Refractory, Ceramic, and Composite Materials
Тугоплавкие, керамические и композиционные материалы

UDC 621.762
https://doi.org/10.17073/1997-308X-2023-2-46-52

Research article
Научная статья

Core/rim microstructure of Ti(C, N) cermets with low nickel-molybdenum binder content

I. G. Grigorov, **V. A. Zhilyaev**

Institute of solid state chemistry, Ural branch of the Russian Academy of Sciences
91 Pervomayskaya Str., Yekaterinburg 620990, Russia

igor.grigorov2012@yandex.ru

Abstract. We investigated the influence of the basic component concentration on the microstructure of the KNT3 and KNT3 tungsten-free hard alloys (TFHA), focusing on ceramic-metal samples (cermets) with a low nickel-molybdenum binder content. The microstructure of the sintered cermets was analyzed using reflected electron images of thin sections obtained with a scanning electron microscope. Our analusis revealed that the KNT alloy exhobits a core/rim structure (CRM). We observed that decreasing the Ni–Mo binder content leads to a significantincrease in the rim size isurrounding the Ti(C, N) core in the sintered alloy. We also investigated the effect of the plasticizer on the formation of the core/rim microstructure with a low binder content. Furthermore, we found that the absence of nitrogen-enriched areas in the Ti(C, N) grains increases the molybdenum diffusion rate across the refractory phase interfaces during the cooling stage, resulting in a higher specific volume fraction of the shell in the cermet microstructure.

Keywords: thin shell micrography, cermets, titanium carbonitride (Ti(CN)), nickel-molybdenum binder, plasticizer

For citation: Grigorov I.G., Zhilyaev V.A. Core/rim microstructure of Ti(C, N) cermets with low nickel-molybdenum binder content. *Powder Metallurgy and Functional Coatings*. 2023;17(2):46–52.
https://doi.org/10.17073/1997-308X-2023-2-46-52

Микроструктура ядро/обод в керметах Ti(C, N) при дефиците никель-молибденовой связки

И. Г. Григоров, **В. А. Жиляев**

Институт химии твердого тела Уральского отделения РАН
Россия, 620990, г. Екатеринбург, ул. Первомайская, 91

igor.grigorov2012@yandex.ru

Аннотация. По результатам, полученным ранее в работах по безвольфрамовым твердым сплавам (БВТС) марок КНТ3 и КНТ7, проведен анализ влияния компонентов, составляющих их основу, на конечное формирование микроструктуры сплавов. Исследования проводились на керамико-металлических образцах (керметах) при дефиците связующей фазы из никеля с молибденом. Для анализа микроструктуры керметов были использованы изображения поверхности их шлифов, полученных с помощью растровой электронной микроскопии в режиме отраженных электронов. Показано, что особенностью микроструктуры сплавов серии КНТ является наличие у них структуры ядро/обод (Core/Rim Structure – CRM). Анализ выявил, что с уменьшением в БВТС серии КНТ содержания связующей фазы из Ni–Mo заметно увеличился размер обода в спеченном сплаве вокруг ядра из Ti(C, N). Дополнительно рассмотрена роль пластификатора в процессе формирования микроструктуры ядро/обод БВТС серии КНТ при дефиците связующей фазы. По результатам исследования микроструктуры керметов сделаны выводы, которые позволяют

предположить, что в отсутствие зон, обогащенных азотом, возрастает вероятность диффузии молибдена через межфазные границы тугоплавких фаз. Следствием этого является увеличение параметра удельной объемной доли оболочки в микроструктуре кермета.

Ключевые слова: анализ изображения шлифов, керметы, карбонитрид титана (Ti(CN)), никель-молибденовая связка, пластификатор

Для цитирования: Григоров И.Г., Жиляев В.А. Микроструктура ядро/ободв керметах Ti(C, N) при дефиците никель-молибденовой связки. *Известия вузов. Порошковая металлургия и функциональные покрытия*. 2023;17(2):46–52. https://doi.org/10.17073/1997-308X-2023-2-46-52

Introduction

The KNT series of tungsten-free hard alloys (TFHA) are composed of titanium carbonitride Ti(C, N) and nickel and molybdenum powders as fusible binders. These alloys can be used as an alternative to tungsten carbide hard alloys. The KNT alloys exhibit unique properties that distinguish them from other TFHAs including high hardness and low specific gravity. For example, the widely used KNT16 alloy (GOST 26530-85) has a hardness of 89 HRA and a density of 5.9 g/cm^3 [1–4].

