S. K. ARINOVA, SV. S. KVON, V. YU. KULIKOV, M. M. ABDILDINA, A. E. OMAROVA

ISSN 0543-5846
METABK 61(2) 341-343 (2022)
UDC / UDK 669.15:539.4/536.45:536.777:536.425:539.26=111

THERMODYNAMIC MODELING AND ANALYSIS OF THE STRUCTURE OF A HEAT-RESISTANT ALLOY OF THE Fe-Cr-Ni SYSTEM

Received – Primljeno: 2021- 09-04
Accepted – Prihvaćeno: 2021-11-16
Preliminary Note – Prethodno priopćenje

There has been carried out thermodynamic modeling of phase transformations of the Fe-Cr Ni alloy alloyed with titanium and niobium in order to predict the phase composition and to substantiate the concentration of alloying elements of the experimental alloy for parts of metallurgical equipment. The results of microstructural analysis and phase composition of an experimental heat-resistant alloy are presented.

Keywords: alloy steel, heat resistance, thermodynamic modeling, phases, X-ray research

INTRODUCTION

A significant part of furnace equipment (rollers, pallets, grates, furnace equipment, etc.) in metallurgical and foundry industries is made of heat-resistant steels, which is associated with the peculiarities of operating conditions: high temperatures, constant load and duration of use. The operation of products at high temperatures and under the impact of constant loading leads to the development of creep with subsequent destruction [1-2]. The phenomenon of creep proceeds mainly by the mechanism of grain boundary sliding, therefore, grain boundaries are an important structural element that affects the material heat resistance. The presence of impurities at the grain boundaries that are not coherently connected with the matrix, impurity segregations and accumulations of micropores are stress concentrators and a source of crack initiation. That is why, an important condition for increasing heat resistance of alloys is alloying with elements that increase the forces of interatomic bonds strengthening the grain boundaries, and decreasing the content of impurities in the alloy that weaken the grain boundaries [3-7].

A promising trend for increasing heat resistance of alloys based on iron-chromium-nickel is dispersed hardening by Laves phases, carbides, borides and nitrides of refractory and transition metals, which simultaneously leads to increasing low-temperature plasticity and decreasing the cold brittleness temperature of alloys [8-9]. The highest strengthening effect is possessed by borides and carbides of niobium, titanium carbide. In works [9-10] it is noted that high- resistant steels alloyed with carbide-forming elements, the evolution of the carbide phase and the appearance of undesirable phases such as Laves and G-phases are responsible for the development of creep and decreasing heat resistance of alloys works [8]. Since the g-phase in a chromium-nickel alloy plays a key role in the process of high-temperature creep, it is of interest to strengthen this phase to increase creep resistance at high temperatures due to alloying with transition metals by analogy with high- resistant nickel alloys, which enrich the grain boundaries in the g-matrix and increase cohesive strength of both the matrix and the boundaries.

In earlier studies [11-13] it is noted that alloying with niobium and titanium leads to stabilization of the structure in heat-resistant alloys of the gelatin-chromium system. Alloying with such elements leads to forming primary and secondary carbides such as TiC, NbC, $M_{23}C_6$ having a high dissociation temperature. However, the exact amount of Nb addition is not precisely known, but some studies have noted that 0,5-1,0 % Nb show a good balance between ductility at the room temperature and high temperature strength.

EXPERIMENTAL STUDIES

Equipment and tools

In order to determine the optimal amount of alloying elements and to predict the amount of various precipitates of carbides and phases, the iron-chromium-nickel system has been calculated using the Thermo-Calc program, which is a well-known method of thermodynamic modeling, which allows building diagrams of the phase state of alloys based on the chemical compositions dependence on the temperature. Preliminary modeling of the phase composition at different temperatures makes it possible to determine the forming phases, their transformations, and predict the phase composition and to determine the range of undesirable phases appearance. The TCFE6 database has been used to calculate the composition of phases and the solubility of elements in structural components.

Heat-resistant alloys are multi-component systems consisting of 5 or more components. This determines their complex phase and structural composition. The Cr18Ni10Ti heat-resistant steel grade has been selected as the base formulation, as it is an attractive candidate

S. K. Arinova, Sv. S. Kvon, V. Yu. Kulikov, M. M. Abbildina, A. E. Omarova (e-mail: sanya_kazah@mail.ru, KTU), Karaganda Technical University, Karaganda, Kazakhstan.

