УДК 620.172.2: 620.18: 620.193.4: 620.199

THE IMPACT OF HAFNIUM ADDITION ON THE PROPERTIES OF HEAT-RESISTANT NICKEL ALLOY SM104

ВПЛИВ ЛЕГУВАННЯ ГАФНІЄМ НА ЕКСПЛУАТАЦІЙНІ ВЛАСТИВОСТІ ЖАРОМІЦНОГО НІКЕЛЕВОГО СПЛАВУ СМ104

DOI 10.15589/SMI. 2018.02.20

Alexander Kostin **О. М. Костін,** канд. техн. наук, проф.
kostin.weld@gmail.com
ORC ID: 0000-0002-4739-660X

Dmytro Gladchenko **Д. С. Гладченко**, магістр
gladchenko.88@mail.ru
ORC ID: —

Admiral Makarov National University of Shipbuilding, Mykolaiv
Національний університет кораблебудування імені адмірала Макарова, м. Миколаїв

Abstract. Improvement of performance properties of heat-resistant nickel alloys remains a pending issue for alloys operating in conditions of high-temperature salt corrosion. Within this context our study examines the impact of hafnium on micro-structure and performance properties of standard heat-resistant nickel alloy CM104 which is widely used in construction of modern marine gas turbine engines. Through computational-analytical method it was determined that the optimal level of hafnium addition shall amount to 1,4 % of the alloy weight. The study included examination of the micro-structure of the alloys, their hardness, plasticity, short-term and long-term strength at a temperature of 900 ºС. It is shown first that hafnium contributes to the grinding of the alloy structure CM104, it stretches the granules boundaries and increases the amount of volumetric fraction of the γ′- phase. Hafnium addition reduces hardness by 3…5 % on average and increases the plasticity of the alloy, it allows to increase resistance to high-temperature salt corrosion while maintaining short-term and long-term strength at 900 ºС. It will allow to improve the performance properties of heat-resistant nickel alloy CM104 and positively impact its bond-ability.

Keywords: micro-structure; hardness; heat resistance; long-term durability; high-temperature salt corrosion.

Анотація. Підвищення експлуатаційних властивостей жароміцних нікелевих сплавів, які працюють в умовах високотемпературної сольової корозії, є актуальною проблемою. У зв’язку із цим було поставлено локальну задачу визначення впливу гафнію на мікроструктуру та експлуатаційні властивості стандартного жароміцного нікелевого сплаву СМ104, який широко використовується для виготовлення сучасних морських газотурбінних двигунів. Розрахунково-аналітичним методом визначено оптимальний рівень легування гафнієм на рівні 1,4 % мас. Виконано дослідження мікроструктури сплавів, визначено їх твердість, пластичність, короткочасну та довготривалу міцність за температури 900 ºС. Уперше показано, що гафній сприяє подрібненню структури сплаву СМ104, збільшує протяжність границь зерен та підвищує кількість об’ємної частки γ′-фази. Додаткове легування гафнієм у середньому на 3…5 % зменшує твердість і підвищує пластичність сплаву, при збереженні короткочасної та довготривалої міцності за температури 900 ºС збільшує стійкість до високотемпературної сольової корозії. Таким чином, додаткове легування гафнієм жароміцного нікелевого сплаву СМ104 підвищує його експлуатаційні властивості та може мати сприятливий вплив на його здатність до зварювання.

Ключові слова: мікроструктура; твердість; жароміцність; довготривала міцність; високотемпературна сольова корозія.