The titanium carbonitride-based cermet offers several advantages, such as its easy availability and simple manufacturing. Moreover it exhibit higher hardness at high temperatures compared to tungsten carbide, along with superior scale resistance. Additionally, a thin oxide film is formed on the surface of the cermet during tool operates at elevated temperatures, which acts as a lubricant. As a result, the KNT alloys exhibit low friction coefficient and good wear resistance. Nonetheless, KNT alloys also possess certain drawbacks, including low impact toughness and thermal conductivity, and a high coefficient of thermal expansion. Consequently, these properties increase the likelihood of cracking when the tool is soldered and sharpened [2].

We developed a TFHA (KNT series) alloy with a reduced amount of No–Mo bonder, to evaluate its suitability as carbide cores for armor-piercing projectiles [3; 5]. These alloy has improved ceramic properties due the presence of a metallic bond improves their [6–12]. The authors presented the sintering conditions, essential TFHA microstructure characteristics, and physical and mechanical properties of the KNT3 and KNT7 alloys [13–15].

The microstructure of the KNT alloy is characterized by a core/rim structure (CRS) [15–20]. The core is comprised of a permanent liquid phase (PLP) consisting of carbonitride $TiC_{1-x}Ni_x$, while the rim (which forms the shell of the core) is a multicomponent carbonitride (Ti, Mo)(C, N). The formation of the cermet microstructure is primarily attributed to the wetting of the solid phase by the molten binder, facilitated by a wetting angle close to zero at the interface between the solid phase and the melt.

The objective of this study is to examine the impact of the carbon-to-nitrogen ratio in the permanent liquid phase (PLP) on the formation of the core/rim structure (CRS).

Alloys with a low binder content

Figure 1 presents composite contrast SEM cross sections of KNT7 and KNT3 alloys. It is apparent from the Fig. 1 that the coaxial shell of the base metal grains, or the rim, around the cermet cores in KNT3 occupies a larger surface area compared to KNT7. This notable difference in the microstructures of KNT3 cermets and conventional hard alloys was previously by Pakholkov V. et al. [3]. The authors suggested variations in the manufacturing process conditions such as sintering temperature and time, as shown in the table, can lead to the formation of different microstructures in cases where the content of the melt liquid phase is inadequate.

The rim (shell) formation by the dissolution-sedimentation reaction [4] is limited by the amount of available molybdenum in the liquid phase. The shell formation may be associated with molybdenum solid-phase mass transfer over the interphase interfaces. There are no available studies of this phenomenon so we decided to investigate the CRS phase and structure formation during the interaction between titanium carbonitride and metallic melts at various stages of sintering.

Formation of CRS ctructure in KNT alloys with a low binder content

The detailed synthesis of KNT3 and KNT7 cermets is presented in references [3; 13]. The values of sintering temperature (t_{sn}) and isothermal holding time (τ_h) for each sample (see the Table) can be attributed to the increased contribution of solid-phase sintering

