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Features of phase and structure formation in obtaining high-entropy alloy of Fe-Ti-Cr-Mn-Si-C system from a powder mixture of ferroalloys

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The peculiarities of the structure and phase composition of the high-entropy alloy of the TiCrFeMnSiC system obtained from the powder mixture of ferrotitanium, ferrochrome and ferrosilicon-manganese ferroalloys are considered in the work. The technological scheme of alloy production included joint grinding of the mixture in a planetary mill, consolidation of the blanks, their heating to 1100 ˚C, hot forging on the dugostator press and subsequent annealing of hot-forged samples at 1200 ˚C. According to the results of X-ray analysis of the obtained alloy, it was found that the main phase of the alloy is the BCC phase with the parameter of the cubic lattice a = 0.2868 nm, which is a solid solution based on alloying components of the original charge. The phase composition of the composite also recorded titanium carbide TiC with FCC lattice with the parameter a = 0.4319 nm, which corresponds to a stoichiometric composition of about $TiC_{0.6}$ and a small amount of FCC phase of iron-chromium carbide $(Cr, Fe)_{23}C_6$ with lattice parameter a = 1.0645 nm. The material has a high hardness (up to 60-61 HRC), which can provide high resistance of this multicomponent alloy.

Keywords: high-entropy alloy, powder metallurgy, hot forging, ferroalloy, microstructure, crystal lattice, phase, carbide.

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Introduction

One of the most promising areas in the field of creating new classes of materials with improved physical, mechanical and operational properties are approaches based on the development of high-entropy alloys (HEAs).

A characteristic feature of such alloys is the content in the composition of the last at least 5 basic elements in an approximately equiatomical ratio. The presence of a large number of heterogeneous elements with different individual properties, imposes its specificity on the formation of a solid solution of high-entropy alloys. The high entropy of mixing minimizes the free Gibbs energy, which leads to better formation of solid solutions with BCC, FCC or FCC + BCC structure. Alloys with such structures are characterized by high hardness and strength, increased thermal stability, high wear resistance and resistance to oxidation, in connection with which they attract the attention of more and more researchers working in the field of modern materials science.

Various foundry technologies have become the most widespread for obtaining HEAs [5-9]. However, the inherent shortcomings of foundry alloys associated with segregation and a high degree of inhomogeneity of the microstructure, contributed to the involvement of high-entropy alloys powder metallurgy methods, including, in particular, mechanical alloying operations of a mixture of elemental powders followed by hot static (isostatic) sintering (SPS) [10, 11].

The vast majority of high-entropy alloys are made using such high-value and scarce elements as Co, V, Nb, Mo, Ta, W, Hf, Zr, etc., which significantly narrows the economic feasibility of their wide practical application. At the same time, there is very little information in the scientific literature on the creation of HEAs based on

cheaper and more affordable raw materials (including non-cobalt) and virtually no data on the possibility of obtaining high-entropy alloys using ferroalloys as starting material.

At the same time, in traditional metallurgical practice, ferroalloys are widely used - alloys of iron with silicon, manganese, chromium and other elements that are intermediate products of metallurgical production. Ferroalloys are used in the smelting of steel and cast iron, for deoxidation and alloying of liquid metal, binding of harmful impurities, providing the metal with the necessary structure and properties, etc [6, 7]. The use of ferroalloys as components for alloying melt has a number of economic and technical advantages over metals in its pure form. In particular, the cost of alloying the melt with a metal in the form of a ferroalloy is significantly lower than in the case of pure metals. Ferroalloys are characterized, as a rule, by lower melting points in comparison with pure metals, which facilitates their dissolution in the melt. In addition, when alloying and deoxidizing steel and alloys, the use of an alloying element in the form of a ferroalloy increases its absorption by the melt and reduces carbon monoxide.

Given the above, ferroalloys are of considerable interest as starting materials for the synthesis of high-entropy alloys.

The aim of this work is to evaluate the possibilities of synthesis of high-entropy alloys from a powder mixture of ferroalloys: ferrotitanium, ferrochrome and ferrosilicon manganese, study of their structure, phase composition and properties.

