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Structural Investigations of Doped Eutectic Alloys Based on Nickel with Niobium Carbide

G. P. Dmytriieva, T. S. Cherepova, T. V. Pryadko, T. A. Kosorukova, and A. V. Nosenko

G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine

The melting temperature, microstructure, and phase composition of cast eutectic alloys with niobium carbide, in which the metal base represented by nickel or nickel and cobalt, are studied by methods of physicochemical analysis. The properties of the studied alloys are comparable with the corresponding properties of the industrial eutectic composite based on cobalt with niobium carbide. The melting point of the eutectic (solidus) of nickel-based alloys is above 1300°C and does not differ from the corresponding value for cobalt serial alloy. The structure of alloys has slightly over-eutectic features and is determined by the presence of primary undeveloped niobium carbide dendrites in the eutectic of dispersed eutectic carbide crystals in an alloyed metal base. In the phase composition of the studied alloys, along with a solid solution of alloying elements in Nickel (γ) and niobium carbide (NbC), there are metastable phases enriched in chromium and rhenium. According to the complex of structural properties, cast eutectic alloys of nickel with niobium carbide are promising for use as an alternative to cobalt alloys of the XTH series.

Key words: cobalt, nickel, niobium carbide, eutectic, melting point, structure, phase composition.

Методами фізико-хемічної аналізи досліджено температуру топлення, мікроструктуру, фазовий склад литих леґованих евтектичних з карбідом Ніобію стопів, в яких металева основа представлена Ніклем, або Ніклем і

Corresponding author: Galyna Petrivna Dmytriieva
E-mail: galina1225@gmail.com

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Кобальтом нарівно. Властивості досліджених стопів порівняні з відповідними властивостями промислового евтектичного композиту на основі Кобальту з карбідом Ніобію. Температура топлення евтектики (солідус) стопів на основі Ніклю вища за 1300°C і не відрізняється від відповідного значення для кобальтового серійного стопу. Структура стопів має ознаки злегка заевтектичної і визначається присутністю первинних нерозвинених дендритів карбіду Ніобію в евтектиці з дисперсних евтектичних кристалів карбіду в леґованій ніклевій, або нікель-кобальтовій металевій основі. В фазовому складі досліджених стопів нарівні з твердим розчином леґувальних елементів в ніклі (γ) і карбіду Ніобію (NbC) присутні метастабільні фази, збагачені Хромом і Ренієм. За комплексом структурних властивостей досліджені литі евтектичні ніклеві з карбідом Ніобію стопи є перспективними для застосування в якості альтернативи кобальтовим стопам серії ХТН.

Ключові слова: Кобальт, Нікель, карбід Ніобію, евтектика, температура топлення, структура, фазовий склад.

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1. INTRODUCTION

Industrial cast eutectic cobalt-carbide alloys of XTH series [1, 2, 3] developed at G. V. Kurdyumov IMPh of the N.A.S.U. are natural composites, which use the advantage of structure formation of highly dispersed metal-carbide stable structure due to eutectic crystallization reaction between solid solution based on metal and monocarbide of refractory metal MeC [4, 5]. Alloys are used as wear-resistant and heat-resistant to protect against wear of the contact surfaces of the blades in turbines GTE and TVD [6–8]. For the purpose of economic expediency, it is important to replace the cobalt base of such alloys with much cheaper nickel without losing the basic properties required of alloys for this purpose. This requires structural studies of the properties of eutectic alloys with niobium carbide, in which the metallic cobalt base is replaced by nickel partially or completely, denoted as Ni (Ni + Co)–NbC. The parameters of structure formation primarily include the eutectic melting point (solidus), microstructure and phase composition.

The advantage of using nickel is seen not only in economic feasibility and in the simplification of the use of nickel protective wear-resistant and heat-resistant alloy on parts of gas turbine engines. It also consists in the absence of polymorphic transformations in nickel-based alloys; in the probable additional strengthening due to γ′-phase; in the same thermodynamic conditions of two-phase equilibrium of nickel and cobalt with niobium carbide with a melting diagram of the eutectic type [9, 10].