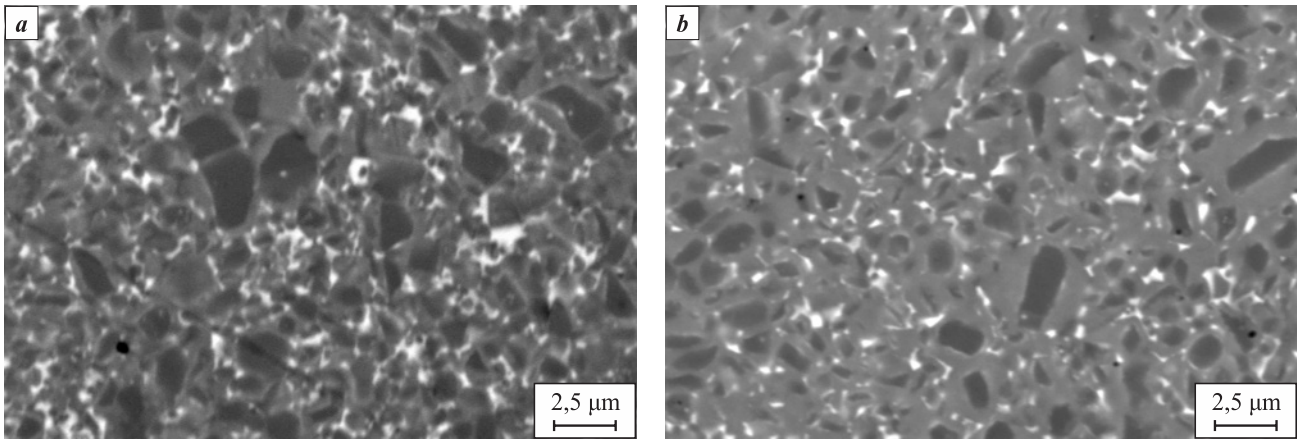

Fig. 1. The core/rim microstructure of KNT7 (***a***) and KNT3 alloys (***b***)
JSM 6390 LA microscope (JEOL Ltd., Japan), ×5000, reflected electron image

Рис. 1. Вид микроструктуры ядро/обод сплавов КНТ7 (***a***) и КНТ3 (***b***)
Микроскоп JSM 6390 LA (JEOL Ltd., Япония), увеличение ×5000, режим съемки – отраженные электроны

Phase composition of the cermets [13]

Фазовый состав исследуемых керметов [13]

Hard alloy grade	Sintering conditions		Content, vol. %		
	t_{sn} ± 10 °C	τ ± 1 %, min	TiC_xN_z core	Rim (Ti, Mo)(C, N)	Ni–Mo binder
KNT7	1480	20	44.64	47.41	6.70
	1480	60	43.95	48.27	6.65
	1500	60	40.42	53.26	6.30
	1520	12	40.97	52.12	6.74
	1520	40	38.64	55.24	6.10
	1520	60	36.67	57.46	5.86
	1540	60	34.06	60.48	5.45
	1560	60	30.89	63.78	5.30
KNT3	1540	20	24.76	72.94	2.22
	1540	60	23.12	74.78	2.02
	1560	60	22.86	75.16	1.94
	1580	60	21.60	76.66	1.70

to cermet formation as the metal component content decreases.

The permanent liquid phase in KNT alloys is titanium carbonitride, which has a double crystal structure consisting of TiC and TiN. Its thermodynamic compatibility with each metal component of the binder phase varies. Cermets are primarily composed on carbon + metal compounds. Nitrogen interacts with metals only at high temperatures and may or may not form weak nitrides. For example, titanium nitride (TiN) is used as an intermediate buffer layer in the electronics industry. It serves as an effective barrier for preventing the diffusion flows between conductive contact components.

The synthesis of the KNT alloy involves three stages of sintering, namely heating, holding at the melting temperature, and cooling in the furnace.

During the heating stage, several reactions take place between the refractory components and the refractory and binder components. These processes occur partially before the liquid phase appears and include gassing, diffusion reactions, and shrinkage of the powder compacts. As the powder mixture is heated, CO is released starting at approximately 900 °C and

reaches its maximum release rate at around 1100 °C. Nitrogen is released at ~1200 °C and reaches its maximum release rate at 1300 °C. The nitrogen release rate decreases at temperatures above 1300 °C is associated with the beginning of CRS growth in cermets.

During the the low-temperature sintering phase, the rubber-based plasticizer (4–5 % gasoline solution) [21; 22] is removed before the liquid metal (melt) emerges. Upon decomposition, the plasticizer yields the Mo_2C molybdenum compound, which may account for another characteristic of the shell microstructure. Figure 2 illustrates the two-layer shell structure of the KNT3 cermet, comprising an inner shell consisting of a solid solution rich in heavy elements, that surrounds the Ti(C, N) grain; and an outer shell is Ti-based material.

The last stage of the two-level shell microstructure formation, particularly its onset, remains ambiguous and conflicting. One proposal suggests that the final shell structure is created during the final stage of sintering, whereby TiC and MoC carbide are deposited on the Ti(C, N) particles. These carbides form a solid solution dissolved in the liquid binder. Another proposal assumes that the inner shell is formed by a solid-phase interaction at the initial sintering stage (up to 900 °C), while the outer shell is formed by dissolution/deposition.

The second sintering stage begins with the interaction between the Ni and Mo binders and refractory phases and the emergence of the liquid phase. The dissolution/deposition process becomes a significant contributor to the formation of the sintered cermet microstructure.