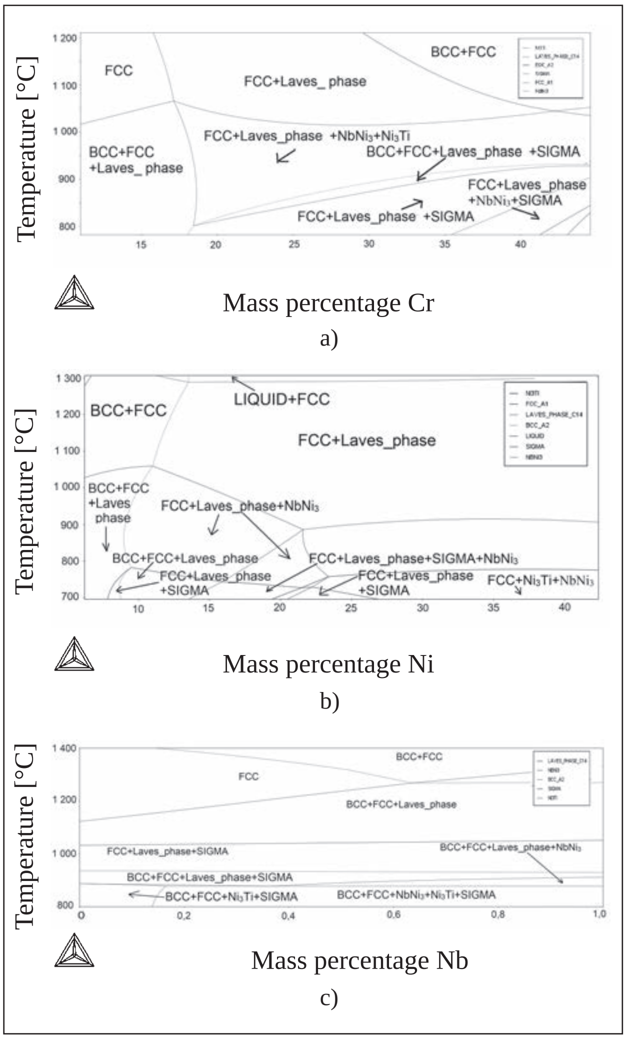

Figure 1 Polythermal cut of the Fe-Cr-Ni system state diagram calculated using the ThermoCalc program

for high temperature use due to their relatively high strength and low cost. Thus, the studied system is iron-chromium-nickel alloyed with titanium and niobium in the amount of up to 1 %. Since the system is multi-component and since Cr and Ni are one of the main components of the alloy under study, binary diagrams have been constructed for the Fe-Ni and Fe-Cr systems, taking into account alloying elements.

Figures 1 show the polythermal sections of the state diagrams of the system under study. The analysis of the diagrams in Figures 1 show that during crystallization there are significant phase changes, when various phases are formed. The crystallization process of the alloy begins with precipitation of the γ-(FCC) phase as the primary phase. By analogy with known analogous alloys, the γ-phase is apparently a solid solution of the type of substitution with a face-centered lattice.

In the range of 800 - 1000 ºC with the amount up to 18% Cr (Figure 1 a), there are formed α-(BCC) phases and Laves phases, however, the presence of the α-phase in the final structure is undesirable, since it leads to decreasing strength properties and corrosion resistance. It is important for alloys operating in high-temperature oxidizing environments in which most of the metallurgical equipment operates.

The Laves phase is present in the entire studied range. It is known that the presence of Laves phases (Cr_2M) is undesirable in most cases, because they slightly harden alloys due to their incoherence with the solid solution and thermal instability. However, for heat-resistant alloys, the presence of the Laves phase has a positive effect, since in the presence of γ' in the structure, Laves phases make it possible to extend the service life of the alloys due to the inherent duration of the incubation period of precipitation.

The greatest interest from the point of view of heat-resistant properties is caused by the formation of such phases, as the intermetallic phase γ' Ni_3Ti, nitride of the type. It is known that the presence of Ti in the composition of alloys based on Fe-Cr-Ni systems stabilizes NbC carbide and prevents its transformation into an undesirable G-phase.

The analysis of the diagram of the iron- nickel system (Figure 1b) shows that at temperatures up to 800 °C and at the nickel content up to 10 %, an extremely undesirable σ-phase is formed. It is known that the presence of the σ-phase leads to sharp embrittlement of the alloy in any temperature range up to melting temperatures [3].

The studied range contains such phases, as α-(BCC) solid solution, γ-(FCC) solid solution, Ni_3Ti intermetallic compound, $NbNi_3$ type nitride. When the nickel content is more than 10 %, a two-phase region α+γ is formed, however, above 800 °C, a favorable phase separation is observed that are optimal from the point of view of increasing the refractoriness.

