

INFLUENCE OF THE SYNTHESIS METHOD ON THE CRYSTALLINE STRUCTURE, PHASE COMPOSITION AND PROPERTIES OF TiCrFeNiCuC EQUIATOMIC ALLOYS

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Abstract: Equiatomic alloys TiCrFeNiCuC were made by two methods of powder metallurgy – vacuum sintering and hot forging followed by annealing. In the process of sintering the TiCrFeNiCuC blanks, the influence of entropy of mixing resulted in the formation of solid substitution solutions mainly on the basis of the FCC lattice, and also formed titanium carbide ($TiC_{0.74}$). In samples obtained by hot forging and subsequent annealing, two carbides TiC and Cr_3C_2 were found, and titanium carbide being formed with lower carbon content ($TiC_{0.58}$). In addition, the forged samples showed significantly higher values of the defect of the crystalline structure, which leads to increase in their hardness.

Keywords: EQUIATOMIC ALLOYS, MICROSTRUCTURE, PHASE COMPOSITION, HARDNESS, SINTERING, HOT FORGING.

1. Introduction

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

A characteristic feature of such alloys is the content in their composition of not less than 5 basic elements, mainly in the equiatomic ratio. The presence of a large (not less than five) number of heterogeneous, but in an equal number of atoms, having different individual properties, imposes its specificity on the formation of a solid solution of high entropy alloys. The high entropy of mixing causes the minimization of the free Gibbs energy, which leads to the preferential formation of solid solutions with a BCC, FCC or FCC + BCC structure. The phases formed on the basis of solid solutions are more stable [1-3]. Alloys with such structures have high hardness, strength, wear resistance, oxidation resistance, etc. These properties of high entropy alloys are due to the slow diffusion of atoms in a multicomponent matrix, a significant distortion of the lattice, which arises in connection with the difference in the atomic dimensions of the constituent elements of the alloy, as well as the interaction between elements in phases based on a solid solution [4-9]. When giving carbon in the alloys, high entropy carbides will form.

To obtain HEAs the most widely used were various casting technologies [1-6]. However, in recent years, the methods of powder metallurgy are gaining increasing popularity in the development and production of these alloys [7-10].

The purpose of the work is to study the influence of the manufacturing method on the crystalline structure, phase composition and properties of the TiCrFeNiCuC equiatomic alloys.

2. Experimental Procedure

The initial Ti, Cr, Ni, Cu, Fe, and C powders with the purity of 99.5 - 99.9% were used as the starting elements for the preparation of the equiatomic alloys of the Ti-Cr-Fe-Ni-Cu-C system. Alloys were produced by two methods of powder metallurgy – vacuum sintering and hot forging with subsequent annealing.

The starting powders were dosed on an electronic scales. The charge of the equiatomic composition was prepared by mixing the powders in a drum mixer with a diagonal axis for 2 hours with the addition of alcohol. From the obtained mixture, cylindrical billets with a diameter of 20 and 40 mm at a pressure of 700 MPa were extruded in a steel matrix. Consolidation of powder blanks by hot forging was carried out on a dougostator press at a temperature of 1050 °C in argon. Sintering of the samples and annealing of the forged samples were carried out in a vacuum induction furnace at 1200 °C for 2 hours.

X-ray diffraction studies were carried out on a DRON-3 X-ray diffractometer in filtered Co radiation by a step-scan method in the angular range 20÷130°. A quantitative micro-X-ray spectral

analysis was performed on a CAMECA MS-46 X-ray microprobe at a probe mode of 20 kV, 12 nA and a probe diameter of 3 μm. The microstructure of the alloys was studied with an XJL-17 optical microscope and with a JEOL Superprobe 733 scanning electron microscope. The density and porosity of the alloys were determined by hydrostatic weighing. The microhardness was measured on a PMT-3 device. The hardness was measured on a TK-14-250 hardness tester. The theoretical density of the alloy, calculated from the additivity formula, is equal to 6.55 g/cm³.