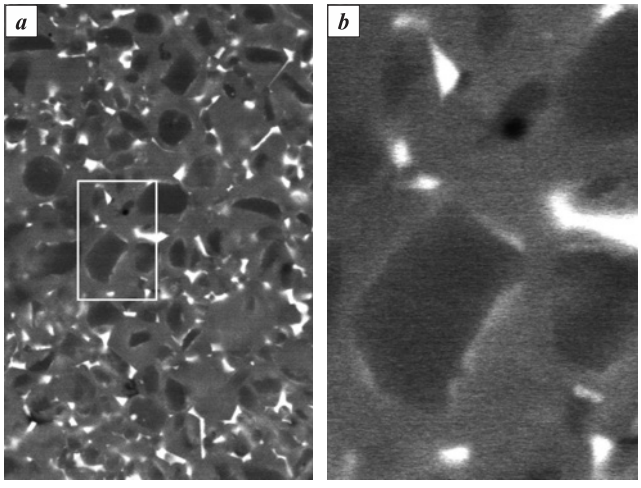

Fig. 2. Two-level microstructure of the KNT3 cermet rim: inner shell (light areas) and outer shell (dark gray areas)
JSM 6390 LA microscope, ×5000 (***a***) and ×20,000 (***b***), reflected electron images

Рис. 2. Вид двухуровневой микроструктуры оболочки (обода) кермета КНТ3: внутренней (светлые участки) и наружной (темно-серые)
Микроскоп JSM 6390 LA, увеличение ×5000 (***a***) и ×20 000 (***b***), режим съемки – отраженные электроны

According to available sources, during the sintering process, Ti(C, N) reacts with the melt such that the liquid molybdenum facilitates the dissolution of titanium and carbon from the PLP, while the nitrogen-rich, poorly soluble carbonitride remains preserved as a solid phase. The enrichment of the refractory phase with titanium nitride is more or less pronounced depending on the liquid/solid phase ratio. The nitrogen-rich areas of the Ti(C, N) grains remain insoluble in the liquid metal bond and act as crystallization nuclei of the (Ti, Mo)C carbide solutions deposited from the melt by dissolution/sedimentation, leading to the formation of the so-called *K*-phase [4].

The formation of the *K*-phase takes place during the liquid-phase sintering of hard alloys in the presence of a carbide-forming element in the melt. As the liquid phase emerges, the TiC component of the PLP begins to dissolve, forming (Ti, Mo)C. The deposition of this compound is possible only when the limit solubility product value $Mo_{1-n}Ti_nC_y$ is reached.

The core size of the Ti(C, N) particles increases with the sintering time primarily due to particle coalescence at their interfaces, which is more intense under liquid-phase sintering than under solid-phase sintering, before the shell structure formation. The rate of shell deposition on the Ti(C, N) grains depends on the sintering temperature and (Ti, Mo)C concentration in the melt. The shell thickness reaches 0.5–3.0 μm as the sintering temperature increases from 1450 to 1540 °C.

Pakholkov V. et al. [3] observed that as the volume fraction of the Ni–Mo binder decreases, the degree of coalescence of the Ti(C, N) grains increases. The specific volume content (V_V) of the Ti shell (rim) consisting of $Ti_{1-x}Mo_xC_yN_z$ exhibits an inverse relationship between the V_V of the shell (as shown in the table) and binder volume, but the reason for this is unclear.

The furnace cooling rate is controlled and does not exceed 10 °C/min to ensure a smooth temperature gradient across the TFHA thickness, thus tavoiding thermal cracking caused by different coefficients of linear thermal expansion of the TFHA components. The shell formation by dissolution-deposition from the melt $(Ti_{1-n}Mo_n)C_x$ in the KNT3 alloy is limited by the volume content of the binder. At the final stage of the CRS formation, significant shell growth can be attributed to a solid-phase molybdenum mass transfer across

the TiC_xN_z – $(Ti_{1-n}Mo_n)C_x$ interface [3]. Figure 3 illustrates the CRS difference for KNT7 and KNT3 cermets for identical sintering conditions (t_{sn} = 1560 °C; τ = 60 min).

Conclusions

We have determined that the synthesis of KNT solid alloy can be divided into three stages: heating, holding at the temperature required for melt formation, and cooling in the furnace. Our conclusion can be summarized as follows.

1. We have observed that the decrease in volume fraction of the Ni–Mo metallic binder leads to an increase in the volume fraction of the $Ti_{1-x}Mo_xC_yN_z$.