Figure 1c shows that the introduction of niobium up to 1 % leads to the appearance of the σ-phase over the entire range and the formation of a two-phase region takes place.

Based on the result of predicting the formation of various phases using Thermo-Calc software, it can be concluded that the recommended concentration of niobium input is at least 1 %, the concentration of chromium is 18 - 20 %, and nickel 8 - 10 %. To confirm the assumption, an experimental high-temperature alloy has been melted based on steel Cr18Ni10Ti and with the recommended alloying limits for the purpose of studying the structure. Smelting has been carried out in the UI-25p induction furnace with an improved cooling system, in a corundum-mullite-zirconium crucible. The smelting has been poured into molds, the weight of the ingots has been 200 - 300 g. The chemical composition of the resulting alloy has been monitored using a Poly Spec-F spectrometer. The composition of the melted alloy is shown in Table 1.

It is known that the properties of heat-resistant alloys depend mainly on the nature, the amount of intermetallic and secondary phases, and on their distribution in the structure. To study the fine structure and elemental chemical composition of the prototypes, X-ray microanalysis of the samples (MRSA) has been used. Mi-

Table 1 **Chemical composition of the melted alloy**

Elements										
No	Cr	Ni	Ti	Al	Mn	Si	Ta	Nb	C	Fe
1	17,9	9,4	0,8	0,04	1,8	0,71	0,003	0,85	0,10	rem

cro X-ray spectral studies, the construction of profiles of the composition and distribution maps of elements have been made on a TESCAN VEGA 3 SBH scanning electron microscope equipped with an energy dispersive attachment, an INCA Energy 15013 X-act microanalyzer manufactured by the Oxford Instruments with an X-act ADD detector and INCA Energy software.

The analysis of the element distribution over the spectra suggests a structure consisting of an alloyed matrix saturated with such elements, as Ni and Cr with the presence of interstitial phases. There have also been found carbides, the nature of which has been identified as M_7C_3 and M_6C, and intermetallic compounds of the Ni_3Ti, $NbNi_3$ type Figure 2. Due to the fine dispersion of these phases and coherence with the solid solution, the alloys at their formation acquire the maximum heat resistance.

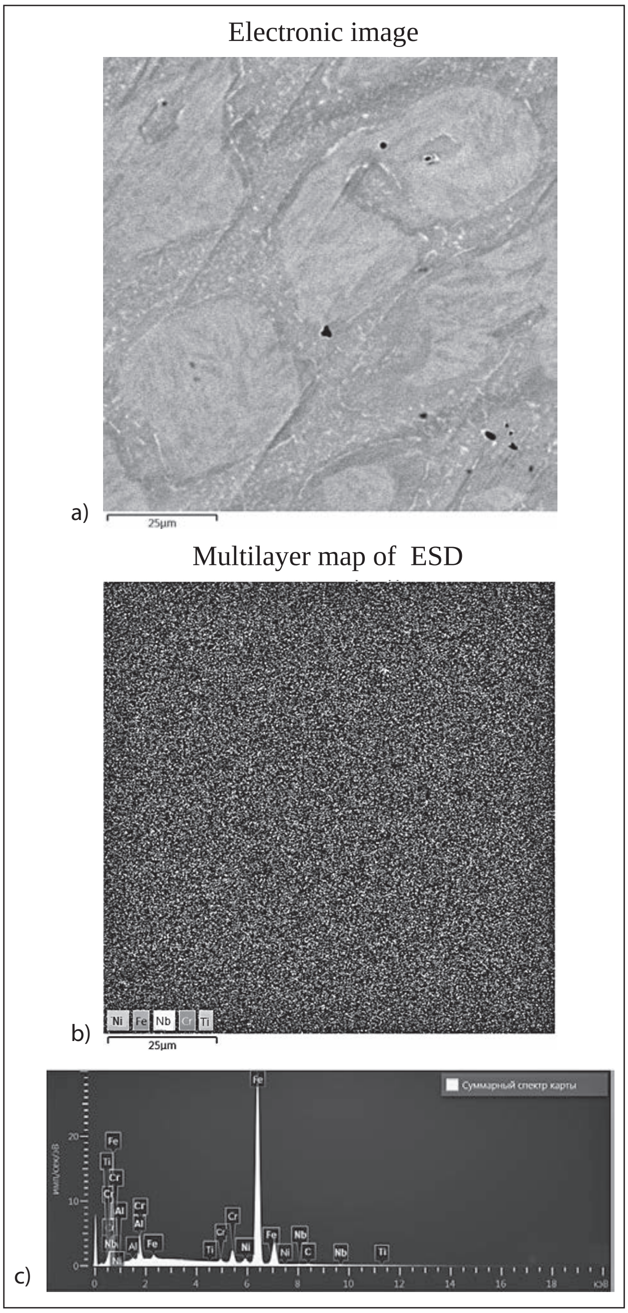

Figure 2 The sample microstructure (a) and the map of element distribution b), MRSA c)