The melting diagram of the quasi-binary cross section of Ni–NbC (NbC0.92) of the ternary system of Ni–Nb–C elements according to the literature data is determined by the following eutectic crystallization parameters: melting point of eutectic in the range from 1330 to 1350°C, the proportion of eutectic in the range from 6 to 12% wt. [11, 12]. According to [13], the eutectic crystallization reaction takes place at a temperature of 1345°C and contains elements (at.%): from 4 to 7.2 Nb and from 3.2 to 6 C, nickel—the rest, and the cross section is deviated from the equiatomic towards niobium (Fig. 1).

To give the eutectic nickel alloy the desired properties, doping similar to cobalt serial alloy is required [14]. Properly determined composition and content of alloying elements in eutectic alloys based on nickel with niobium carbide and study of their melting point, structure and phase composition is an important step in creating new industrial alloys to protect against wear of contact surfaces of gas turbine blades.

2. EXPERIMENTAL DETAILS

Samples for the study weighing 25–30 grams were made in an arc furnace by the method of electric arc melting with a non-consumable tungsten electrode in argon, on a copper water-cooled hearth. The crys-

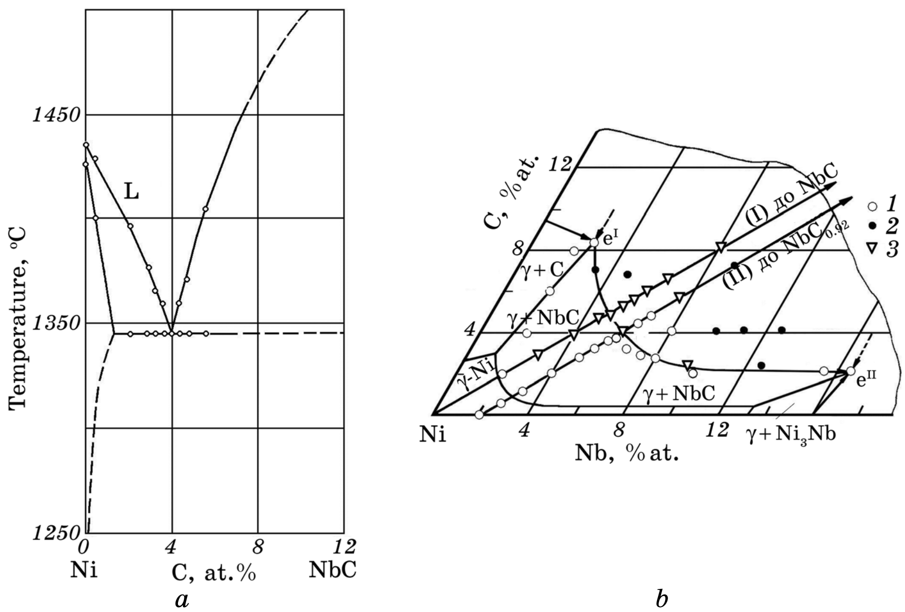


Fig. 1. Phase diagram of the Ni–Nb–C system [13]: quasi-binary cross section of Ni–NbC (*a*), Ni-angle of the melting diagram of the ternary system of elements C–Ni–Nb (*b*).

tallization rate of the melt is ≈ 150°/s. The study of structural properties was performed on cast samples, as serial cobalt alloys XTH are used in the cast state. The charge materials for the smelting of alloys were: nickel grade (99.9%), cobalt K1 (99.35%), electrolytic chromium ERC (99.5%), tungsten in HTP rods (99.95%), aluminium A-995 (99.95%), rhenium powder, niobium NBSH-00 (99.95%), spectrally pure graphite. The chemical composition of the alloys, determined by fluorescence X-ray spectral analysis on a VRA-30 spectrometer, coincides with the nominal composition within an error of ±0.5%. The melting point was investigated by the method of high-temperature differential thermal analysis (VDTA) in an atmosphere of ultra-high argon pressure thermal analyser VDTA-8M with a heating and cooling rate of 80 °/min, or by the method of differential scanning calorimeter (DSC) on the calorimeter 'Netzsch DSC 404 F1 Pegasus'. Analysis of the content of metal components in the phase components of alloys was performed according to the data of energy-dispersive X-ray spectroscopy, obtained on the equipment: JSM-7100F Schottky Field Emission Scanning Electron Microscope (Jeol). Microstructural analysis (ISA) was performed using an optical microscope 'Neophot-32'.

