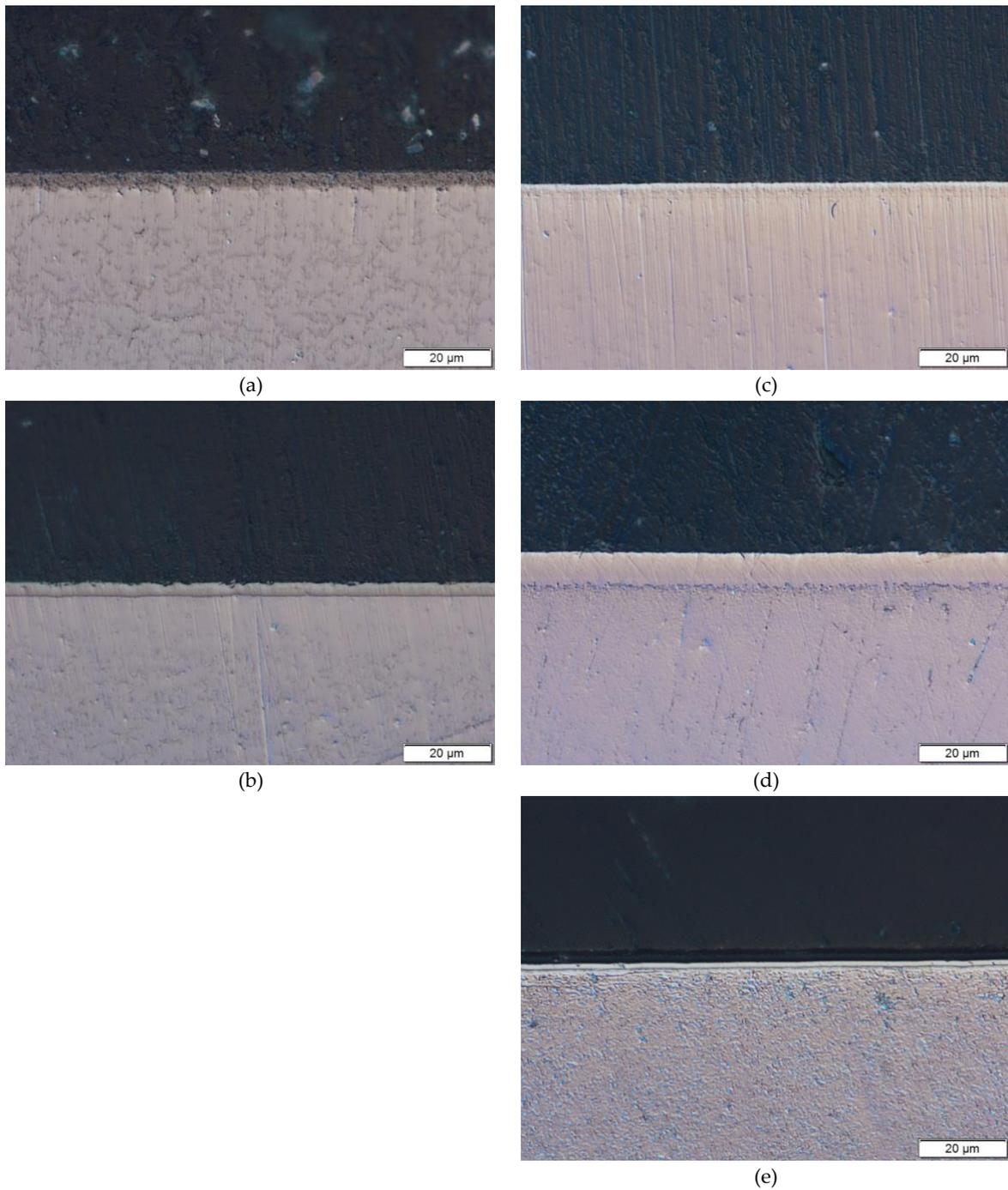


Fig. 3. Structures of molybdenum substrates with different coatings deposited: a) TiC, b) ZrC, c) Cr₃C₂, d) Mo₂C, e) WC. Optical microscope, Nomarski interference contrast

Table I. Thickness of carbide coatings (average value of 5 measurements)