Аннотация. Повышение эксплуатационных свойств жаропрочных никелевых сплавов, которые работают в условиях высокотемпературной солевой коррозии, является актуальной проблемой. В связи с этим была поставлена локальная задача определения влияния гафния на микроструктуру и эксплуатационные свойства стандартного жаропрочного никелевого сплава СМ104, который широко используется для изготовления современных морских газотурбинных двигателей. Расчетно-аналитическим методом определён оптимальный уровень легирования гафнием на уровне 1,4 % мас. Выполнено исследование микроструктуры сплавов, определены их твердость, пластичность, кратковременная и длительная прочность при температуре 900 ºС. Впервые показано, что гафний способствует измельчению структуры сплава СМ104, увеличивает протяженность границ зерен и повышает объемную долю γ′-фазы. Дополнительное легирование гафнием в среднем на 3…5 % уменьшает твердость и повышает пластичность сплава СМ104, при сохранении кратковременной и длительной прочности при температуре 900 ºС увеличивает стойкость к высокотемпературной солевой коррозии. Таким образом, дополнительное легирование гафнием жаропрочного никелевого сплава СМ104 повышает его эксплуатационные свойства и может оказывать благоприятное влияние на его свариваемость.

Ключевые слова: микроструктура; твердость; жаропрочность; долговременная прочность; высокотемпературная солевая коррозия.

References

[1] Sims, Ch. T. Supersplavy II: Zharoprochnye materialy dlya aerokosmicheskikh i promyshlennykh energoustanovok / Ch. T. Sims, N. S. Stoloff, U. K. Khagel. M.: Metallugiya, 1995. T. I. 384 s.

[2] Kablov, Ye. N. Litye lopatki gazoturbinnykh dvigateley / Ye. N. Kablov. M.: MISIS, 2001. 632 s.

[3] Kablov, Ye. N. Strategicheskie napravleniya razvitiya materialov i tekhnologiy ikh pererabotki na period do 2030 goda [Tekst] / Ye. N. Kablov // Aviatsionnye materialy i tekhnologii. 2012. № 8. S. 7–17.

[4] Kvasnitskiy, V. F. Vliyanie elementov-depressantov na svoystva nikelevykh pripoev i zharoprochnykh splavov [Tekst] / Kvasnitskiy V. F., Kostin A. M., Kvasnitskiy V. V. // Adgeziya rasplavov i payka materialov. 2002. № 35. S. 129–139.

[5] Zharoprochnost liteynykh nikelevykh splavov i zashchita ikh ot okisleniya / Pod red. B.Ye. Patona. Kiev: Nauka. dumka. 1997. 336 s.

[6] Effect of hafnium on creep behavior of a corrosion resistant nickel base superalloy [Text] / J. S. Houa, J. T. Guoa, Y. X. Wub, L. Z. Zhoua, H. Q. Yea // Materials Science and Engineering. 2010. A 527. P. 1548–1554.

[7] Anisotropy in creep properties of DS200 + Hf alloy [Text] / L. Mataveli Suave, J. Cormier, P. Villechaise, D. Bertheau // Materials at High Temperatures. 2016. Vol. 33. P. 361–371.

[8] Issledovanie vliyaniya gafniya na strukturu i svoystva liteynogo zharoprochnogo korrozionnostoykogo nikelevogo splava [Tekst] / A. D. Koval, A. G. Andrienko, S. V. Gayduk, V. V. Kononov // Vestnik dvigatelestroeniya. 2012. № 1. S. 196–200.

[9] Vliyanie sootnosheniya volframa k molibdenu na mekhanicheskie svoystva splava ZhS3LS, optimalno legirovannogo gafniem i tantalom [Tekst] / A. D. Koval, A. G. Andrienko, S. V. Gayduk, V. V. Kononov // Novi materialy i tekhnolohii v metalurhii ta mashynobuduvanni. 2012. № 1. S. 31–35.

[10] Optimizatsiya rezhima termicheskoy obrabotki dlya splava ZhSZLS, legirovannogo gafniem i tantalom [Tekst] / A. D. Koval, A. G. Andrienko, S. V. Gayduk, V. V. Kononov // Novi materialy i tekhnolohii v metalurhii ta mashynobuduvanni. 2012. № 2. S. 15–19.