3. RESULTS AND DISCUSSION

According to an experimental study, the melting point of the alloy of the eutectic composition of the Ni–NbC system is defined as 1335°C, and the composition of the alloy contains ≈ 12% vol. (11% wt.) NbC.

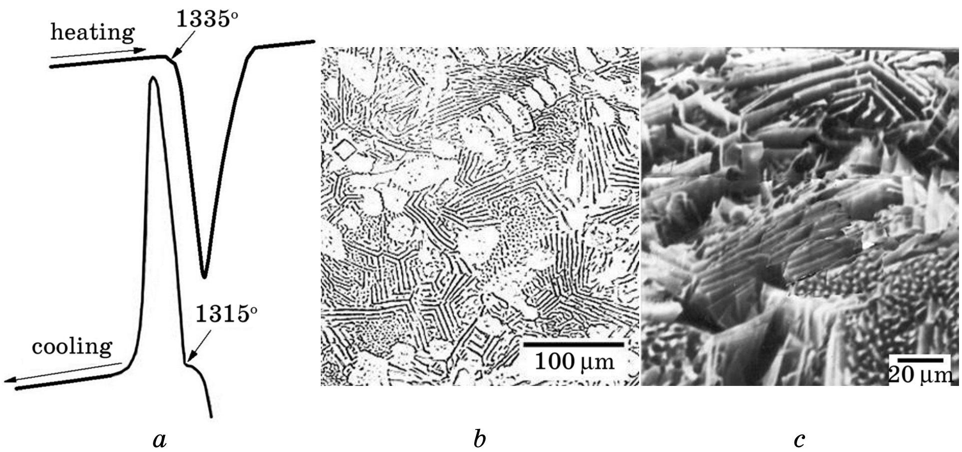


Fig. 2. Parameters of crystallization of the eutectic composition of the Ni–NbC system: thermal curves of heating and cooling (*a*), nickel-carbide eutectic colonies in the microstructure of the alloy (*b*), the shape of carbide crystals in the structure of the eutectic colony of the alloy with etched metal phase (*c*).

TABLE 1. Solubility of alloying elements in Nickel.

Element	Maximum solubility in Ni		Maximum solubility temperature and type of reaction, °C
	% mas.	at.%	
Cr	46.97	50	1345 (eutectic)
W	39.9	17.5	1500 (eutectic)
Al	10.4	21	1385 (eutectic)
Re	40	17.4	1620 (peritectics)
Nb	20.83	13.5	1285 (eutectic)
C	0.71	3.4	1314 (eutectic)

The crystallization interval is ≈ 20°C. Thermal curves of heating with the melting temperature of the alloy (1335°C) and cooling with the crystallization temperature (1315°C) are shown in Fig. 2, *a*. In the structure of the eutectic alloy there are primary crystals of the embodiment phase—niobium monocarbide, which generates and conducts crystallization (Fig. 2, *b*). Carbide crystals in the eutectic colony (Ni + NbC) with a thickness of ≈ 1 μm and a length of ≈ 20 μm have a lamellar-rod shape (Fig. 2, *c*).

Alloying of nickel-carbide eutectic alloys is made for a number of reasons, including to ensure the phase and structural stability of γ-solid solution at high temperatures by stabilizing and strengthening elements such as Cr, W, Mo. Al and Ti are used to ensure the optimal ratio of the total content of γ'-forming elements [15]. Re, Cr, and W take part in the strengthening of a nickel-based solid solution by slowing down the mobility of grain boundaries. Rhenium most intensively slows down the diffusion of atoms of alloy components [16].

In the studied in the work of nickel with niobium carbide alloys used the same alloying complex as in the industrial cobalt alloy XTH based on the eutectic Co + NbC [17], alloying elements which serve in the following amount (% wt.): chromium (18–20), tungsten (9–10), aluminium (2–4), (possible introduction of molybdenum in the amount of up to 2%). When dissolved in cobalt and nickel, these elements reduce their melting point. To prevent this, based on the analysis of modern heat-resistant nickel alloys for casting blades GTE [18], the content of alloying elements in the studied alloys is further supplemented with rhenium, which increases the melting point of cobalt and nickel, according

TABLE 2. Chemical composition of the studied alloys.

Element	Cr	W	Al	Re	Mo	Nb	C	Ni (Ni + Co)
% mas.	18–20	3–9.5	2–3	4.5–6	≤ 2	15–15.5	1.8–2	rest

to the phase equilibrium diagram.