Type of the coating	TiC	ZrC	Cr ₃ C ₂	Mo ₂ C	WC
Thickness of the coating [μm]	4.74	3	2.4	7.8	1.3

Table II. Chemical composition of prepared Ni alloy as determined by AAS method (wt.%)

	C	Si	B	Fe	Ni
Stop NiBSi	not tested	2.453	1.174	0.190	rest

Samples after interaction with the NiBSi alloy

Table III presents the results of the measurement of the droplet's spreading area (average of 2 trials), temperature of process termination and the total time of liquid – substrate contact, measured from the beginning of the formation of the liquid phase (for the ZrC sample, the wetted surface was highly asymmetrical). The obtained results indicate a more intense interaction of the Ni alloy with carbides from the VIB group: a significantly larger surface of the droplets' spreading was obtained, the temperature at which the spreadability stabilized was lower, and the interaction time – shorter.

Table III. Spreadability of liquid NiBSi alloy on carbide substrates along with the temperature of process termination and the total time of liquid - substrate contact

Type of the substrate	TiC	ZrC	Cr ₃ C ₂	MoC	WC
Temperature of process termination [°C]	1350	1350	1310	1330	1320
Total time of liquid – substrate contact [min]	6	6	4	5	4,5
Droplet's spreading area [mm ²]	48.9	57.8	–*	113.3	191.9