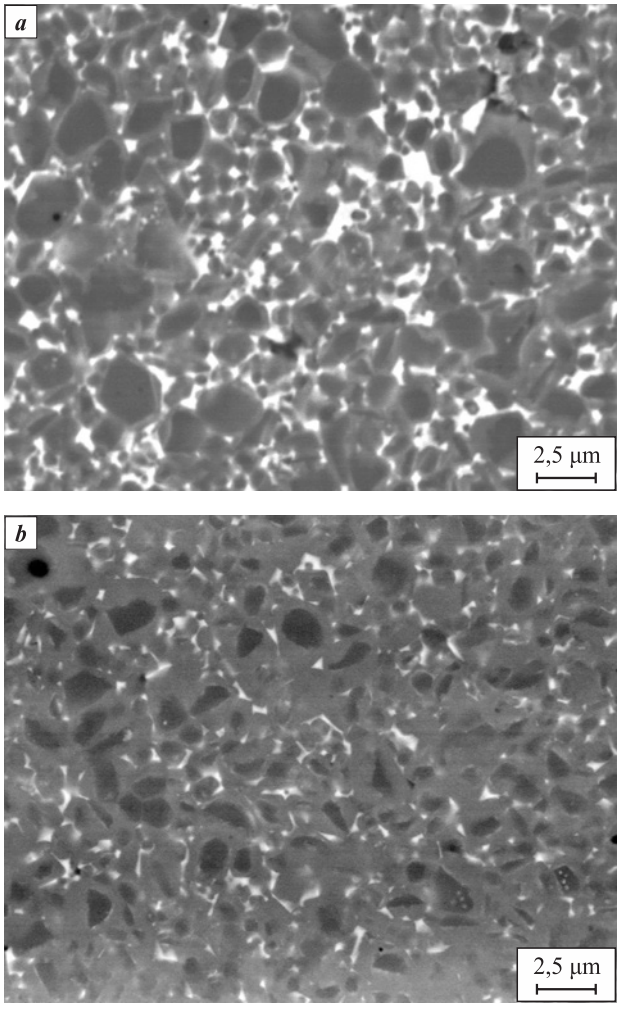

Fig. 3. Microstructure of KNT7 (***a***) and KNT3 (***b***) cermets
JSM 6390 LA microscope, ×3000, t_{sn} = 1560 °C, τ = 60 min, reflected electron images

Рис. 3. Вид микроструктуры керметов марок КНТ7 (***а***) и КНТ3 (***б***)
Микроскоп JSM 6390 LA, увеличение ×3000, $t_{сп}$ = 1560 °C, τ = 60 мин, режим – отраженные электроны

2. The absence of nitrogen-enriched areas in the Ti(C, N) grains leads to an increase in the diffusion rate of molybdenum across the refractory phase interfaces during the cooling stage.

3. We have discovered a two-level structure of the cermet shell with inner and outer layers. The inner shell (appearing as light areas in the SEM image) is molybdenum-rich, while the outer shell is Ti-rich (appearing as dark gray areas).

4. We propose a chemical explanation for the formation of the inner cermet shell as a result of the decomposition of the rubber-based plasticizer (4–5 % gasoline solution) during the heating stage.

References / Список литературы

1. Panov V.S., Chuvilin A.M. Technology and properties of sintered hard alloys and products from them. Moscow: MISIS, 2001. 426 p. (In Russ.).

Панов В.С., Чувилин А.М. Технология и свойства спеченных твердых сплавов и изделий из них. М.: МИСИС, 2001. 426 с.

2. Yanushkin A.S., Yakimov S.A., Petrov I.P., Arkhipov P.V. Studies of the surface of tungsten-free hard alloys ground by the combined method. *Nauchnyi zhurnal Bratskogo gosudarstvennogo universiteta*. 2009;(2):70–77. (In Russ.).

Янюшкин А.С., Якимов С.А., Петров И.П., Архипов П.В. Исследования поверхности безвольфрамовых твердых сплавов, шлифованного комбинированным методом. *Научный журнал Братского государственного университета*. 2009;(2):70–77.

3. Pakholkov V.V., Melnikov B.V., Grigorov I.G., Zainulin Yu.G., Alyamovsky S.I. Features of the formation of the microstructure of hard alloys based on $TiC_{0.5}N_{0.47}$ with a deficiency of nickel–molybdenum bond. *Neorganicheskie materialy*. 1990;26(2):292–296. (In Russ.).