I. Materials and methods of research

Ferroalloys: ferrotitanium FTi30, ferrochrome FH850 and ferrosilicon manganese MnS17 were used as starting components for the production of high-entropy alloys. The chemical composition and density of each of the ferroalloys are given in table 1.

Pieces of ferroalloys were ground first on a hydraulic press (to obtain granules up to 2 mm in size), followed by joint grinding of their mixture of the appropriate ratio in a planetary mill. The initial mixture for the synthesis of high-entropy alloy was formed at the rate of 33.3% (wt.) of each of the ferroalloys. The ratio of the mass of the charge to the mass of the grinding bodies was 1:10. The frequency of rotation of the drums of the mill was about 800 rpm. Grinding was carried out in ethyl alcohol for 30 minutes.

From the resulting mixture on a hydraulic press under a pressure of 700 MPa were pressed cylindrical samples with a diameter of 40 mm and a height of 20 mm, further consolidation of which was carried out by hot forging on a dugostator press FB1732 with a force of 1600 kN. Heating under hot forging was carried out in running argon at a temperature of 1100 °C for 20 minutes After hot forging, the forgings were annealed in an electric furnace Termolab at 1200 °C for 2 hours. The starting samples for forging had a porosity of about 36%, while after hot forging their porosity did not exceed 2 ÷ 3 %.

The microstructure of the obtained alloy was studied on an XJL-17 optical microscope. Studies of the phase composition and defects of the structural components of the studied materials were performed by radiography: X-ray phase analysis and X-ray diffraction analysis. X-ray sampling was performed on a DRON-3 diffractometer in filtered cobalt radiation, by step scanning in the range of angles 20 ÷ 1300. Scanning step was 0.05 deg, angular velocity of rotation of the goniometer - ¼ deg / min. The analysis of the parameters of the substructure of the samples was carried out according to the parameters of the fine structure.

The hardness of the obtained alloy was determined on a hardness tester TK-14-250 according to GOST 9013-75, and microhardness - on a microhardness tester PMT-3.

II. Analysis of experimental results and their discussion

As a result of grinding granules from a mixture of ferroalloys in a planetary mill, the fractional composition of the obtained powder mixture is represented mainly by dispersed fractions in the range of 5-20 μm (Fig. 1). Grinding of granules of starting materials was also accompanied by mechanical activation of the formed charge, which has a positive effect on the further formation of the structure during high-temperature processes.

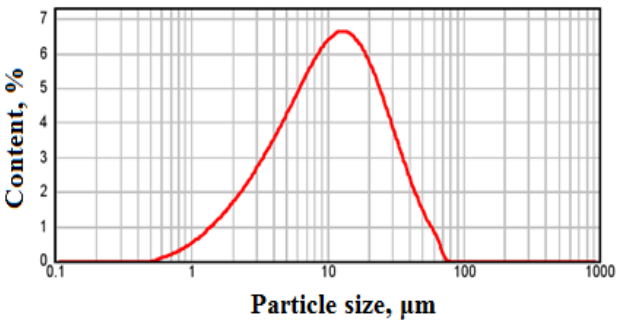

Fig. 1. Fractional composition of the powder mixture of ferroalloys after grinding for 30 minutes.

The bulk density of the obtained powder is 2.42 g/cm^3, the density of the shake is 3.53 g/cm^3, and the

Table 1

Chemical composition and density of starting ferroalloys.

Ferroaloy	Content of chemical elements (wt. %)					Density, g/cm^3
	C	Cr	Ti	Si	Mn	
Ferrotitanium FTi30	0.08	--	35.7	--	--	5.0
Ferrochrome FX850	8.3	69.4	--	--	--	6.8
Ferrosilicon manganese MnS17	2.1	--	--	15.8	62.6	5.3

calculated theoretical density of the alloy is 6.7 g/cm^3.