* the correct measurement result was not obtained

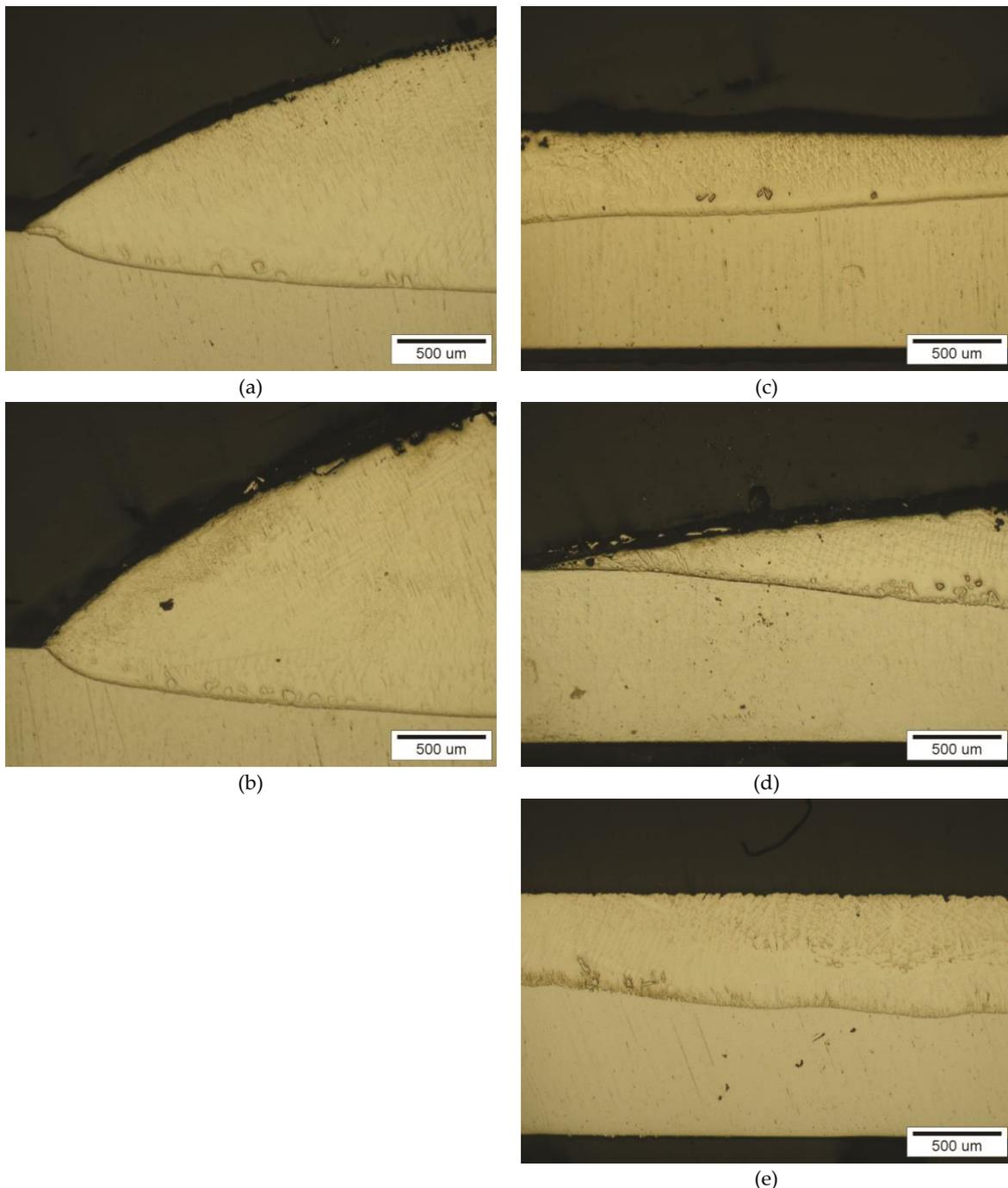


Fig. 4. Interfaces of Ni alloy - molybdenum substrate with a carbide layer: a) TiC, b) ZrC, c) Cr₃C₂, d) Mo₂C, e) WC

The results of the research on the interface between carbide and Ni alloy are shown in Figures 4 and 5 at different magnifications. The presented photos show that the liquid Ni alloy dissolved both the carbide layers and – after their destruction – molybdenum substrates (Fig. 5). The liquid erosion of the substrate was the highest for TiC and ZrC. In other cases, this effect was less intense, but also clearly visible. Images of structures at higher magnifications reveal a continuous intermediate layer between the Ni alloy and the molybdenum substrate in each of the tested systems (Fig. 5). These layers were formed as a result of the direct interaction of the liquid Ni alloy with carbide coatings during the wetting process. A more detailed study of this area was performed using scanning microscopy for each of the carbides.