Пахолков В.В., Мельников Б.В., Григоров И.Г., Зайнулин Ю.Г., Алямовский С.И. Особенности формирования микроструктуры твердых сплавов на основе $TiC_{0,5}N_{0,47}$ при дефиците никель – молибденовой связки. *Неорганические материалы*. 1990;26(2):292–296.

4. Zhilyaev V.A., Patrakov E.I. Regularities of the contact interaction of double carbides $(Ti_{1-n}Me_n)C$ with nickel. *Russian Journal of Non-Ferrous Metals*. 2015;56(3):329–332. https://doi.org/10.3103/S1067821215030232

Жиляев В.А., Патраков Е.И. Кинетика и механизм контактного взаимодействия карбонитрида титана с Ni–Mo-расплавом. *Известия вузов. Порошковая металлургия и функциональные покрытия*. 2015;(2):30–37. https://doi.org/10.17073/1997-308X-2015-2-30-37

5. Kieffer R., Benesovsky F. Hard alloys. (Translated from German). Moscow: Metallurgiya. 1971. 392 p. (In Russ.).

Киффер Р., Бенезовский Ф. Твердые сплавы. Перевод с нем. М.: Металлургия, 1971. 392 с.

6. Bolognini S., Feusier G., Mari D., Viatte T., Benoit W. TiMoCN-based cermets: high-temperature deformation.

International journal of refractory metals and hard materials. 2003;21(1–2):19–29. https://doi.org/10.1016/S0263-4368(02)00091-4

7. Mari D., Bolognini S., Feusier G., Cutard T., Verdon C., Viatte T., Benoit W. TiMoCN based cermets: Part I. Morphology and phase composition. *International Journal of Refractory Metals and Hard Materials*. 2003;21(1):37–46. https://doi.org/10.1016/S0263-4368(03)00010-6
8. Mari D., Bolognini S., Feusier G., Cutard T., Viatte T., Benoit W. TiMoCN based cermets Part II. Microstructure and room temperature mechanical properties. *International Journal of Refractory Metals and Hard Materials*. 2003;21(1):47–53. https://doi.org/10.1016/S0263-4368(03)00011-8
9. Zhou S., Zhao W., Xiong W. Microstructure and properties of the cermets based on Ti(C, N). *International Journal of Refractory Metals and Hard Materials*. 2009;27(1):26–32. https://doi.org/10.1016/j.ijrmhm.2008.01.011
10. Bellosi A., Calzavarini R., Faga M.G., Monteverde F., Zancolo C., D'Errico G.E. Characterization and application of titanium carbonitride-based cutting tools. *Journal of Materials Processing Technology*. 2003;143-144:527–532. https://doi.org/10.1016/S0924-0136(03)00339-X
11. Xiong J., Guo Z., Wen B., Li C., Shen B. Microstructure and properties of ultra-fine $TiC_{0.7}N_{0.3}$ cermet. *Materials Science and Engineering: A*. 2006;416(1-2):51–58. https://doi.org/10.1016/j.msea.2005.08.060
12. Peng Y., Miao H., Peng Z. Development of TiCN-based cermets: Mechanical propertiesand wear mechanism. *International Journal of Refractory Metals and Hard Materials*. 2013;39:78–89. https://doi.org/10.1016/j.ijrmhm.2012.07.001
13. Grigorov I.G., Zhilyaev V.A., Ermakov A.N., Zainulin Yu.G., Shveykin G.P. On the methodology of forecasting some physical and mechanical properties of kermets. *Materialovedenie*. 2004;(8):14–20. (In Russ.).

    Григоров И.Г., Жиляев В.А., Ермаков А.Н., Зайнулин Ю.Г., Швейкин Г.П. О методике прогнозирования некоторых физико-механических свойств керметов. *Материаловедение*. 2004;(8):14–20.
14. Grigorov I.G., Zainulin Y.G. Analysis of fracture of metal ceramic hard alloys of KNT brand. *Materialovedenie*. 2019;10(4):987–994. (In Russ.).