[11] Gayduk, S. V. Issledovanie vliyaniya gafniya na fazovyy sostav liteynogo zharoprochnogo korrozionnostoykogo nikelevogo splava s primeneniem metoda passivnogo eksperimenta [Tekst] / S. V. Gayduk, V. V. Kononov // Novi materialy i tekhnolohii v metalurhii ta mashynobuduvanni. 2014. № 1. S. 45–51.

[12] Oryshich, I. V. Razrabotka metodiki ispytaniya zharoprochnykh splavov v rasplavakh soley [Tekst] / I. V. Oryshich // Zashchita metallov. 1981. T. 17. № 1. S. 74–79.

[13] Gayduk, S. V. Kompleksnaya raschetno-analiticheskaya metodika dlya proektirovaniya liteynykh zharoprochnykh nikelevykh splavov [Tekst] / S. V. Gayduk // Novi materialy i tekhnolohii v metalurhii ta mashynobuduvanni. 2015. № 2. S. 92–103.

[14] Kolomytsev, P. T. Gazovaya korroziya i prochnost nikelevykh splavov / P. T. Kolomytsev. M.: Metalurgiya, 1984. 216 s.

[15] Oryshich, I. V. Vliyanie sostava sulfatokhloridnogo rasplava natriya na stoykost k vysokotemperaturnoy solevoy korrozii nikelevykh splavov [Tekst] / I. V. Oryshich // Aviatsionnaya promyshlennost. 1983. № 4. S. 50–52.

Problem statement. The development of modern shipboard gas-turbine construction is characterized by a constant search for ways to increase the specific power and efficiency of turbine engines, which certainly leads to the need to increase the operating temperature at the turbine inlet. The temperature of the first turbine stage can reach 950…1050 ^{o}C. In this regard, improving the performance properties of heat-resistant nickel alloys is relevant.

Nickel-base superalloys are a heterophase precipitation hardening alloys, the main structural components of which are γ-phase (austenitic matrix with BCC lattice) and γ′-phase (eutectoid intermetallic structure based on Ni_3(Al, Ti), which is released from the gamma phase solid solution). The solubility limit of the γ′-phase changes significantly with decreasing alloy temperature, which leads to its active release in a dispersed form during a special heat treatment [1]. The performance properties of heat-resistant nickel alloys increase significantly with increasing volume concentration of the γ′-phase to 50…65 %, while reducing their weldability [2, 3].

Latest research and publications analysis. It is known that the addition of hafnium improves the performance characteristics of nickel alloys due to a favorable change in the morphology of carbides of the type $M_{23}C_6$, as well as their resistance to oxidation and high-temperature salt corrosion [4, 5]. In addition, hafnium increases the proportion of the eutectic γ′-phase, which optimizes the structure and increases the creep resistance [1, 6]. For example, additional alloying with hafnium alloys MAR-M200 and DS200 to 2 % wt. improves their performance properties [7]. A similar effect is observed with additional alloying with hafnium of the ZhS3LS alloy in an amount up to 0.9 % wt. [8–10]. The alloying of nickel superalloys with hafnium also contributes to an increase in the thermal stability of the γ′-phase by increasing the temperature of its complete dissolution in the γ-solid solution by more than 70 °C [11]. However, a change in the matrix alloying system of the alloy affects the optimal concentration limits for alloying with hafnium and is the subject of additional research.

THE ARTICLE AIM — determining the effect of hafnium on the microstructure and performance properties of the standard heat-resistant nickel alloy CM104, which is widely used for the manufacture of modern gas-turbine engines.

Methods, object and subject of research. We used standard methods for studying the properties of metallic materials: we measured the HRC hardness according to ISO 6508-1: 2013; determined the characteristics of heat resistance and limiting stress according to GOST 9651–84 / Trans. 1: 2008 and GOST 10145–81 / Trans. 1: 2018; investigated the electronic structure and determined the chemical composition of the alloys by the method of micro-X-ray spectral analysis using the PEMMA 102-02 installation; measured their resistance to high-temperature salt corrosion according to method [12].