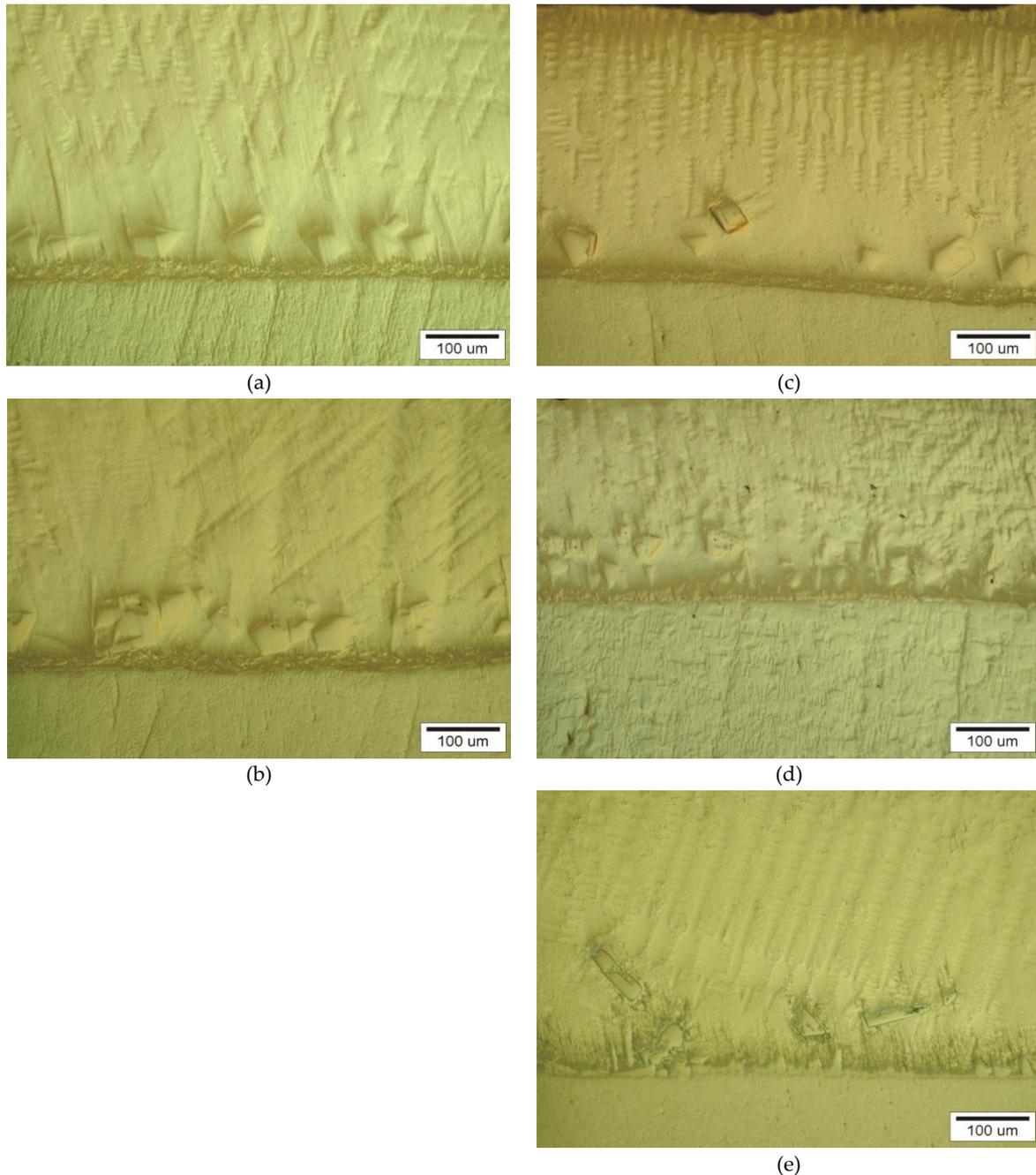


Fig. 5. Structure of interfaces from Fig. 4 at higher magnification: a) TiC, b) ZrC, c) Cr₃C₂, d) Mo₂C, e) WC. Not etched, Nomarski contrast

The results of the analysis indicated a similar mechanism for each of the studied cases. Figure 6 shows an example of the final structure of the interface created for the initial system Mo substrate – TiC coating – Ni alloy, and the maps of element concentrations for this area. During the contact with the liquid Ni alloy, the carbide layer on the Mo surface was completely destroyed. The carbide dissolved in the liquid Ni alloy, as it is evidenced by the surface distribution of Ti in the matrix. However, a thin layer of TiC remained, which

did not completely dissolve, but was detached from the substrate as a result of liquid penetration along the molybdenum – carbide interface. Removal of the TiC barrier allowed the metallic liquid to contact the substrate, dissolving the molybdenum and forming Ni – Mo intermetallic phases. This effect was observed for all tested carbide layers.