The atomic content of each element in the alloy was determined by X-ray fluorescence analysis on the EXPERT 3L unit and chemical analysis (Table 2).

Table 2

Atomic concentration of elements in the alloy.

Element	Ti	Cr	Fe	Mn	Si	C
Content (at. %)	9.5	16.3	39.1	15.0	6.5	13.6

The nature of phase formation in the synthesis of alloys is largely determined by the main crystallographic parameters of the elements that make up the alloy, as well as the melting temperatures given in table 3.

According to [12], at a concentration of valence electrons (CVE) ≥ 8 in the alloy, solid solutions with a FCC lattice are formed, and at CVE ≥ 6.8, BCC solid solutions are formed. The value of the concentration of valence electrons of the alloy is determined by the dependence:

$$\text{KBE} = \sum_{i=1}^{n} c_i \cdot \text{CBE}_i, \qquad (1)$$

where c_i is the concentration of the i-th element of the alloy (at. %), CVE_i is the concentration of valence electrons of the i-th element.

Taking into account the data of table. 3, the concentration of valence electrons of the alloy obtained from the elements, the content of which is given in table 2, is according to the dependence (1) 6.34 el./at., which should lead to the formation of mainly solid solutions with BCC structure.

According to the results of X-ray diffraction analysis of the alloy obtained after hot forging and subsequent annealing (Fig. 2), it was found that the latter is in a substantially nonequilibrium state. The peaks of the highest intensity, forming the main phase of the alloy, belong to the BCC phase with the parameter of the cubic lattice a = 0.2868 nm, which is a solid solution based on a-Fe. This indicates a solid-soluble mechanism for strengthening the matrix by dissolving the components of the charge.

The phase composition of the composite also recorded clear peaks of FCC titanium carbide phase, with the FCC lattice parameter a = 0.4319 nm, which corresponds to a stoichiometric composition of about $TiC_{0.6}$, and lines corresponding to the FCC phase of iron-chromium carbide $(Cr, Fe)_{23}C_6$ with the lattice parameter a = 1.0645 (Fig. 2, Table 4).

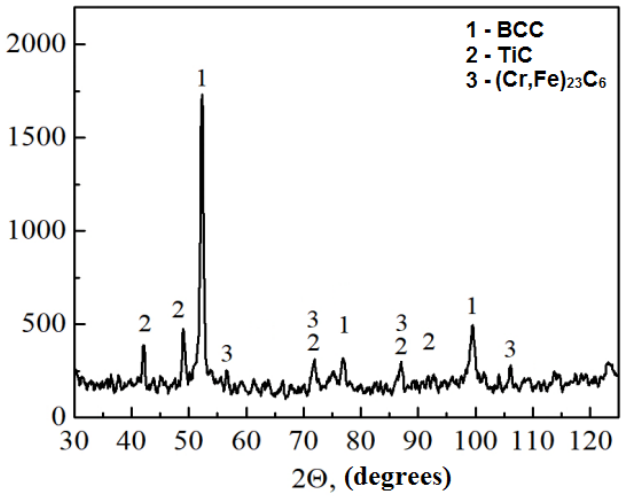

Fig. 2. Diffractogram of hot-forged alloy TiCrFeMnSiC.

Calculation of the content of these phases in the structure of the alloy, performed using the software package Match, showed that the BCC content of the phase - a solid solution based on a-Fe, is 39.2%, iron-chromium carbide $(Cr, Fe)_{23}C_6$ - 38.3%, titanium carbide - 22.5%.

X-ray diffraction analysis of the sample allowed to detect the defect of the crystal lattice of the matrix BCC phase and to calculate the parameters of the elements of the fine structure (substructure) of the crystal lattice of the matrix.

The dispersion of the coherent scattering regions is 26.7 nm, which is in the region of nanoscale, micro-distortion ($\Delta a/a = 16.5 * 10^{-2}$) and high dislocation density ($1.53 * 10^{12}$ cm^{-2}) indicate a significant defect of the crystal lattice matrix (Table 4). The lattice parameter of the BCC phase (0.2868 nm) is close to the lattice parameter α-Fe (0.2866 nm). The ratio of the expansion of the lines β_{220} and β_{110} indicates a significantly chaotic nature of the distribution of dislocations, which causes high hardness of the alloy.

