PHYSICAL-CHEMICAL MODELING AND INVESTIGATION OF THE "HIGH-ENTROPY METAL MATRIX / TiC" SYSTEM COMPONENTS INTERACTION

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ABSTRACT

The research carried out is aimed at developing the scientific basis for obtaining new composite materials based on high-entropy alloys, as well as developing the basic principles of processing and operation of such materials. It was necessary to conduct a theoretical and experimental study of the physical-chemical processes occurring during the interaction of high-entropy alloys with reinforcing TiC particles, as well as to study the effect of temperature and composition of interacting phases on the interaction process and its results. Thermodynamic and kinetic modeling of the interaction processes of the matrix components of high-entropy alloys based on the Cantor alloy (FeCoCrNiMn), including titanium and carbon with the formation of titanium carbide was carried out. Modern modeling approaches were used, which makes it possible to implement modern software. In particular, thermodynamic modeling using methods developed within the framework of the Calphad approach was carried out. Thermo-Calc software (including TC-PRISMA kinetic modeling software) and FactSage software were used in the research process. An experimental study of the composition and structure of samples of TiC-reinforced metal matrix materials (using electron microscopy, X-ray spectral microanalysis and XRD) was also carried out. The distribution of various elements in the microstructure of materials and their phase composition were investigated. Comparison of the simulation results with experimental data allowed to make conclusions about the qualitative adequacy of thermodynamic and kinetic models of phase equilibria and phase transformations occurring during the formation, possible heat treatment and operation of TiC-reinforced metal matrix materials at high temperatures to the observed experimental data.

Keywords: composite materials, high-entropy alloys, ceramic materials, interaction.

INTRODUCTION

Over the past two decades, one of the new and promising directions in the scientific research of materials has been the creation and study of "high - entropy materials" - metal and ceramic materials characterized by high configuration entropy of mixing [1 - 4]. Research on high-entropy materials is developing very quickly and despite the relative novelty of this field, many interesting and useful results have been obtained within its framework.

The interest in the study of materials based on high-entropy phases is due not only to the desire to obtain new substances, but also to the possibility of creating materials with improved properties important for applied applications. It has been shown that such materials can have attractive mechanical properties, such as high toughness at low temperatures or high strength at high temperatures, surpassing similar properties of industrially used materials. The possibilities of using high-entropy alloys as radiation-resistant materials and biomedical alloys are also considered.

It is shown that the processes of structure formation of such alloys, as well as the diffusion of atoms, thermal

stability and mechanical properties of such alloys differ significantly from the processes occurring in traditional alloys, which are based on one or two elements. High-entropy alloys have increased thermal stability of their structure, which is an advantage not only when used, but also in the process of manufacturing products, for example, in developing additive technologies and modern methods of surface engineering [3 - 7].

One of the promising areas of research of high-entropy alloys is the creation and study of new composite materials based on them. The matrix in such materials consists of a high-entropy alloy, and other metals, carbon materials, intermetallides, ceramics can serve as reinforcing components). Inclusions of reinforcing phases can have both exogenous and endogenous origin [8 - 17]. Such composite materials can significantly exceed in their properties both composites with matrices from traditional alloys and special alloys, including high-entropy ones. In addition to high hardness and strength, delayed diffusion in a high-entropy matrix material contributes to the stabilization of reinforcing phases at high temperatures. It can be expected that such materials will have high heat resistance, superior to traditional heat-resistant alloys (for example, nickel-based). They will also be characterized by low brittleness, which is an advantage compared to heat-resistant ceramics. Analysis of the published data shows that the use of ceramic particles (oxides, carbides, and nitrides, first of all) as reinforcing, strengthening additives leads to significant positive changes in the properties of the material (the resulting metal matrix composite) from the point of view of its use as a structural material or as a coating base.