By reducing the solubility in nickel, the elements that make up the alloy are distributed in a number: Cr, Al, W, Re, Nb, C [19]. Analysis of the maximum dissolution temperature (Table 1) tungsten and rhenium may have a positive effect on the melting point of the studied alloys.

Taking into account the results of the analysis of the solubility of alloying elements in nickel, the technological regulation of smelting alloy ingots requires certain conditions when loading the charge and the melt temperature ≥ 1700°C. The most optimal doping limits are given in Table. 2.

The influence of nickel on the melting temperature of a serial cobalt alloy without rhenium is represented by thermal heating and cooling curves (VDTA method) for alloys, the alloying complex of elements of which includes (% wt.): 20 Cr, 9.5 W, 2 Al, 15 Nb, 2 C (Fig. 3). The metal base of the studied alloys is nickel, or nickel and cobalt in equal proportions, or only cobalt. Melting of eutectic in a nickel-based alloy (Fig. 3, *a*) begins at a temperature of 1300°C (solidus), crystallization occurs at 1290°C, interval of melting–crystallization is 10°C, which minimizes possible segregation. The obtained data of thermal analysis prove a decrease in the alloying temperature of the alloy of the eutectic composition in the Ni–NbC system by 35°C.

The presence of in the metal base of alloy the nickel in equal proportions with cobalt does not change the melting temperature (Fig. 3, *b*), because these elements are completely mutually soluble. The melting point of the base alloy based on cobalt exceeds the melting point of nickel alloys, reaching 1320°C (Fig. 3, *c*). This is obviously due to the higher melting point of cobalt (1494°C) than nickel (1453°C).

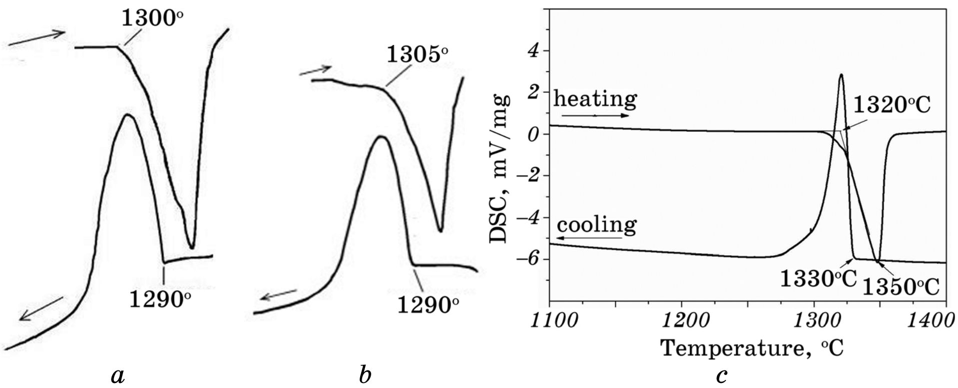


Fig. 3. Thermal curves of heating and cooling of alloys of the system of elements Ni (Ni + Co)–NbC and alloy XTH: based on nickel (*a*), based on nickel and cobalt equally (*b*), XTH based on cobalt (*c*).

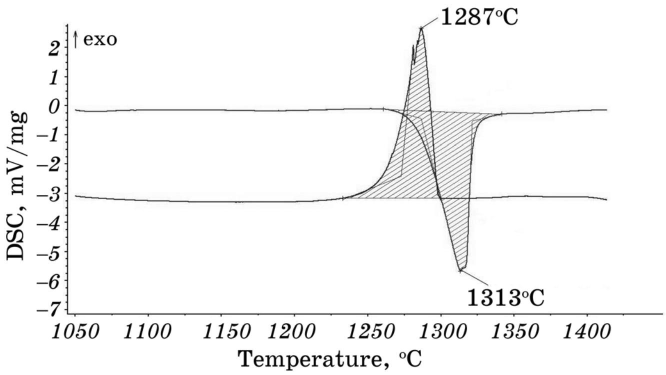


Fig. 4. Thermal heating and cooling curves of an alloy based on nickel with niobium carbide additionally doped with rhenium (DSC method).