3. Experimental results and their discussion

X-ray diffraction studies of high entropy TiCrFeNiCuC alloys, obtained by different methods, revealed features both in the phase composition and in the defectiveness of their crystal unit cell. Regardless of the method of preparation, alloys had a heterogeneous structure. On the X-ray diffraction pattern of the alloy obtained after sintering at 1200 °C for two hours, a number of lines characterizing the phase with a FCC lattice are fixed, as well as TiC carbide. On the lines with the indices of the atomic planes (311) and (222), we can assume the presence of two phases with FCC lattices with close values of the crystal lattice parameter (Fig. 1, a). The phase with the BCC structure is fixed weakly.

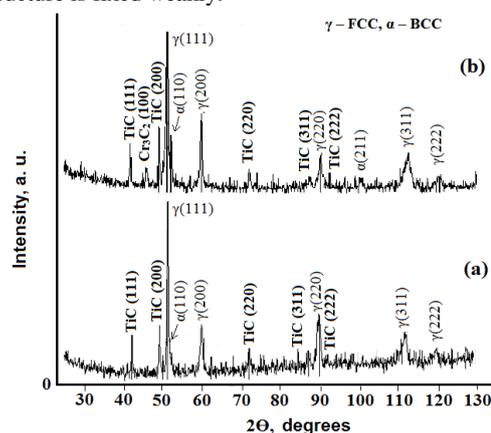


Fig. 1. XRD patterns of TiCrFeNiCuC alloys, obtained by vacuum sintering (a) and hot forging with subsequent annealing (b)

On the X-ray diffraction pattern of the sintered alloy, the diffraction maxima (111) and (222) were divided into two components (Fig. 2). The calculated crystal lattice parameters for both FCC phases are: $a = 0.36098$ nm and $a = 0.35877$ nm. It is known that nickel and copper are systems with unrestricted solubility based on the structural type of FCC. It should be assumed that one phase of FCC with $a = 0.36098$ nm is formed with a high copper content ($a_{Cu} = 0.36176$ nm), another phase $a = 0.35877$ nm – with a high nickel content ($a_{Ni} = 0.35195$ nm). An analysis of the structural state of phases with a FCC structure indicates that both

phases of the FCC have a number of imperfections in their crystal lattice and a difference in the quantitative ratio of their defectiveness, characterized by the values of the parameters of the fine structure elements. Thus, for FCC with a high copper content with $a = 0.30988$ nm, the defectiveness of the crystal structure is denoted by the following parameters: coherent scattering region (CSR) = 36.2 nm, microdistortion $\Delta a/a = 54.6 \times 10^{-3}$, dislocation density $\rho = 8.2 \times 10^{11} \text{ cm}^{-2}$. For a FCC structure with a high nickel content $a = 0.35877$ nm. Data on the imperfections of the FCC alloy structure is much higher in comparison with the analogous results for the phase with the predominant copper content and are denoted by the following parameters: CSR = 10.0 nm, $\Delta a/a = 77.2 \times 10^{-3}$, $\rho = 17.3 \times 10^{11} \text{ cm}^{-2}$. The FCC phase, which is formed with the predominant content of the more ductile element of copper, naturally has a less distorted crystal lattice in comparison with the FCC lattice with a harder nickel base. This conclusion is confirmed by microhardness measurements: a FCC structure with a crystal lattice parameter equal to $a = 0.36098$ nm has a microhardness of 4.9 GPa, a structure with a crystal lattice parameter equal to $a = 0.35877$ nm has a microhardness of 6.8 GPa.