The results of studies of the microstructure of the material after hot forging and subsequent annealing (Fig. 3) confirmed the data of X-ray phase analysis for the presence in the alloy structure of three main phases, which differ significantly in color and morphology.

According to the results of local micro-X-ray spectral analysis (Fig. 3, b; Table 5), matrix phase 1 of dark color is identified as BCC solid solution based on a-Fe, which

Table 3

Basic crystallographic parameters of elements and their melting temperature.

Element	Atomic radius, nm	Crystal lattice type	Number of valence electrons	Melting temperature, °C
Ti	0.147	Hexagonal	4	1670
Cr	0.130	BCC	6	1857
Fe	0.126	BCC	8	1539
Mn	0.127	FCC	7	1244
Si	0.132	FCC	4	1415
C	0.070	Hexagonal	4	-

Table 4

Parameters of fine structure of components of hot-forged sample.

Thin structure parameters (substructures)						Parameters of the crystal lattice of phases	
						Фаза	*a*, нм
β_{110}, мрад	β_{220}, мрад	β_{220}/β_{110}	ОКР, нм	$\rho*10^{12}$, см$^{-2}$	$(\Delta a/a)*10^{-2}$	BCC TiC (FCC) $(Cr, Fe)_{23}C_6$ (FCC)	0.2868 0.4319 1.0645
5.6	21.15	3.83	26.70	9.25	16.5		

Table 5

Chemical composition of the alloy phases of the TiCrFeMnSiC system (mass (a) and atomic (b) content of elements).

Phase	Content of elements, % (wt.)					
	Fe	Cr	Mn	Ti	Si	C
1	53.78	17.52	14.97	6.33	6.45	0.81
2	16.44	54.47	11.06	2.25	0.09	15.69
3	32.20	11.10	1.64	27.20	12.80	12.82

(a)

Phase	Content of elements, % (wt.)					
	Fe	Cr	Mn	Ti	Si	C
1	47.98	16.79	13.58	6.59	11.44	3.39
2	10.15	36.13	6.94	1.62	0.15	45.05
3	20.62	7.64	8.34	20.30	4.75	38.16

(b)

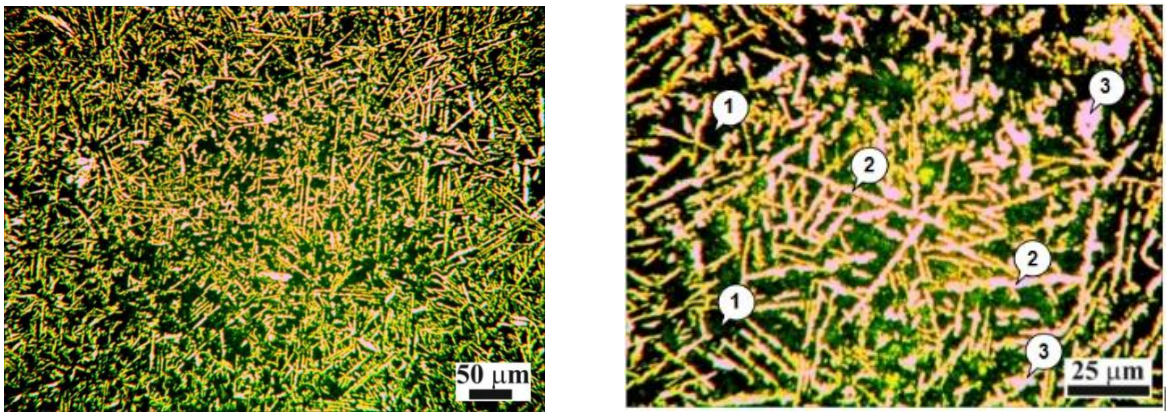

Fig. 3. Microstructure of samples of the obtained alloy system TiCrFeMnSiC.

includes all components of the original charge in different ratios.