One of the key problems that arise when creating such materials is the chemical interaction between reinforcing additives and metal. Heterogeneous reactions between metal components and exogenous particles can lead to the disappearance of the reinforcing component or to modification of its chemical structure, which will significantly affect its characteristics and affect the properties of the composite. On the other hand, the interaction of metal components (melt or solid solution) can lead to the formation (both in liquid and in crystallized metal) of endogenous hardening particles. This method of hardening has its advantages. Managing the course and results of heterogeneous interaction processes involving components of high-entropy alloys requires the development of modeling techniques for such processes, including modeling based on thermodynamic and kinetic laws.

The purpose of this work is the theoretical and experimental study of the interaction possibility of carbon and titanium in a matrix based on a Cantor alloy (FeCoCrNiMn) for the endogenous production of titanium carbide hardening particles in a metal matrix. Of particular interest was the extent to which modern methods of thermodynamic and kinetic modeling allow predicting the course and results of TiC formation processes from components based on Cantor alloy.

EXPERIMENTAL

Modeling and simulation

For work on thermodynamic modeling, aimed primarily at establishing possible directions of processes occurring during the implementation of processes for obtaining metal matrix composites, as well as processes that may occur during the use of the obtained materials, the FactSage software package version 8.0 was used. In the process of modeling using FactSage, the FTlite and FactPS databases were used [18 - 20]. The composition FeCoCrNiMn as the model compositions of the metal matrix was used. TiC as reinforcing components was considered.

The simulation made it possible to calculate the phase diagrams, examples of which are shown in Fig. 1. The information provided allows to make conclusions both about the processes occurring during the smelting and crystallization of metal, and about the processes that can occur during the long-term operation of composite materials at elevated temperatures. It can be seen how changes in the composition of the systems under consideration and changes in temperature lead to changes in the composition of equilibrium phase compositions. The diagrams show the boundaries of the phase equilibrium regions and, in particular, the concentration boundaries, within which we can count on the thermodynamically stable coexistence of the high-entropy phase (with the FCC structure) with the reinforcing phase (also with the FCC structure). Among other things, you can see which alloy compositions can be in equilibrium with reinforcing particles based on titanium carbide.

Titanium carbide particles can be formed in the metal both during its crystallization and during solid-phase processes. To simulate the process of

TiC formation during crystallization, the ThermoCalc software package was used, including the possibility of modeling based on the Sheil crystallization model [21 - 23]. In the process of use for modeling, a specialized database of thermodynamic data was used to describe high - entropy alloys - TCHEA5.

Fig. 2 shows the results of modeling the crystallization of the FeCoCrNiMn + xTi + xC melt using the classical Sheil model for various variants of the presence of carbon and titanium in the system (x = 0; 0.05; 0.25). Among other things, they demonstrate the temperature at which an additional phase with the FCC structure begins to stand out from the metal melt, the basis of which is titanium carbide. This temperature corresponds to the point of contact of the red line and the line consisting of black dots in Fig. 2(b) and 2(c).

When considering the process of endogenous formation of hardening phase particles in the volume of crystallized metal, kinetic factors play an important role, determining the rate and actual possibility of hardening particles formation as a result of diffusion-controlled chemical reactions, as well as determining the possible size of such particles. Kinetic modeling performed using the TC-PRISMA module of the Thermo-Calc software package allows to take into account such factors. This