    Григоров И.Г., Зайнулин Ю.Г. Анализ изломов металлокерамических твердых сплавов марки КНТ. *Материаловедение*. 2019;(2):17–24.
15. Grigorov I.G., Zainulin Y.G., Shveykin G.P. Fractal analysis of fracture of powder metallurgical hard alloy. *Materialovedenie*. 2017;8(1):67–74. (In Russ.).

    Григоров И.Г., Зайнулин Ю.Г., Швейкин Г.П. Фрактальный анализ разрушения металлокерамических твердых сплавов. *Материаловедение*. 2016;(6):16–22.
16. Li P., Ye J., Liu Y., Yang D., Yu H. Study on the formation of core–rim structure in Ti(CN)-based cermets. *International Journal of Refractory Metals and Hard Materials*. 2012;35:27–31. https://doi.org/10.1016/j.ijrmhm.2012.03.012
17. Ahn S., Kang S. Formation of core/rim structures in Ti(C,N)–WC–Ni cermets via a dissolution and precipitation process. *Journal of the American Ceramic Society*. 2000;83(6):1489–1494. https://doi.org/10.1111/j.1151-2916.2000.tb01415.x
18. Kim S., Min K., Kang S. Rim structure in $Ti(C_{0.7}N_{0.3})$–WC–Ni cermets. *Journal of the American Ceramic Society*. 2003;86(10):1761–1766. https://doi.org/10.1111/j.1151-2916.2003.tb03551.x
19. Bellosi A., Medri V., Monteverde F. Processing and properties of Ti(C,N)–WC-based materials. *Journal of the American Ceramic Society*. 2001;84(11):2669–2676. https://doi.org/10.1111/j.1151-2916.2001.tb01069.x
20. Zheng Y., Lin W., Wang S., Xiong W. Effect of carbont on the microstructure and mechanical properties of Ti(C, N)-based cermets. *Ceramics International*. 2004;30(8):2111–2115. https://doi.org/10.1016/j.ceramint.2003.11.016
21. Ermakov A.N., Grigorov I.G., Ermakova O.N., Pushin V.G., Zainulin Yu.G. Influence of plasticizer on microstructure and properties of titanium carbonitride – titanium nickelide system. *Perspetkivnye materialy*. 2006;(5):42–48. (In Russ.).

    Ермаков А.Н., Григоров И.Г., Ермакова О.Н., Пушин В.Г., Зайнулин Ю.Г. Влияние пластификатора на микроструктуру и свойства системы карбонитрид титана – никелид титана. *Перспективные материалы*. 2006;(5):42–48.
22. Grigorov I.G., Zhilyaev V.A., Ermakov A.N., Zainulin Yu.G. The effect of plasticizer on the microstructure of an alloy based on carbonitride and titanium nickelide. *Konstruktsii iz kompozitsionnykh materialov*. 2006;(4):46–49. (In Russ).

    Григоров И.Г., Жиляев В.А., Ермаков А.Н., Зайнулин Ю.Г. Влияние пластификатора на микроструктуру сплава на основе карбонитрида и никелида титана. *Конструкции из композиционных материалов*. 2006;(4):46–49.

Information about the Authors

Igor' G. Grigorov – Cand. Sci. (Chem.), Research Scientist of Laboratory of Structural and Phase Analysis, Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences (ISSC UB RAS)
ORCID: 0000-0003-1906-7654
E-mail: igor.grigorov2012@yandex.ru

Viktor. A. Zhilyaev – Dr. Sci. (Eng.), ISSC UB RAS

Сведения об авторах

Игорь Георгиевич Григоров – к.х.н., вед. науч. сотрудник лаборатории структурного и фазового анализа, Институт химии твердого тела УрО РАН (ИХТТ УрО РАН)
ORCID: 0000-0003-1906-7654
E-mail: igor.grigorov2012@yandex.ru

Виктор Александрович Жиляев – д.т.н., ИХТТ УрО РАН

Contribution of the Authors

I. G. Grigorov – basic concept, problem statement, paper authoring, conclusions.

V. A. Zhilyaev – research supervision, article proofreading, editing the conclusions.

Вклад авторов

И. Г. Григоров – формирование основной концепции, постановка цели и задачи исследования, подготовка текста, формулировка выводов.

В. А. Жиляев – научное руководство, корректировка текста, корректировка выводов.

Received 26.05.2022
Revised 24.11.2022
Accepted 01.12.2022

Статья поступила 26.05.2022 г.
Доработана 24.11.2022 г.
Принята к публикации 01.12.2022 г.