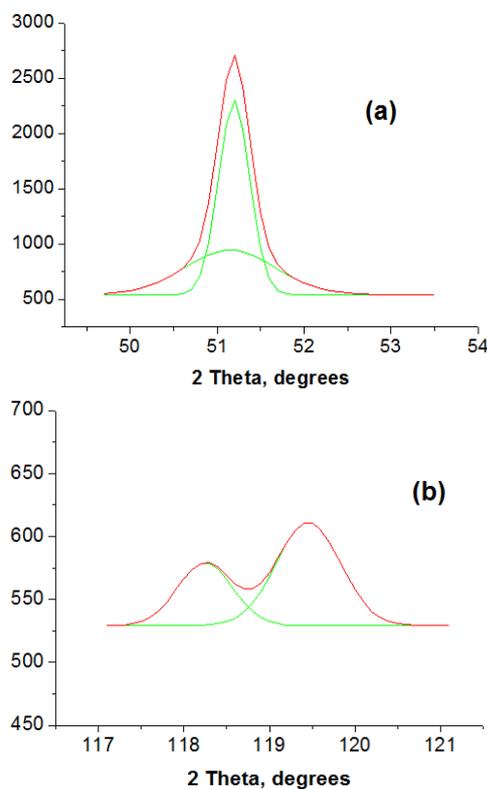


Fig. 2. Fragments of the XRD pattern of the TiCrFeNiCu alloy, obtained by sintering at 1200 °C for 2 hours, in the peak region (a) (111); (b) (222)

Along with solid solutions of the FCC type in the highly entropic TiCrFeNiCu alloy obtained by sintering at 1200 °C for two hours, titanium carbide with a crystal lattice parameter of 0.43215 nm is formed. According to the dependence of the TiC cell parameter on the amount of carbon bound in it [12] in the sintered alloy, there is a TiC phase with an atomic ratio of carbon to titanium of 0.74 (TiC_{0.74}).

The formation of phases in highly entropic alloys, the appearance of two or three phases is associated with a certain electronic concentration in the alloy, with the difference in the atomic radii of the components that make up the alloy. Hot forging is a significant influence on the formation of the crystal structure of high entropy alloys. Hot forging of porous blanks can be considered one of the cycles of thermomechanical processing, during which a developed substructure is created. This developed substructure is the primary factor determining all other structural causes of thermomechanical hardening of steel. [11].

X-ray diffraction studies of the alloy TiCrFeNiCuC, obtained by hot forging and subsequent high-temperature annealing, indicate the formation of a heterophase structure of the alloy. The X-ray spectrum of the alloy is represented by phases of FCC, BCC, TiC and Cr₃C₂ carbides (Fig. 1 b).

Analysis of the X-ray spectrum of the alloy revealed the following features. Estimating the nature of the profiles of the X-ray lines of the FCC structure, several blurred profiles should be noted that describe the phase with the FCC grating, which is especially noticeable at large reflection angles. Thus, for a FCC lattice along lines with indices of atomic planes (311) and (222), it is possible to assume the presence of two phases with FCC lattices with close parameters. This is confirmed by calculations on the lines (222): $a_1 = 0.36460$ nm and $a_2 = 0.35815$. On the XRD pattern of the forging alloy, the diffraction maxima (111) and (222) were decomposed into two components (Fig. 3).

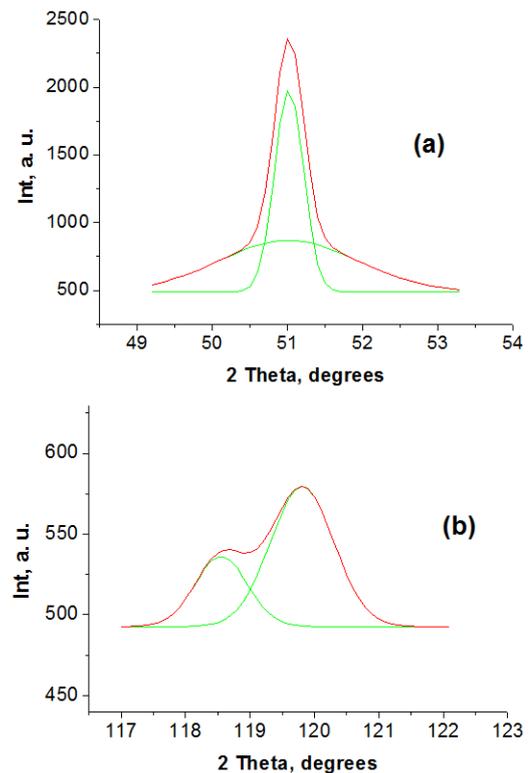


Fig. 3. Fragments of the XRD pattern of the TiCrFeNiCu alloy obtained by hot forging at 1050 °C, followed by annealing at 1200 °C for 2 hours, in the peak region: a) (111), b) (222)

One of the phases with the parameter $a_1 = 0.36046$ nm $a_2 = 0.35815$ copper i.e. with a high copper content, another phase of FCC with $a_2 = 0.35815$ nm is closer to the nickel parameter, i.e. with a high content of nickel.