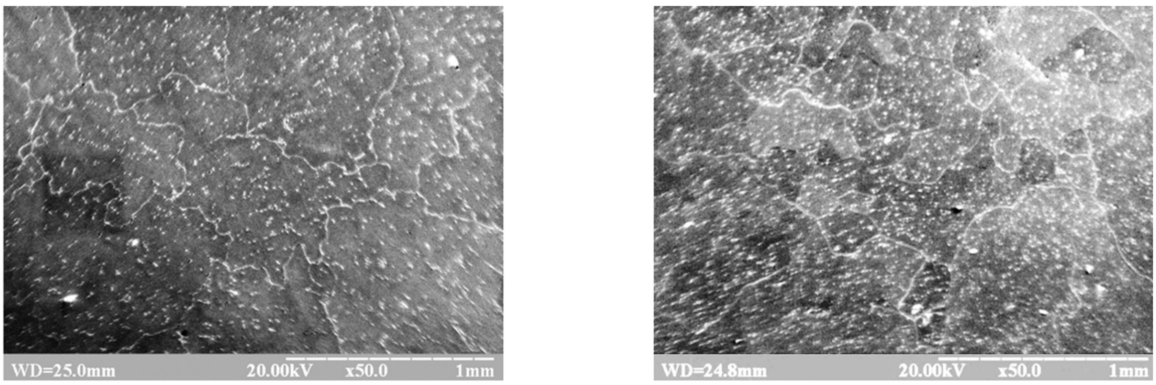
The object of the research is the microstructure, chemical composition, mechanical properties of alloys at a temperature of 900 °C and their resistance to high-temperature salt corrosion.

The subject of the research is the structure and operational properties of heat-resistant nickel alloys.

Basic material. To determine the optimal concentration of hafnium in the experimental alloy, an express method of a comprehensive analytical solution method (CASM) was used, which allowed with a sufficient degree of accuracy to carry out preliminary calculations for the main groups of operating parameters of the alloy [13]. The calculation showed that an increase in the operational properties of the alloy CM104 is possible due to the additional alloying with hafnium at an optimum level of 1.4 % by weight.

In this regard, we have produced CM104 alloys (basic composition and an alloy with additional doping with hafnium – further SM104Hf). Using spectral analysis, it was found that the concentration of alloying elements in the experimental composition with hafnium is at the following level (% wt.): 21.2 Cr; 10.35 Co; 1.4 Hf; 2.64 Al; 3.45 Ti; 0.66 Mo; 3.9 W; 0.3 Nb; 0.03 Mn; 0.1 Fe; 0.08 C; 0.008 Si; 0.003 S; 0.005 P; Ni – base. The basic composition is characterized by the absence of hafnium. The characteristic structure of the alloys is shown in Figure 1.

X-ray studies have shown the absence of internal defects in castings. Castings underwent a standard full heat treatment cycle: homogenization



a) ×50 *b)* ×50

Fig. 1. The characteristic structure of the alloys CM104 (*a*) and CM104Hf (*b*)

T = 1170 °C —3.5 hours; + hot quenching T = 1050 °C – 3.5 hours; + aging T = = 850 °C – 16 hours. The distribution of the average concentration of alloying elements in the phase components of the experimental alloys is given in Table 1.

Measurements of the hardness of samples of experimental alloys showed that the hardness of the HRC alloy CM104 is within 35.4...36.5 units, with an average of 35.8 units, and the alloy CM104Hf – 34.8...36.0 units, with an average value of 34.7 units. Thus, the additional alloying of the CM104 alloy with hafnium slightly reduces its hardness. To determine the characteristics of heat resistance and limiting stress, samples were made from experimental alloys according to GOST 9651–84 / Per. 1: 2008 and GOST 10145–81 / Trans. 1: 2018 for stretching at operating temperatures. The test results are shown in table 2.