CONCLUSIONS

The simulation of phase transformations in the iron-chromium-nickel system has made it possible to determine the concentration of Nb in the amount of at least 1 % and to confirm the concentration of Cr, Ni and Ti, thus avoiding the formation of undesirable phases (σ-phase and α-solution) in the final structure and identifying the limits of concentration regions in which the appearance of these phases is possible. This prediction has experimentally been confirmed by comparing the phases in the microstructure of the experimental alloy. The preliminary obtained data on phase and structural changes will make it possible to predict the phase composition, thereby reducing the number of experiments and melting.

REFERENCES

[1] Kireyeva V. B. Steels and alloys for high-temperature service. In the book “Heat-resistant metal materials. Physicochemical principles of development”. M.: Nauka, 1987. p. 40.

[2] Kablov E.N. Casting heat-resistant alloys. The effect of S. T. Kishkina, Scientific and technical. To the 100th anniversary of S. T. Kishkin. M.: Nauka, 2006, 272.

[3] F. Tancret, F. Christen, J. Laigo// Phase transformations in Fe-Ni-Cr heat-resistant alloys for reformer tube applications// March, Materials Science and Technology 34(2018)11,1-11. Doi:10.1080/02670836.2018.1449177

[4] L. Wang, R. Kamachali. Density-based grain boundary phase diagrams: Application to Fe-Mn-Cr, Fe-Mn-Ni, Fe-Mn-Co, Fe-Cr-Ni and Fe-Cr-Co alloy systems // Acta Materialia. Volume 207 (2021)1. Doi:10.1016/j.actamat.2021.116668.

[5] G. N. Haidemenopoulos , K. Polychronopoulou, A. D. Zervaki , H. Kamoutsi , S. I. Alkhoori, S. Jaffar, P. Cho and H. Mavros, Aging Phenomena during In-Service Creep Exposure of Heat-Resistant Steels, Metals 9(2019)7, 800. doi:10.3390/met9070800

[6] Yu Z.,H. Lianyong X. L., Yongdian H. J. Microstructure and texture study on an advanced heat-resistant alloy during creep Materials Characterization, 130 (2017), 156-172.

[7] P. Yanyan, Yu. Liming, L. Yongchang, Microstructures and tensile properties of an austenitic ODS heat resistance steel, Materials science and engineering a-structural materials properties microstructure and processing, 767(2019). doi.org/10.1016/j.msea. 2019.138419

[8] Kozlov E. V., Nikonenko E. L., Popova N. A., Koneva N. A. Mechanisms of hardening heat-resistant alloys on a nickel base. Fundamental problems of modern materials science, (2016)1, 39-42.

[9] N. Nabiran, S. Weber, W. Theisena. Influence of intermetallic precipitates and heat treatment on the mechanical properties of high-temperature corrosion resistant ferritic steels. Procedia Engineering 10 (2011), 1651-1656.

[10] Dmytrieva, H. P.; Cherepova, T. S.; Kosorukova, T. A. Influence of Rhenium on the Heat Resistance of the Alloy of Cobalt with Niobium Carbide, Materials science, 55 (2019)2, 181-186.

[11] Kulikov, V. Y., Issagulov, A. Z., Kvon, S. S., Sidorina, Y. A. Studying the effect of boron on heat-resistance properties of Ni-Cr alloys, Metalurgija, 56(2017)3-4, 409-411.

[12] Kvon Sv., Issagulov A., Kulikov V., Medvedeva I., Arinova S. Studying heat treatment impact on heat resisting properties of Cr-Ni- a.e. system alloy/ Metalurgija 56(2017)3-4, 382-384.

[13] Kvon Sv., Kulikov V., Shcherbakova Y., Arinova S. Effect of inoculant introducing on improving ingot structure / Metalurgija 58(2019)3-4, 315-318.

Note: Responsible for the English language is Natalya Drak, Karaganda, Kazakhstan