However, despite the fact that the melting point of Ni (Ni + Co) NbC alloys is lower than the melting point of cobalt alloy by ≈ 10–15°C, it remains within the technological requirements for the melting point of industrial wear-resistant and heat-resistant alloys (≥ 1300°C).

Figure 4 shows the heating and cooling curves of an alloy based on nickel with niobium carbide, which further contains rhenium and the content of alloying elements in which is (% wt.): 20 Cr, 9 W, 3 Al, 4.5 Re, 15 Nb, 2 C, Ni—the rest.

The solidus temperature of the alloy containing rhenium, and the melting point of which is 1314°C, is preceded by the thermal effect of solid-phase transformation, similar to that in the alloy XTH based on cobalt [20]. Additional doping with rhenium raises the melting point of

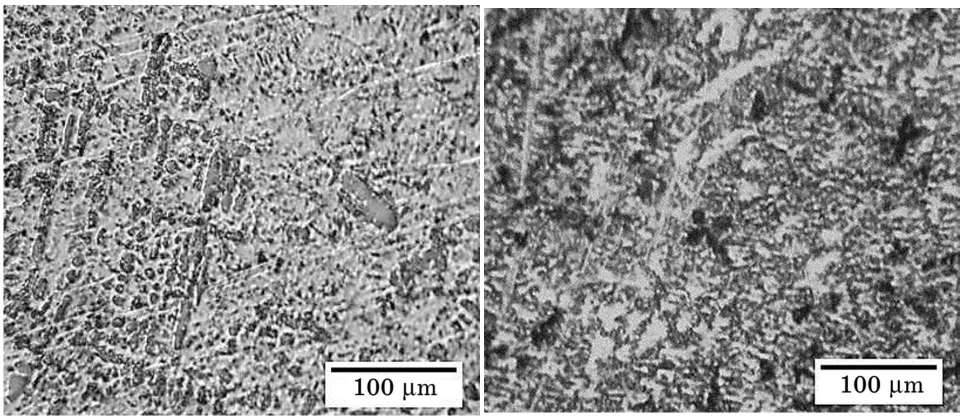
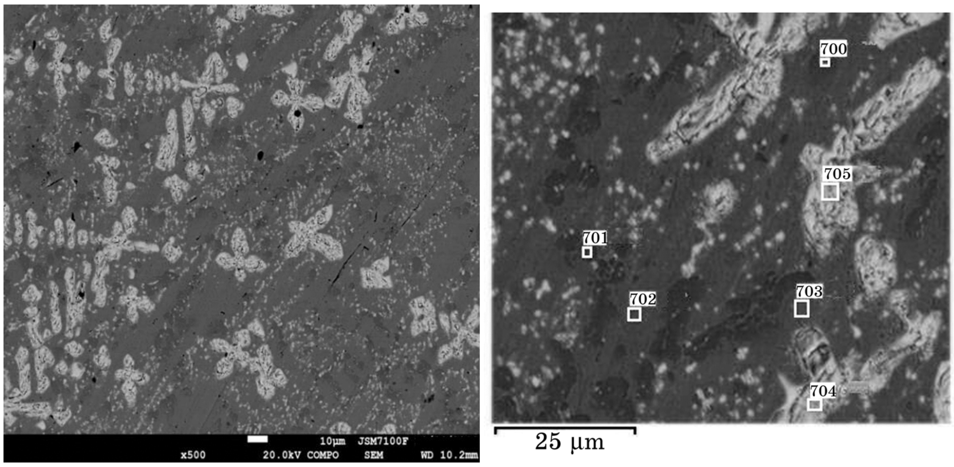


Fig. 5. Typical structure of eutectic alloys with niobium carbide: nickel-based alloy (*a*), cobalt-based alloy (*b*).



a *b*

Fig. 6. Phase components of eutectic alloy based on nickel with niobium carbide: microstructure (*a*), zones for determining the phase composition (*b*).

the nickel-based alloy to the level of serial cobalt—niobium carbide eutectic composite XTH.