Another important factor, which also plays a decisive role in the operation of marine gas turbine engines, is the resistance of materials against high-temperature salt corrosion. High temperature salt corrosion occurs in the presence of sulfur compounds in products of combustion of fuel, among which the most important role is played by the compounds with sodium. Sulfur at combustion forms oxides of SO_2 and SO_3. The proportions of NaCl salts deposited on the parts of the hot tract are involved in the reactions of sulfidation. Numerous studies have shown that sodium sulfate is present in carbon generated on the blades of marine turbines, while corrosion affects parts at temperatures 650...950 ºC [14]. In addition, sulfatochloride sodium melts containing up to 70...80 % NaCl produce oxysulphidation processes [15].

Thus, the mechanism of corrosion destruction in most cases is associated with the dissolution of a protective film, which is on the surface of the alloy, in the presence of Na_2SO_4. The amount of sulfides, of course, affects the intensity of corrosion damage. To determine the actual rate of corrosion the most informative are the natural tests of gas turbine engines, however, their cost and duration makes use of intermediate laboratory test methods. The most common is the crucible test method in the melt salts of 75 % Na_2SO_4 + 25 % NaCl at the operating temperature of the engines for 10 ... 20 hours, followed by the calculation of the average rate of corrosion by the formula $V_c = m_c/S_s \times t_s$, where V_c – average rate of corrosion, mg/cm²·hour; m_c – mass loss, mg; S_s – surface area of the sample, cm²; t_s – test time, hours [12].

According to this method, studies of resistance to high-temperature salt corrosion of experimental alloys CM104 and CM104Hf were conducted. Samples of test alloys were kept in the molten salt of 75 % Na_2SO_4 + 25 % NaCl at a temperature of 900 °C for 20 hours. The electronic structure of the surface layer of samples from the CM104Hf alloy is shown in Figure 2. The distribution of chemical elements in zones of corrosion destruction is given in Table 3.

According to the results of the tests it was established that the geometry of all samples practically did not change. On the surface of the samples there is a small amount of corrosive destruction products of dark green color, which hold tight on the surface. Measurement of the rate of high-temperature salt corrosion of experimental alloys confirmed that additional alloying with hafnium increases the corrosion resistance of the CM104 alloy. The average rate of corrosion of the CM104 alloy is

Table 1. The distribution of the concentration of alloying elements in the phase components of the experimental alloys

Alloy		The average concentration of alloying elements, % wt.										
		Al	Si	Ti	Cr	Fe	Co	Ni	Nb	Mo	W	Hf
CM104	Solid solution	3,06	0,06	4,52	21,53	0,29	10,98	56,61	0,38	0,68	1,99	–
	Hardening phase	2,41	0,00	16,44	19,46	0,89	6,39	40,52	6,77	1,67	5,45	–
CM104Hf	Solid solution	2,08	0,03	4,08	19,98	2,87	10,37	55,12	0,46	0,37	1,53	3,38
	Hardening phase	1,05	0,00	19,26	16,53	1,71	7,48	39,44	2,60	0,01	1,46	10,47

Table 2. Mechanical properties and limiting stress of experimental alloys at a temperature of 900 °C

Alloy	Sample number	Limiting stress		Mechanical tensile properties		
		Weight, MPa	Time, hours	Tensile Strength, MPa	δ, %	Ψ, %
CM104	1	200	50	646	14	30
	2	200	50	642	8	21
CM104Hf	3	200	50	592	20	37
	4	200	50	653	14	35

Table 3. Distribution of alloying elements in the CM104Hf alloy according to Figure 2

Zone	Average concentration of alloying elements, % wt.										
	Al	Si	Ti	Cr	Fe	Co	Ni	Nb	Mo	W	Hf
1	2,15	0,00	4,52	19,35	3,25	10,53	52,81	1,69	0,24	1,62	3,83
2	2,03	0,43	2,03	14,28	4,92	11,67	58,54	1,02	1,99	1,41	1,66
3	1,64	0,96	10,95	70,70	1,19	2,71	6,37	1,85	1,05	0,32	2,27