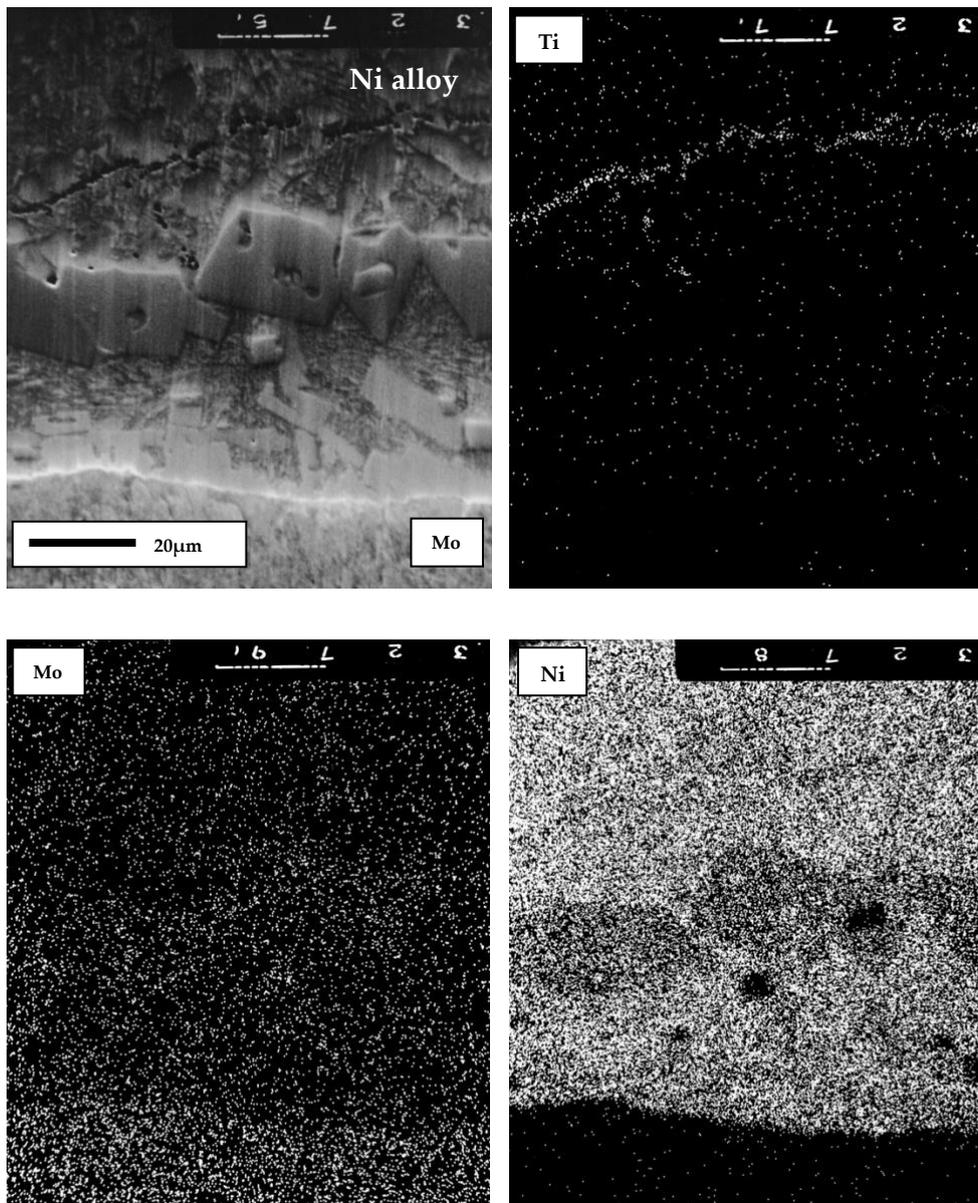


Fig. 6. Structure of Mo - TiC - Ni alloy interface with the maps of Ti, Mo and Ni concentration

The complete annihilation of the carbide layers with the subsequent erosion of the molybdenum substrates proves the intense interaction of the liquid NiBSi alloy with both the carbide ceramics and free metallic substrate. For the molybdenum substrate it is consistent with the theoretical predictions [13]. However, despite the final complete destruction of the carbide layers, there was a noticeable difference in the process of this interaction between metal carbides of VIB (relatively fast) and IVB (less intense) groups. This corresponds to some observations for curved, small objects (carbide particles in padding welds deposited by plasma and laser surfacing) [14].

Conclusions

- Continuous transition metal carbide layers on molybdenum plates can be obtained using the reactive magnetron sputtering method. The surface morphology of the coatings reflects the initial state of the substrate's surface. However, due to the slow thickness build-up with this method, it is difficult to obtain thick coatings.
- The layers of transition metal carbides of IVB and VIB groups are destroyed during contact with the liquid NiBSi alloy through their dissolution, intensified by the penetration of the liquid along

the coating – substrate interface, which proves the strong interaction of the liquid with both carbide ceramics and refractory metal substrate. The effect differs for both tested carbide groups: VIB (relatively fast) and IVB (less intense).

Author Contributions: conceptualization, M.B. and J.S.; methodology, J.S., B.G. and M.B.; validation, M.B., J.S. and B.G.; formal analysis, M.B. and J.S.; investigation, M.B. and B.G.; writing—original draft preparation, M.B. and J.S.; writing—review and editing, J.S. and M.B.; visualization, M.B.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