The structure formation of doped cast alloys of Ni (Ni + Co)–NbC begins with the crystallization of niobium carbide from liquid, and ends with the crystallization of eutectic and this process looks like P → NbC → (γ + NbC). The shape and dispersion of the carbide phase crystals depends on the composition of the alloy and the cooling rate during crystallization. The studied alloys have a typical structure, which is characteristic of slightly over-eutectic two-phase serial cobalt alloys with niobium carbide. The structural components of alloys, both

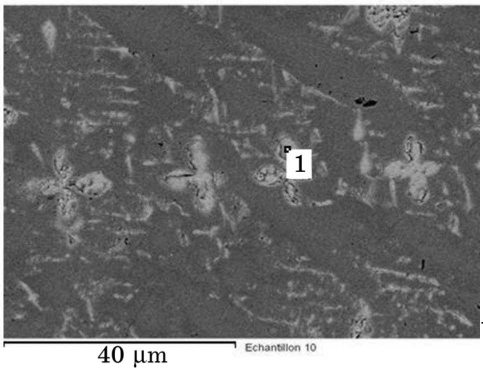
TABLE 3. Phase composition of the alloy based on nickel without carbon.

No. zone	Composition, % mas.					
	Ni	Cr	W	Nb	Al	Mo
700	9.03	74.13	9.85	0	0	6.99
701	17.18	66.86	9.11	0	0.32	6.54
702	70.15	19.69	3.36	1.75	2.93	2.12
703	70.54	19.53	3.54	1.69	2.64	2.06
704	2.06	1.43	2.99	93.52	0	0
705	1.78	1.35	3.34	93.52	0	0
Nominal composition	58	18	3	15	2	2

cobalt-based and nickel-based, are undeveloped niobium carbide dendrites (dark phase) in eutectic (Fig. 5). A feature of the structure of such natural composites is the dispersion of structural elements and its stability up to temperatures close to the melting point.

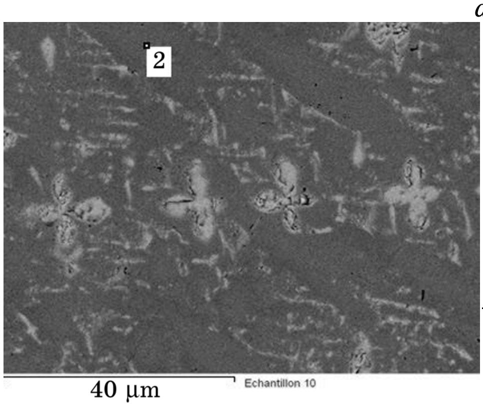
The content of niobium carbide in nickel alloys ≈ 15%, which is commensurate with the corresponding value for the alloy XTH. The high content of carbide in the form of dispersed structural components in combination with heat-resistant metal base should provide sufficient properties of hardness and wear resistance of nickel-based alloys when used as protective materials for contact surfaces of gas turbine blades at high temperatures.

Determination of the distribution of alloying elements in the phase components of Ni (Ni + Co)–NbC alloys was performed by the EMF method. The results of the study of the phase composition of alloys based on nickel, or nickel and cobalt were compared with the phase composition of the base alloy XTH, smelted under identical conditions.



Element	% mas.	at.%
Al	0.71	2.17
Cr	5.03	7.9
Co	8.14	11.27
Ni	7.73	10.74
Nb	76.57	67.00
W	1.82	0.92
Total	100%	

a



Element	% mas.	at.%
Al	3.33	7.08
Cr	20.81	22.76
Co	35.53	34.33
Ni	34.61	33.35
Nb	2,13	1.36
W	3.59	1.12
Total	100%	

b

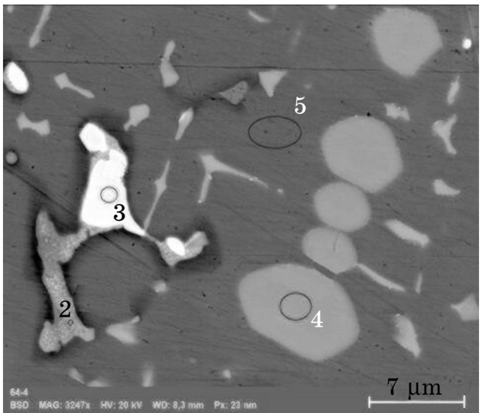
Fig. 7. Content of metallic elements: in niobium carbide crystal (*a*), in eutectic component of cobalt-nickel alloy (*b*).

The phase composition of the alloy, which contains (% wt.): 18 Cr, 3 W, 2 Al, 2 Mo, 15 Nb, 2 C, Ni—the rest, is shown in Fig. 6 and in Table 3. According to the study, it is determined that the specified alloy is two-phase, as well as the base cobalt alloy. The alloy phases are niobium carbide and eutectic (Ni + NbC).