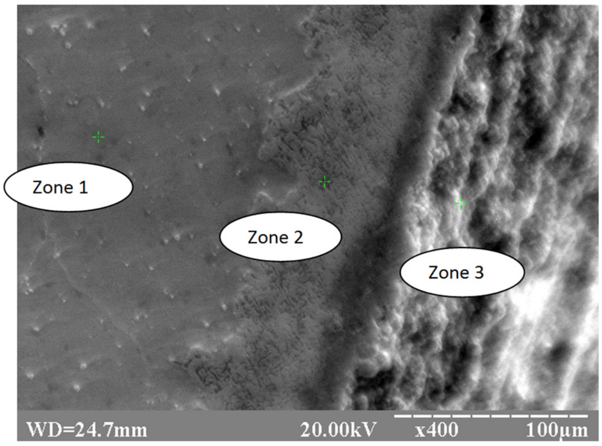


Fig. 2. The electronic structure of the surface layer of the CM104Hf alloy after corrosion tests, × 400

V_c = 0.21 mg/cm²·h, and for the CM104Hf alloy, this indicator is much lower – V_s = 0.12 mg/cm²·h. The total average mass loss of the test alloy CM104 is 0.19 %, and the CM104Hf alloy is 0.12 %.

DISCUSSIONS. Analysis of the microstructure showed (see Figure 1) that additional alloying with hafnium contributes to the fragmentation of grains, smoothes their boundaries and increases the volume fraction of the γ′-phase, which fully coincides with the conclusions of the works [1, 6].

The determined concentrations of the alloying elements according to the phase components of the alloys shown in Table 1 show that the hafnium is unevenly distributed in phases. It is predominantly predicted to be part of the strengthening phases and stand out in the form of minor eutectic inclusions along the grain boundaries, which corresponds to the conclusions of the works [4, 6].

The results of tests of mechanical properties of alloys during stretching and their long-term durability at a temperature of 900 °C showed (see Table 2) that the additional alloying with the hafnium of the alloy CM104 to a level of 1,4 % by weight. improves its mechanical properties, with a slight decrease in hardness and increased plasticity. This fact has a beneficial effect on its welding ability, which is extremely important and is the subject of additional research.

An analysis of the microstructure of the samples after testing their resistance to high-temperature salt corrosion, as shown in Figure 2, and the distribution of chemical elements in the zones of corrosion fracture (see Table 3), gives a clear idea of the mechanism of destruction On the surface of the sample, a protective layer (zone 3) is formed in which the concentration of nickel and cobalt is sharply reduced due to their intense interaction with the active medium, which leads to a significant increase in the concentration of chromium (up to 70 % by weight), which plays a major role in the containment of corrosion destruction. At the same time, there is a moderate increase in the concentration of titanium and hafnium. The total concentration of these three elements in the surface layer reaches about 85 %, which greatly increases the stability of the alloy against high-temperature salt corrosion. In the near-surface transition layer (zone 2), on the contrary, there is a slight increase in the concentration of nickel and cobalt in comparison with the base metal (zone 1) due to the diffusion of the alloying elements on the surface.

In this regard, the results of the tests clearly prove that the presence of hafnium in the surface layer plays a positive role in the deterrence of corrosion fracture, which is quite logical and coincides with the conclusions of work [4].

Thus, the additional alloying with a hafnium of a heat-resistant nickel alloy CM104 at a level of 1.4 % by weight. increases its operational properties and may have a beneficial effect on its welding ability, which is extremely important and requires additional research.

CONCLUSIONS. Additional alloying hafnium alloy CM104 at 1.4 % by weight positively affects its operational properties:

1. Hafnium promotes the grinding of grains, ramparts their boundaries and increases the volume fraction of the γ'-phase.

2. An average of 3–5 % decreases hardness and increases the plasticity of the alloy while maintaining short-term and long-term strength at 900 ºC.

3. The stability of the alloy against high-temperature salt corrosion at a temperature of 900 ºC increases qualitatively.