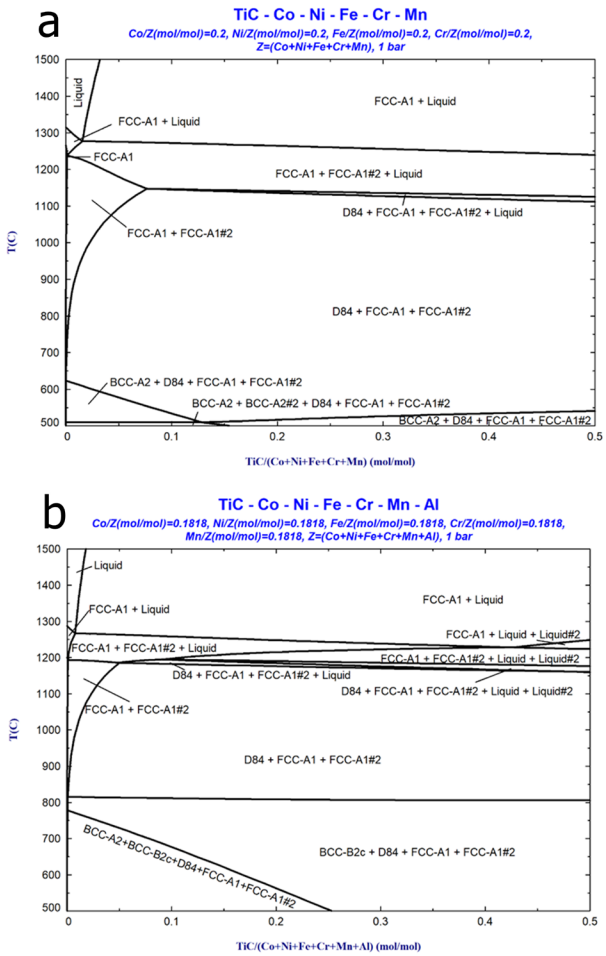

Fig. 1. Phase diagrams of Fe-Co-Ni-Mn-Cr/TiC (a) and AlFeCoNiMnCr/TiC (b) systems.

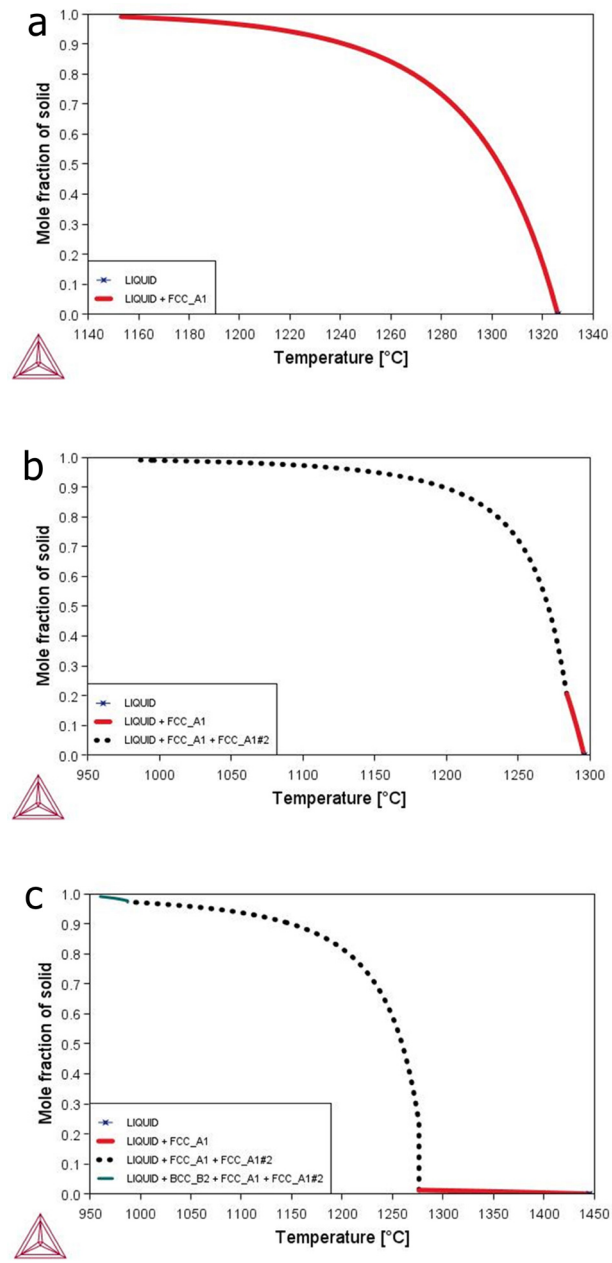

Fig. 2. Result of the crystallization modeling of the melt FeCoCrNiMn + xTi + xC using the classical Sheil model (Thermo-Calc): a) x = 0; b) x = 0.05; c) x = 0.25.

module makes it possible to model the nucleation, growth/dissolution and enlargement of crystallites under arbitrary heat treatment conditions in multicomponent and multiphase systems using Langer-Schwarz theory and the numerical Kampmann-Wagner approach. TC-PRISMA extends the functionality available in Thermo-Calc, allows you to perform calculations related to the crystallization and recrystallization of materials.