An analysis of the structural state of phases with a FCC structure indicates that both phases of the FCC have a number of imperfections in their crystal lattice and a difference in the quantitative ratio of their defectiveness, characterized by the values of the parameters of the fine structure elements. Thus, for the FCC lattice with a high copper content $a = 0.36098$ nm, the defectiveness of the crystal structure is denoted by the following parameters: CSR = 5.2 nm, microdistortion $\Delta a/a = 90.4 \times 10^{-3}$, dislocation density $\rho = 22.6 \times 10^{11} \text{ cm}^{-2}$. For a FCC structure with a high nickel content $a = 0.35815$ nm. Data on distortion of the lattice of the FCC structure of the alloy is much higher in comparison with the analogous results for the phase with the predominant content of copper and are denoted by the following parameters: $\Delta a/a = 119.8 \times 10^{-3}$, $\rho = 42.0 \times 10^{11} \text{ cm}^{-2}$. There is no grain fragmentation in the coherent scattering region (CSR = 112.3 nm, i.e. commensurate with the grain size), the structural defect is due to the distortion of the crystal lattice. The FCC phase, which is formed with the predominant

content of the more ductile element of copper, naturally has a less distorted crystal lattice in comparison with the FCC lattice with a harder nickel base. This conclusion is confirmed by microhardness measurements: a FCC structure with a crystal lattice parameter $a = 0.36098$ nm has a microhardness of 5.5 GPa, a structure with a lattice parameter $a = 0.35877$ nm has a microhardness of 7.3 GPa.

The most intense line (110) of the structure with a BCC lattice on the x-ray spectrum of the sample is indicated by a line of weak intensity, which indicates a small amount in the sample alloy. In addition to line (110), we can consider the line (211) belonging to the BCC structure as a weak diffuse reflex. Line (220) is almost overlapped with the background. The diffuse character of the BCC reflections is due to the distortion of the crystal lattice, which is confirmed by the quantitative characteristics of the fine structure elements. So the value of the regions of coherent scattering is 50.0 nm (probably somewhat overestimated as a result of overlapping of the part of the profile from the side of the small angle by the line of the FCC lattice (110)), microdistortions equal to 175.87×10^{-3} , the dislocation density is $\rho = 62.0 \times 10^{11} \text{ cm}^{-2}$. The results on the distortion of the crystal lattice of the BCC phase are the largest for all the emerging highly entropic phases. The phase with the BCC structure is formed upon mutual dissolution of iron and chromium, has the parameter $a_{\text{bcc}} = 0.2858$ nm, has so small a grain that it was impossible to measure the microhardness.

It was pointed out that on the XRD pattern of the alloy, in addition to a series of phase lines of FCC and BCC structures, a number of reflections belonging to TiC and Cr_3C_2 carbides. The TiC lattice parameter is 0.4311 nm, hence, the TiC phase is present in the alloy with an atomic carbon to titanium ratio of 0.58 ($\text{TiC}_{0.58}$). In the sintered alloy, the atomic ratio of carbon to titanium is 0.74.

The microstructure of the sintered and forged alloys consists mainly of two structural regions. According to micro-X-ray spectral analysis, the light phase has an increased content of Cu, Fe, and Cr. The darker phase is the result of the maximum interdiffusion of all elements of the alloy and has an increased concentration of Ni, Ti and C. Consequently, the dark phase contains TiC. In the forged alloy, a much greater dispersion of the structural elements is observed compared to the sintered alloy, as well as the presence of two carbides – TiC and Cr_3C_2 , which is explained by the influence of hot forging.