Light phase 2 with needle-shaped grains 1-2 μm thick and 20-50 μm long, enriched with chromium and iron. Given the high carbon content, this allows us to identify it as iron-chromium carbide type $(Cr, Fe)_{23}C_6$.

The results of local microanalysis of light gray phase 3 taking into account the data of X-ray phase analysis of the alloy (Fig. 2) allow us to conclude that it contains titanium carbide grains formed in situ on the basis of ferrotitanium grains as a result of exothermic reaction in Fe-Ti-C [13], which was accompanied by a redistribution in the direction of titanium carbon from particles of high-carbon ferrochrome.

As shown by the results of the evaluation of the mechanical characteristics of the obtained alloy by micro- and macroindentation, the matrix phase 1 of dark color has a microhardness of about 9.0 GPa. The microhardness of the light phase 2 needles could not be measured due to the inability of the indenter to enter a fairly thin needle, but the microhardness of globules (conglomerates) of the same phase is about 10.3 GPa. The average microhardness of phase 2 containing titanium carbide is 12.4 GPa.

The value of the macrohardness of the alloy is 60.0-61.0 HRC. Sufficiently high micro- and macrohardness characteristics are due to solid-soluble hardening with strong distortion of the crystal lattice of solid solutions due to a significant difference in the atomic radii of the substitution elements, as well as the predominant BCC phase content.

Conclusions

1. Using powder metallurgy methods, which included high-energy grinding of powder mixture, hot forging of pressed blanks and their subsequent annealing, from the initial mixture of three ferroalloys: ferrotitanium, ferrochrome and ferrosilicon manganese, obtained high-entropy alloy, based Ti-Cr-Fe-Mn-Si-C system.

2. According to the results of X-ray diffraction analysis and local micro X-ray spectral analysis it was found that after hot forging and annealing at 1200 °C the alloy consists of matrix BCC phase, which is a solid solution based on a-Fe, which includes all components of the initial charge in different ratios, and two FCC phases identified as titanium carbide with a stoichiometry of about $TiC_{0.6}$, and iron-chromium carbide $(Cr, Fe)_{23}C_6$.

3. High values of microhardness of individual phases and macrohardness of hot-forged samples, which significantly exceed the hardness of the initial components of the alloy, indicates a solid-soluble mechanism of matrix strengthening by dissolving components of the charge.

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Особливості фазо- та структуроутворення при отриманні високоентропійного сплаву системи Fe-Ti-Cr-Mn-Si-C із порошкової суміші феросплавів

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В роботі розглянуті особливості структури та фазового складу високоентропійного сплаву системи TiCrFeMnSiC, отриманого із порошкової суміші феросплавів феротитану, ферохрому та феросилікомарганцю. Технологічна схема виготовлення сплаву включала спільне розмелювання суміші в планетарному млині, пресування вихідних заготовок, їх нагрів до 1100 ^{0}C, гаряче штампування на дугостаторному пресі та наступний відпал гарячештампованих зразків при 1200 ^{0}C. За результатами рентгенофазового аналізу отриманого сплаву встановлено, що основною фазою сплаву є ОЦК фаза з параметром кубічної гратки a = 0,2868 нм, що представляє твердий розчин на основі легуючих компонентів складу вихідної шихти. У фазовому складі композиту зафіксовані також карбід титану з ГЦК граткою з параметром a = 0,4319 нм, що відповідає стехіометричному співвідношенню $TiC_{0,6}$, та ГЦК фаза залізо-хромового карбіду $(Cr, Fe)_{23}C_6$ з параметром решітки a = 1.0645 nm. Матеріал відзначається підвищеною твердістю (до 60-61 HRC), що має забезпечувати високу зностійкість даного полікомпонентного сплаву.

Ключові слова: високоентропійний сплав, порошкова металургія, гаряче штампування, феросплав, мікроструктура, кристалічна решітка, фазовий склад, карбід.