The modeling of the formation and growth of embryos performed for the systems (FeCoCrNiMn + xTi + xC) using the TC-PRISMA module was based on the use of the TCHEA5 and MOBHEA2 bases. The results of such modeling are presented in Figs. 3 and 4. The calculation results allow to estimate how the temperature and concentrations of titanium and carbon should affect the rate of release of TiC particles and their size during the heat treatment of castings (FeCoCrNiMn + xTi + xC). This kind of modeling makes it possible to rationally select the modes of heat treatment aimed at obtaining endogenous reinforcing TiC particles in the volume of the matrix based on high-entropy alloys. The main conclusions that can be drawn from the results of this simulation part are that at 1000°C, TiC particle nuclei appear in fractions of a second (at lower temperatures,

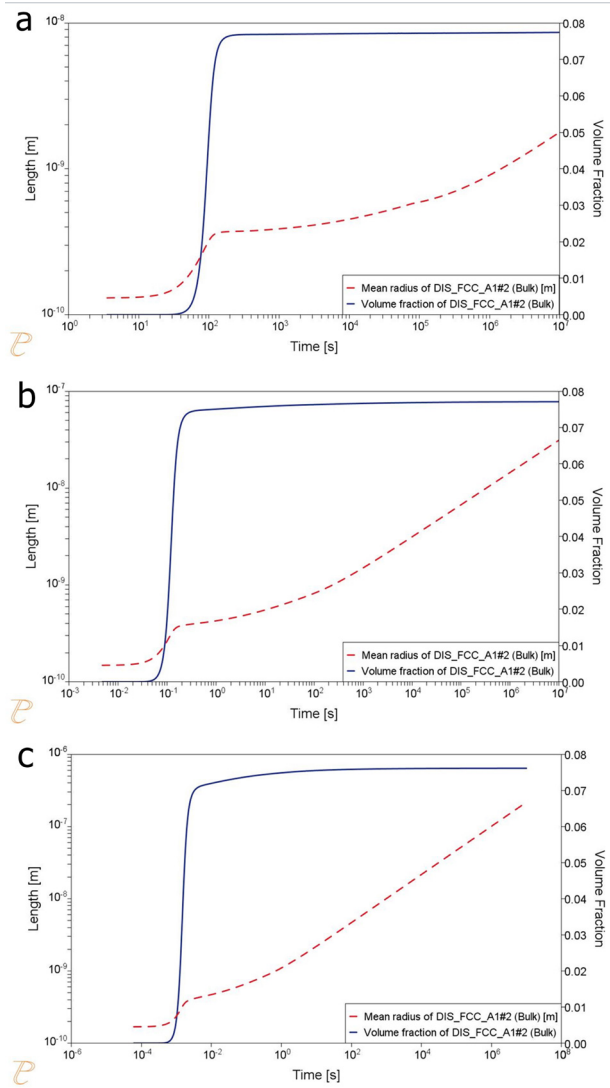

Fig. 3. Result of modeling the formation and growth over time of TiC inclusions in the system sample (FeCoCrNiMn + 0.05Ti + 0.05C) at 600°C (a), 800°C (b), 1000°C (c). The average particle radius and total volume fraction were simulated.