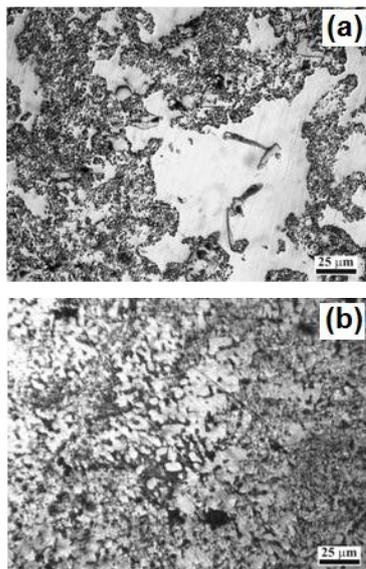


Fig. 4. Microstructures of sintered (a) and forged (b) equiatomic TiCrFeNiCuC alloys

Analysis of the processes of structure formation of high entropy phases formed in alloys of TiCrFeNiCuC composition, inclusions of various compounds showed a significant increase in the defectiveness of crystal structures and, accordingly, an increase in the microhardness of both individual structural components and hardness of the alloy as a whole, using preliminary hot forging of

porous blanks. In the sintered alloy, the hardness is 30 HRC, in the alloy with the preliminary hot forging, the hardness increased to 42 HRC (Table 1).

Table 1. Characteristics of TiCrFeNiCuC alloys obtained

No	Production method	Density, g/cm^3	Porosity, %	Hardness, HRC
1	Sintering	6,28	4,0	30
2	Hot forging and annealing	6,40	2,2	42

3. Conclusions

Thus, preliminary hot forging during the formation of a high entropy alloy intensifies the processes of structure formation, causes redistribution of carbon (with the formation of chromium carbide Cr_3C_2 , titanium carbide TiC is formed with a smaller carbon content in TiC to 0.58), and also provides processes that lead to significant distortion of the crystalline lattice of the forming phases, which contributes to the strength of the alloys.

References

1. Wang Y.P. *et al.*, "Microstructure and compressive properties of AlCrFeCoNi high entropy alloy," *Mat. Sci. and Eng. A* 491, pp. 154—158, 2008.
2. Wang F.J., Zhang Y. Effect of Co Addition on Crystal Structure and Mechanical Properties of Ti0.5CrFeNiAlCo High entropy alloy // *J. Mater. Sci. Eng. A* 496, pp. 214 — 216, 2008.
3. Zhang Ch. *et al.*, Computational Thermodynamics Aided High-Entropy Alloy Design // *JOM*, vol. 64, No. 7, pp. 839—845, 2012.
4. Yeh J.W. Recent progress in high-entropy alloys // *Ann. Chim. Sci. Mat.*, vol. 31, pp. 633—648, 2006.
5. Tang W.-Y. *et al.* Microstructure and Mechanical Performance of Brand-New Al0.3CrFe1.5MnNi0.5 High-Entropy Alloys // *Advanced Engineering Materials*, vol. 11, No. 10, pp.788—794, 2009.
6. Firstov S.A., Gorban V.F., Krapivka N.A. Mechanical properties of cast multicomponent alloys at high temperatures // *Current problems of physics material science. - 2008. - Issue. 17. - P. 126-139.*
7. Fan Y. H, Zhang Y. P, Guan H. G, Suo H. M, He L. AlNiCrFeMo_{0.2}CoCu High Entropy Alloys Prepared by Powder Metallurgy // *Rare Metal Materials and Engineering. - 2013. Vol. 42, No.6. - P. 1127-1129.*
8. Qiu X. W. Microstructure and properties of AlCrFeNiCoCu high entropy alloy prepared by powder metallurgy // *Journal of Alloys and Compounds. - 2013. - Vol. 555. - P. 246-249.*
9. Yurkova A.I., Chernyavsky V.V., Gorban V.F. Structure and mechanical properties of high entropy AlCuNiFeTi and AlCuNiFeCr alloys, obtained by mechanical alloying with subsequent sintering under pressure // *Powder Metallurgy. - 2016. - No. 3/4. - P. 37-52.*
10. Bagliuk G.A., Marych M.V., Mamonova A.A., Gripachevsky A.N. Features of the structure formation in the sintering of compacts from a multicomponent charge of the TiCrFeNiCu system // *Powder Metallurgy. - 2015. - No. 9/10. - P. 46-52.*
11. Bernstein M.L. Structure of deformed metals. - Moscow: Metallurgy, 1977. - 432 p.
12. Kyparisov S. S., Levinsky Yu. V., Petrov A. I. Titanium carbide: production, properties, application. - Moscow: Metallurgy. 1987. - 216 p.