- [1] Eustathopoulos N., Nicholas M.G., Drevet B.; *Wettability at High Temperatures*, Pergamon Press, 1999.
- [2] Lengauer W., *Transition Metal Carbides, Nitrides, and Carbonitrides*, in: *Handbook of Ceramic Hard Materials*, Wiley - VCH, 2000.
- [3] Senkara J., Windyga A., *Podstawy teorii procesów spajania*, Wyd. Politechniki Warszawskiej, 1990.
- [4] Bober M., Jakubowski J., Radziszewski A., Senkara J., *Microstructure and mechanical properties of Ni-WC thermal sprayed composite coatings*, *Advances in Materials Science*, 2018, vol. 18, 24-34.
- [5] Bober M., Grześ J., *The structure of Ni-TiC composite coatings deposited by PPTAW method*, *Composites Theory and Practice*, 2015, vol. 2, 72-77.
- [6] Jakubowski J., Wysocki P., Senkara J., *Selektywne regeneracyjne napawanie plazmowe warstw Ni-WC na tytanowe łopatkę sprężarki silnika lotniczego*, *Welding Technology Review*, 2011, vol. 83, 38-42.
- [7] Bober M., Senkara J., *Badania struktury kompozytowych powłok Ni-WC napawanych plazmowo*, *Welding Technology Review*, 2016, vol. 88, 67-70.
- [8] Bober M., Senkara J., *Comparative tests of plasma-surfaced nickel layers with chromium and titanium carbides*, *Welding International*, 2016, vol. 30, 32-37.
- [9] Dul I., Kopeć J. i in., *Wpływ wybranych czynników technologicznych na proces lutowania próżniowego stopów Ni i stali wysokostopowej 18-8*, *Welding Technology Review*, 2009, 77-80.
- [10] Babul T., Jakubowski J. i in., *Lutowanie próżniowe uszczelnień ulowych w aparatach kierujących wykonanych ze stopów Hastelloy i Inconel z zastosowaniem luty NiCrSiB*, *Welding Technology Review*, 2007, 79, 124-129.
- [11] *CRC Handbook of Chemistry and Physics*, 99th Edition, Taylor&Francis, 2018.
- [12] Bober M., *Oddziaływania międzyfazowe w technologii napawania plazmowego warstw na osnowie Ni z węglkami metali przejściowych*. PhD Thesis, Warsaw University of Technology, Warsaw, 2009.
- [13] Senkara J., *Sterowanie energią adhezji pomiędzy molibdenem i wolframem a ciekłymi metalami w procesach spajania*, Wydawnictwa Politechniki Warszawskiej, 1993.
- [14] Oukach S., Pateyron B., Pawłowski L., *Physical and chemical phenomena occurring between solid ceramics and liquid metals and alloys at laser and plasma composite coatings formation: A review*, *Surface Science Reports*, 2019, vol. 74, 213-241
- [15] Jansson U., Lewin E., *Sputter deposition of transition-metal carbide films – a critical review from a chemical perspective*. *Thin Solid Films*, 2013, vol. 536, 1-24.
- [16] Tokunaga T., Nishio K., Ohtani H., Hasebe M., *Phase equilibria in the Ni-Si-B system*. *Materials Transactions*, 2003, vol. 44, 1651-1654.
- [17] Peng H., Liu C., Guo H., Yuan Y., Gong S., Xu H., *Fabrication of WCp/NiBSi metal matrix composite by electron beam melting*, *Materials Science and Engineering: A*, 2016, vol. 666, 320-323.
- [18] Liu C., H Peng H., Y Zhao Y., Y Yuan Y., Guo H.B., Xu H.B., *Microstructure, mechanical and corrosion properties of electron-beam-melted and plasma-transferred arc-welded WC_p/NiBSi metal matrix composites*, *Rare Metals*, 2019, vol. 38, 814–823.
- [19] Żak A., Sawras K., Dudziński W., *Wpływ składu mieszanin NiCrBSiFe+ WSC i NiBSi+ WSC na ich mikrostrukturę i twardość*, *Welding Technology Review*, 2016, vol. 88, 39-41.
- [20] Reeks W., Davies H., Marchisio S., *A review: Interlayer joining of nickel base alloys*, *Journal of Advanced Joining Processes*, 2020, vol. 2, 1000302020, <https://doi.org/10.1016/j.jajp.2020.100030>.
- [21] Sundaramoorthy R., Tong S.X., Parekh D., Subramanian C., *Effect of matrix chemistry and WC types on the performance of Ni-WC based MMC overlays deposited by plasma transferred arc (PTA) welding*, *Wear*, 2017, vol. 376–377, 1720-1727.



© 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).