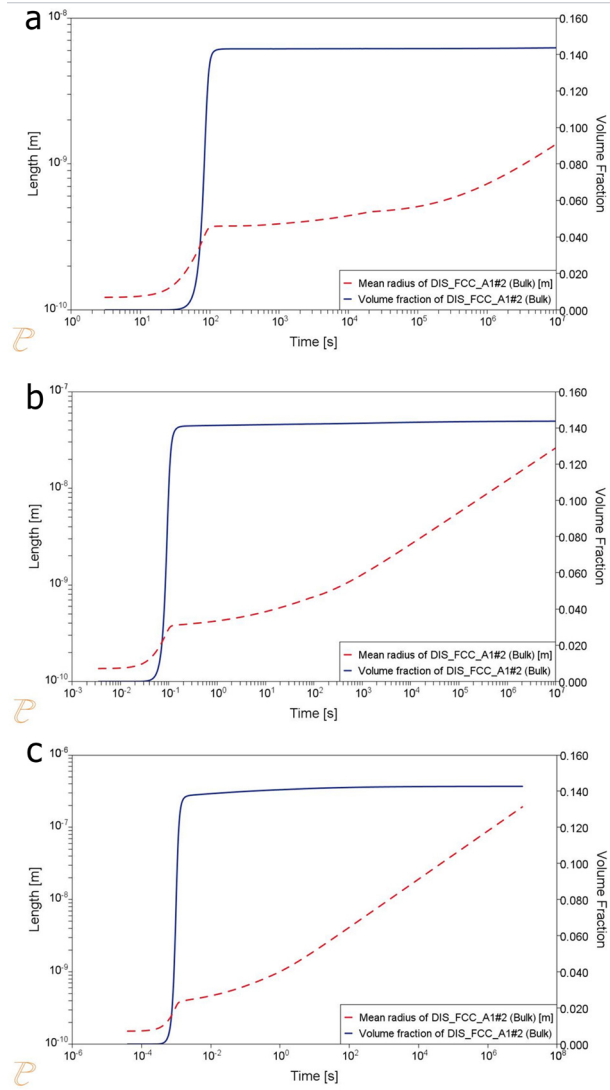

Fig. 4. Result of modeling the formation and growth over time of TiC inclusions in the system sample (FeCoCrNiMn + 0.25Ti + 0.25C) at 600°C (a), 800°C (b), 1000°C (c). The average particle radius and total volume fraction were simulated.

this takes a noticeable time), and the particle size can be successfully controlled within large limits by controlling the time of the heat treatment process.

Experiment description

For the manufacture of the experimental samples, samples of mixtures of simple substances (metals and graphite) were used, the composition of which is reflected in Table 1. The calculation of the masses is based on the required total mass of each sample of 20 g. Powders and pieces of simple substances with a purity of at least 99.99 % were used to produce alloys. The composition of each sample (with the exception of the zero one, which is made for comparison) includes equivalent amounts of titanium and carbon. It was assumed that as a result of crystallization and subsequent heat treatment, a composite material will be obtained in a high-entropy matrix of which reinforcing particles of titanium carbide will be distributed.

The alloys were smelted in corundum crucibles at a reducing atmosphere in a laboratory induction furnace. The crucibles were heated up to 1650°C and then kept for at least 15 minutes to average the composition of the samples, after which the crucibles were removed from the furnace and cooled on a cast-iron plate on air.

After that the ingots obtained were removed from the crucibles (the crucibles were broken) and cut in half (along the vertical axis). Samples for examination by electron microscopy and XRD were made from half of each obtained ingot, and the other half was heat-treated in order to ensure the most complete isolation of TiC inclusions in the metal volume. To do this, the ingots in a protective atmosphere in a resistance furnace were heated to 1000°C (the time to reach the desired temperature was about 30 minutes), kept at this temperature for 2 hours, and then gradually cooled to a temperature of 500°C for 5 hours. Then samples were made from the ingot halves processed in this way for examination by electron microscopy and XRD methods.

RESULTS AND DISCUSSION

The phase structure of the obtained samples (X-ray phase analysis) was studied by powder diffractometry (XRD) using a Rigaku Ultima IV powder diffractometer using Cu-Kα radiation (wavelength λ = 0.154 nm). Measurements were carried out in the range of angles of 5° - 95° with a scanning speed of 2°/min. The structure of the experimental samples was studied using a scanning electron microscope (SEM) Jeol JSM7001F. equipped with an X-MAX 80 energy dispersive X-ray spectrometer for qualitative and quantitative X-ray spectral microanalysis (RSMA). This study allowed to obtain information about the microstructure of the obtained materials (including data on the distribution and size of TiC particles found in the metal, see Fig. 5),