Список літератури

[1] **Симс, Ч. Т.** Суперсплавы II: Жаропрочные материалы для аэрокосмических и промышленных энергоустановок [Текст] / Ч. Т. Симс, Н. С. Столофф, У. К. Хагель. М. : Металлугия, 1995. Т. I. 384 с.

[2] **Каблов, Е. Н.** Литые лопатки газотурбинных двигателей [Текст] / Е. Н. Каблов. М. : МИСИС, 2001. 632 с.

[3] **Каблов, Е. Н.** Стратегические направления развития материалов и технологий их переработки на период до 2030 года [Текст] / Е. Н. Каблов // Авиационные материалы и технологии. 2012. № 8. С. 7–17.

[4] **Квасницкий, В. Ф.** Влияние элементов-депрессантов на свойства никелевых припоев и жаропрочных сплавов [Текст] / В. Ф. Квасницкий, А. М. Костин, В. В. Квасницкий // Адгезия расплавов и пайка материалов. 2002. № 35. С. 129–139.

[5] Жаропрочность литейных никелевых сплавов и защита их от окисления [Текст] ; под ред. Б. Е. Патона. К. : Наука. думка, 1997. 336 с.

[6] Effect of hafnium on creep behavior of a corrosion resistant nickel base superalloy [Text] / J. S. Houa, J. T. Guoa, Y. X. Wub, L. Z. Zhoua, H. Q. Yea // Materials Science and Engineering. 2010. A 527. P. 1548–1554.

[7] Anisotropy in creep properties of DS200 + Hf alloy [Text] / L. Mataveli Suave, J. Cormier, P. Villechaise, D. Bertheau // Materials at High Temperatures. – 2016. Vol. 33. P. 361–371.

[8] Исследование влияния гафния на структуру и свойства литейного жаропрочного коррозионностойкого никелевого сплава [Текст] / А. Д. Коваль, А. Г. Андриенко, С. В. Гайдук, В. В. Кононов // Вестник двигателестроения. 2012. № 1. С. 196–200.

[9] Влияние соотношения вольфрама к молибдену на механические свойства сплава ЖС3ЛС, оптимально легированного гафнием и танталом [Текст] / А. Д. Коваль, А. Г. Андриенко, С. В. Гайдук, В. В. Кононов // Нові матеріали і технології в металургії та машинобудуванні. 2012. № 1. С. 31–35.

[10] Оптимизация режима термической обработки для сплава ЖС3ЛС, легированного гафнием и танталом [Текст] / А. Д. Коваль, А. Г. Андриенко, С. В. Гайдук, В. В. Кононов // Нові матеріали і технології в металургії та машинобудуванні. 2012. № 2. С. 15–19.

[11] **Гайдук, С. В.** Исследование влияния гафния на фазовый состав литейного жаропрочного коррозионностойкого никелевого сплава с применением метода пассивного эксперимента [Текст] / С. В. Гайдук, В. В. Кононов // Нові матеріали і технології в металургії та машинобудуванні. 2014. № 1. С. 45–51.

[12] **Орышич, И. В.** Разработка методики испытания жаропрочных сплавов в расплавах солей [Текст] / И. В. Орышич // Защита металлов. 1981. Т. 17, № 1. С. 74–79.

[13] **Гайдук, С. В.** Комплексная расчетно-аналитическая методика для проектирования литейных жаропрочных никелевых сплавов [Текст] / С. В. Гайдук // Нові матеріали і технології в металургії та машинобудуванні. 2015. № 2. С. 92–103.

[14] **Коломыцев, П. Т.** Газовая коррозия и прочность никелевых сплавов [Текст] / П. Т. Коломыцев. М. : Металургия, 1984. 216 с.

[15] **Орышич, И. В.** Влияние состава сульфатохлоридного расплава натрия на стойкость к высокотемпературной солевой коррозии никелевых сплавов [Текст] / И. В. Орышич // Авиационная промышленность. 1983. № 4. С. 50–52.

Статтю рекомендує до друку
д-р техн. наук, проф. *Н. О. Макаренко*