Other carbide-forming elements present in the primary crystals of niobium carbide present in the alloy structure (samples 704, 405) are almost insoluble. The metal base of the eutectic component of the alloy is a solid solution of chromium, tungsten, aluminium and molybdenum in nickel (samples 702, 703). The chromium-based phase component (samples 700, 701) can be interpreted as a metastable carbide based on it.

The result of the study of the phase composition of the structural components of the alloy, the metal base of which consists of nickel and cobalt equally, and which contains the following elements (% wt.): 18.2 Cr, 3 W, 2 Al, 15 Nb, 2 C are presented in Fig. 7.

The obtained results indicate that in the case of replacement of the cobalt base of the alloy equally by nickel, the quantitative phase composition of the alloy does not change, it remains two-phase and is represented by primary crystals of niobium carbide in eutectic. The amount of niobium in carbide is approaching 77% (spectre 1, Fig. 7, *a*), and the eutectic consists of solid solution on base nickel-cobalt and dispersed crystals of niobium carbide (spectre 2, Fig. 7, *b*).



Zone	Ni	Cr	W	Al	Re	C	Nb
2	42.45	18.87	6.66	2.69	4.82	2.51	21.99
3	21.61	47,2	19.65	0.63	6.35	3.05	1.49
4	1.37	1.23	4.89	0.13	0.36	7.09	84.93
5	55.68	24.66	6.63	3.63	6.35	1.96	1.09

Fig. 8. Structure and chemical composition of the phases of nickel-niobium carbide alloy additionally doped with rhenium.

With additional rhenium doping, the quantitative phase composition of the nickel alloy changes. In Figure 8 shows the phase composition of the alloy containing (% wt.): 18 Cr, 9.5 W, 3 Al, 6 Re, 15.5 Nb, 1.8 C, nickel—the rest. According to experimental data, this alloy is not two-phase. Niobium carbide (grey phase, spectre 4) contains some tungsten. The metal base of the alloy is a γ-solid solution of alloying elements in nickel (spectre 5) with dispersed particles of niobium carbide. Besides, the alloy contains additional phase components. One of them is enriched with chromium (spectre 3) and is determined alloyed by carbide based on it. The formation of this phase is explained by the fact that when the alloy contains several carbide-forming elements (in this alloy—Nb, Cr, W), then with sufficient carbon may be their carbides, and in the phase composition may be present phases not only based on niobium-carbide, but and based on chromium and tungsten.

The increase in the number of phase components of the alloy can also be explained by the fact that in a cast multicomponent eutectic alloy at a high crystallization rate from a liquid, the solubility of the components in the solid state does not correspond to phase equilibrium and promotes the formation of metastable intermediate phases [21]. The appearance of such phases can also be caused by segregation, which alloys with rhenium are prone to [22]. Thus, the results of the study prove that the phase composition of a natural eutectic cast composite based on nickel with niobium carbide, additionally alloyed with rhenium, is not two-phase.

4. CONCLUSION

The process of structure formation in alloyed eutectic composites Ni (Ni + Co)–NbC, which occurs under non-equilibrium conditions of ultrafast eutectic crystallization is determined by the following parameters:

1. The melting point of the studied alloys with niobium carbide, in which as a metal component contain nickel, or nickel and cobalt equally, is obtained as 1300°C. Additional doping with rhenium raises the melting temperature to the level of alloy of cobalt with niobium carbide—the serial industrial eutectic composite XTH.
2. Alloys have a typical structure, which is characteristic of slightly over-eutectic two-phase serial cobalt alloys with niobium carbide series XTH. The main structural components are undeveloped NbC dendrites in nickel-carbide eutectic (γ + NbC).
3. The phase composition of the studied alloys contains a multicomponent solid solution based on nickel and also doped niobium carbide. With additional doping with rhenium, alloys change the phase composition, supplemented by met stable phases containing rhenium and chromium.

The data obtained on the structure formation of Ni (Ni + Co)–NbC alloys provide a basis to investigate their high-temperature physical and mechanical properties, in particular heat-resistance and wear-resistance to determine the feasibility of using as an alternative to cobalt industrial alloys XTH.