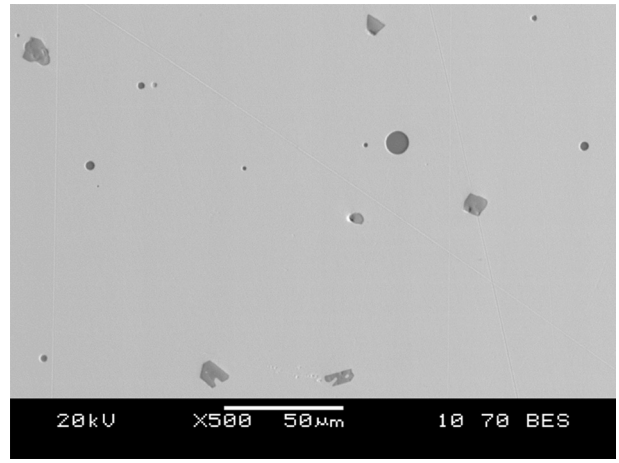

Fig 5. Microstructure of sample 6/1 (dark gray inclusions - TiC particles).

Table 1. Compositions of hangings (in g for 20 g of total weight) for the samples production.

Designation and formula of the sample	Ti	Fe	Co	Cr	Ni	Mn	C
0: FeCoCrNiMn	0,0000	3,9833	4,2034	3,7086	4,1861	3,9185	0,0000
1: FeCoCrNiMn + 0,05Ti + 0,05C	0,1693	3,9496	4,1679	3,6773	4,1507	3,8853	0,0427
2: FeCoCrNiMn + 0,1Ti + 0,1C	0,3358	3,9164	4,1329	3,6464	4,1158	3,8527	0,0852
3: FeCoCrNiMn + 0,2Ti + 0,2C	0,6605	3,8518	4,0646	3,5862	4,0479	3,7891	0,1697
4: FeCoCrNiMn + 0,3Ti + 0,3C	0,9746	3,7892	3,9986	3,5279	3,9821	3,7275	0,2535
5: FeCoCrNiMn + 0,4Ti + 0,4C	1,2787	3,7287	3,9347	3,4715	3,9185	3,6680	0,3366
6: FeCoCrNiMn + 0,5Ti + 0,5C	1,5732	3,6700	3,8728	3,4169	3,8568	3,6103	0,4190

Table 2. Results of the study of the samples microstructure and phase composition.

Cast samples			Samples after heat treatment		
Sample	Phase composition according to XRD data	Results of electron microscopic examination including results of micro-X-ray spectral analysis and mapping	Sample	Phase composition according to XRD data	Results of electron microscopic examination including results of micro-X-ray spectral analysis and mapping
0/1	HCC	The investigated surface is homogeneous. Composition (at.%) Fe 21.93; Co 20.35; Cr 21.80; Ni 20.23, Mn 15.69.	0/2	HCC	The investigated surface is homogeneous. Composition (at.%) Fe 20.13; Co 22.97; Cr 23.06; Ni 21.18, Mn 12.66.
1/1	HCC	The investigated surface is almost homogeneous. Composition (at.%) Fe 20.40; Co 21.88; Cr 20.18; Ni 21.33, Mn 16.21. Traces of titanium in the metal composition	1/2	HCC	The investigated surface is almost homogeneous. Composition (at.%) Fe 21.15; Co 22.03; Cr 24.72; Ni 20.13, Mn 11.97.
2/1	HCC	Matrix composition (at.%) Fe 21.36; Co 20.29; Cr 22.73; Ni 22.68, Mn 14.94. Single TiC inclusions are detected	2/2	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 21.41; Co 22.37; Cr 21.25; Ni 21.22, Mn 13.75. Uniformly distributed inclusions of TiC with a size of 2 microns are detected
3/1	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 20.88; Co 20.76; Cr 20.70; Ni 22.22, Mn 15.44. Uniformly distributed inclusions of TiC with a size of 1 micron are detected	3/2	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 20.40; Co 22.47; Cr 20.89; Ni 21.02, Mn 15.22. Uniformly distributed inclusions of TiC with a size of 2 microns are detected.
4/1	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 20.26; Co 20.90; Cr 20.07; Ni 22.03, Mn 16.74. Uniformly distributed TiC inclusions larger than 1 microns are detected	4/2	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 21.38; Co 21.57; Cr 20.91; Ni 21.28, Mn 14.86. Uniformly distributed inclusions of TiC up to 10 microns in size are detected
5/1	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 22.77; Co 20.32; Cr 18.30; Ni 21.58, Mn 17.03. Uniformly distributed TiC inclusions larger than 2 microns are detected	5/2	HCC1+ CC2(TiC)+Ti	Matrix composition (at.%) Fe 22.33; Co 21.50; Cr 20.53; Ni 21.74, Mn 13.90. Uniformly distributed inclusions of TiC up to 10 microns in size are detected
6/1	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 21.07; Co 22.28; Cr 18.84; Ni 21.74, Mn 16.07. Uniformly distributed inclusions of TiC with a size of 2-10 microns are detected	6/2	HCC1+ HCC2(TiC)	Matrix composition (at.%) Fe 22.28; Co 21.93; Cr 18.84; Ni 21.27, Mn 15.68. Uniformly distributed inclusions of TiC up to 15 microns in size are detected

as well as data on the chemical composition of the metal matrix and the inclusions found in it.

The results of the analysis of the obtained powder diffractograms and compositions of microstructural components by the RSMA method are presented in Table 2. The samples marked X/1 did not undergo additional heat treatment. Samples marked X/2 have undergone additional heat treatment according to the procedure described above.

The obtained data indicate that the smelting and subsequent heat treatment of alloys based on the Cantor alloy with the participation of titanium and carbon makes it possible to obtain materials with reinforcing TiC particles. From Table 2 it can be concluded that heat treatment had a positive effect on the process of separating reinforcing particles, however, samples that did not pass it contain such particles. This may be due to the (predicted in the process of kinetic modeling) high rate of particle separation at temperatures of the order of 1000°C, and these temperatures the ingots cooling after smelting had for several tens of seconds.

CONCLUSIONS

The works aimed at theoretical and experimental study of the possibility of interaction of carbon and titanium in a matrix based on a Cantor alloy (FeCoCrNiMn) with the formation of TiC, aimed at developing methods for obtaining titanium carbide hardening particles in a multicomponent metal matrix, have been carried out.

The analysis of the results of the calculations and experiments allows to obtain the following conclusions:

The results of thermodynamic modeling demonstrate the possibility that titanium carbide can partially dissolve in the matrix, and the resulting carbon interacts with chromium, forming phases based on chromium carbide. At the same time, in the studied concentration ranges, most of the titanium carbide is thermodynamically stable.

The temperature range of the stability of the composite structure can be determined using thermodynamic modeling. The calculations show that for the studied system, the stability region is limited from above by the melting point of the matrix, and the lower limit of stability (the temperature at which other phases besides the matrix and the main filler phase can appear) depends on the amount of titanium and carbon in the system.

Sheil crystallization modeling allows to estimate the maximum temperature at which an additional phase with the FCC structure, based on titanium carbide, can be released from the metal melt.

The conducted modeling allows to estimate the alloys of which compositions can be in equilibrium with the reinforcing component based on TiC, as well as how long and at what temperatures it is necessary to heat-treat alloys with titanium and carbon so that their predominant part forms a phase based on titanium carbide.

The data obtained indicate that the smelting and subsequent heat treatment of alloys based on the Cantor alloy with the participation of titanium and carbon makes it possible to obtain materials with reinforcing TiC particles. In general, the obtained results demonstrate the capabilities of modern thermodynamic and kinetic modeling techniques in the process of predicting the course and results of TiC formation processes from components of a multicomponent alloy based on a Cantor alloy including titanium and carbon. Comparison of the simulation results with experimental data allowed us to draw conclusions about the qualitative adequacy of thermodynamic and kinetic models of phase equilibria and phase transformations occurring during the formation, possible heat treatment and operation of TiC-reinforced metal matrix materials at high temperatures to the observed experimental data.

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