REFERENCES

1. G. P. Dmitrieva, T. S. Cherepova, T. A. Kosorukova, and V. I. Nichiporenko, *Metallofiz. Noveishie Tekhnol.*, **37**, No. 7: 973 (2015) (in Russian).
2. T. S. Cherepova, G. P. Dmitrieva, A. V. Nosenko, and A. M. Semirga, *Science and Innovation*, **10**, No. 4: 20 (2014).
3. H. P. Dmytrieva, T. S. Cherepova, T. A. Kosorukova, and T. V. Pryadko, *Materials Science*, **55**, No. 2: 181 (2019).
4. A. K. Shurin and G. P. Dmitrieva, *Metallofizika*, **53**: 91 (1974) (in Russian).
5. A. K. Shurin, O. M. Barabash, G. P. Dmitrieva, V. E. Panarin, and T. N. Legkaya, *Metally*, No. 6: 184 (1974) (in Russian).
6. G. I. Peychev, A. K. Shurin, V. E. Zamkovoy, G. P. Kalashnikov, and N. V. Andreychenko, *Aviatsionno-Kosmicheskaya Tekhnika i Tekhnologiya*, No. 3: 58 (2000) (in Russian).
7. G. I. Peychev, V. E. Zamkovoy, and N. V. Akhrameev, *Tekhnologicheskie Sistemy*, No. 2: 5 (2000) (in Russian).
8. V. A. Boguslaev, Yu. F. Basov, and Yu. D. Kurchenko, *Tekhnologicheskie Sistemy*, No. 3: 9 (2001) (in Russian).
9. A. K. Shurin, G. P. Dmitrieva, and N. V. Razumova, *Metally*, No. 6: 67 (1988) (in Russian).
10. H. P. Dmytriyeva, T. S. Cherepova, and A. K. Shurin, *Poroshkovaya Metallurgiya*, No. 1/12: 44 (1996) (in Ukrainian).
11. G. M. Leyderman and G. M. Nikolaeva, *Neorganicheskie materialy*, **9**, No. 10: 1721 (1973) (in Russian).
12. G. P. Dmitrieva. A. K. Shurin, V. V. Polotnyuk, and S. V. Zolkina, *Metallofizika*, **3**, No. 6: 38 (1981) (in Russian).
13. V. N. Gridnev, O. M. Barabash, and T. N. Legkaya, *Metally*, No. 6: 221 (1985) (in Russian).
14. T. S. Cherepova, G. P. Dmytriieva, T. V. Pryadko, M. V. Kindrachuk, O. V. Tisov, O. I. Dukhota, A. O. Yurchuk, and O. V. Gerasymova, *Functional Materials*, **28**, No. 1: 69 (2021).
15. T. Gayger, R. Shtikler, and Dzh. X. Uayt, *Zharoprochnye Splavy dlya Gazovykh Turbin* [Heat Resistant Alloys for Gas Turbines] (Moscow: Metallurgiya: 1981), p. 174 (in Russian).
16. E. N. Kablov, N. V. Petrushin, L. B. Vasilenok, and G. I. Morozova, *Materialovedenie*, No. 2: 23 (2000) (in Russian).
17. G. Dmytriieva and T. Cherepova, *Chemistry of Metals and Alloys*, **8**, No. 3/4: 83 (2015).
18. *Supersplavy II. Zharoprochnye Materialy dlya Aerokosmicheskikh i Promyshlennykh Energoustanovok* [Superalloys II. Heat-Resistant Materials for Aerospace and Industrial Power Plants] (Moscow: Metallurgiya: 1995) Vol. 2 (in Russian).

19. O. M. Barabash and Yu. N. Koval', *Struktura i Svoystva Metallov i Splavov* [Structure and Properties of Metals and Alloys] (Kyiv: Naukova Dumka: 1986) (in Russian)
20. G. P. Dmytriieva, T. S. Cherepova, and T. V. Pryadko, *Prog. Phys. Met.*, **22**, No. 4: 678 (2021).
21. Yu. M. Taran, I. M. Spyrydonova, and O. Yu. Bereza, *Metaloznavstvo ta Obrobka Materialiv*, No. 1: 3 (2008) (in Ukrainian).
22. E. N. Kablov, I. L. Svetlov, and N. V. Pervushin, *Materialovedenie*, No. 4: 32 (1997) (in Russian).