

INFLUENCE OF CHROMIUM ON THE PHASE COMPOSITION AND SPECIFIC FEATURES OF HARDENING OF THE MnFeCoNiCu HIGH-ENTROPY ALLOY

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A six-component system of CoNiCuCr_x high-entropy alloys with different contents of chromium (where $x = 0, 0.5, 1.0, 2.0,$ and 3.0 mole) is obtained by the method of argon-arc melting in a F-9 study. By the methods of X-ray diffraction analysis, scanning-electron microscopy, and indentation, we investigate the influence of chromium on the crystalline structure, microstructure, and hardness of these alloys in the as-cast state. In their structure, depending on the chromium content, we detect a mixture of the following phase components: two face-centered cubes + a body-centered cube + an intermetallic σ -phase (FCC1 + FCC2 + BCC + σ). It is also established that, as the chromium content increases, we observe the formation of the bcc structure and the σ -phase, which is the predominant factor of hardening of the alloy.

Keywords: high-entropy alloys, phase composition, hardness.

Introduction

Most alloys currently used in industry were developed on the basis of a single main element (metal), namely, Fe, Al, Cu, Ti, etc. A new class of alloys was created in [1]. These alloys were called high-entropy alloys (HEA) due to their high entropy of mixing in the liquid state as compared with traditional alloys. By definition, any HEA must have at least five components with a concentration of each component varying within the range 5–35 at.%. For some compositions, these alloys may have high characteristics of hardness, wear resistance, oxidation resistance, and corrosion resistance [2, 3].

During the last decade, high-entropy alloys of different compositions were obtained and investigated. Among them, we can especially mention a single-phase fcc MnFeCoNiCu alloy, which has been sufficiently well investigated and exhibits high strength and thermally stable mechanical properties [4, 5]. The aim of the present work is to study the influence of chromium on the structure, phase composition, and hardness of the MnFeCoNiCu HEA. This choice is determined by the fact that chromium is a relatively low-cost metal, which is commonly used as an alloying element in the compositions of steels and, moreover, according to the binary diagrams of state, may form the σ -phase with several components of the alloy.

Procedure

The alloys were obtained in a F-9 argon-arc furnace in the atmosphere of high-purity argon. The procedure of melting was performed with a nonconsumable tungsten electrode on a copper water-cooled hearth.

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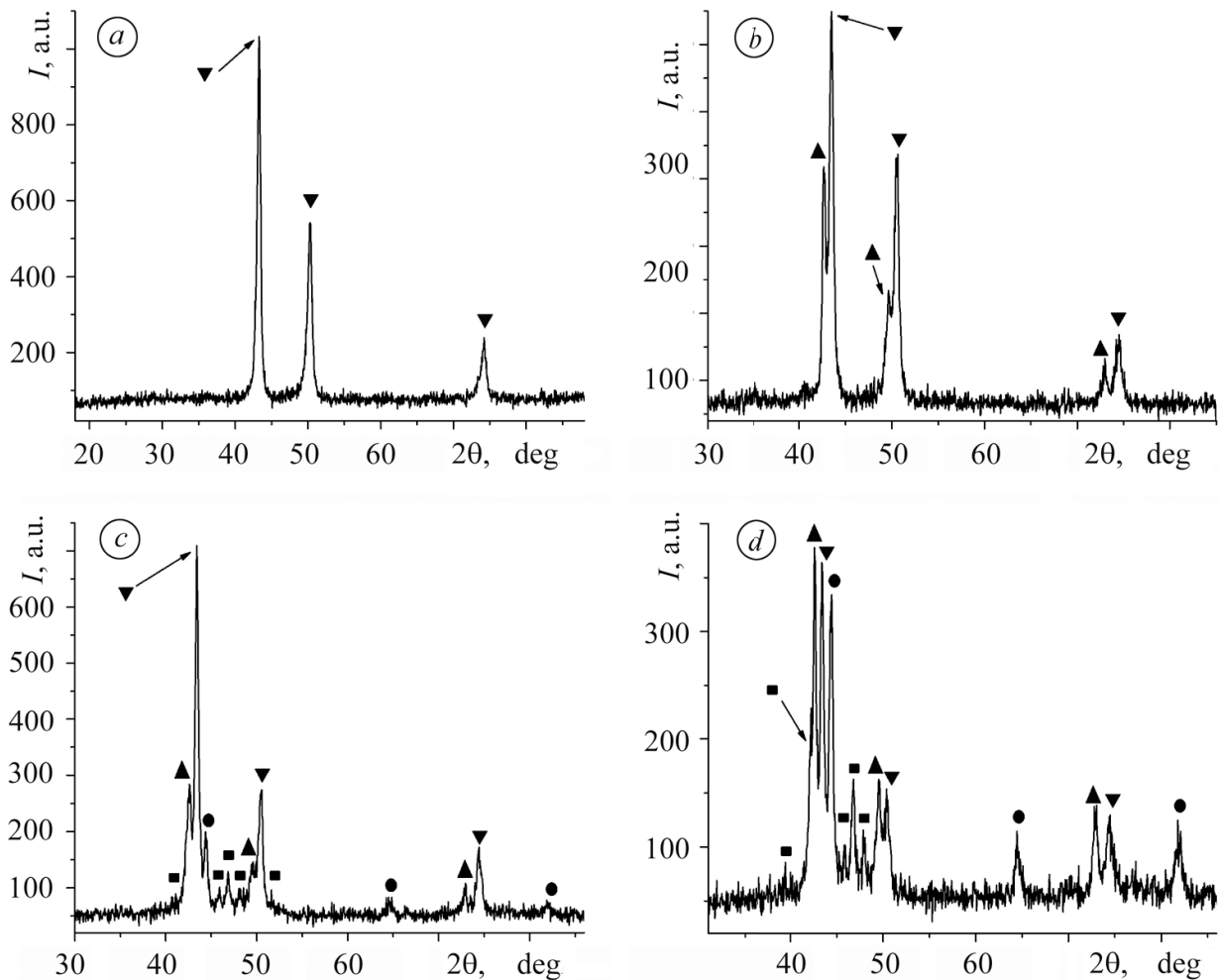


Fig. 1. Diffraction patterns of alloys of the MnFeCoNiCuCr system with different chromium contents: (a) $x = 0$, (∇) FCC; (b) $x = 0.5$ mole, (∇) FCC1, (\blacktriangle) FCC2; (c) $x = 2.0$, (\bullet) BCC, (∇) FCC1, (\blacktriangle) FCC2, (\blacksquare) FeCr -type phase; (d) $x = 3.0$ mole, (\bullet) BCC, (∇) FCC1, (\blacktriangle) FCC2, (\blacksquare) FeCr -type phase. The arrows mark the diffraction maxima.

The obtained castings were remelted 6–7 times in order to homogenize their compositions and cooled at a rate of 80–100°K/sec. The original MnFeCoNiCu alloy contained 20 at.% of each component.

The phase composition was determined by the X-ray diffraction method in the Bragg–Brentano focusing geometry in a DRON-3 diffractometer in the monochromatic $\text{CuK}\alpha$ -radiation. The microstructures of polished microsections (without etching) were studied by using a TESCAN VEGA3 scanning electron microscope equipped with a detector for recording reflected electrons. The Vickers microhardness (HV) was measured on polished surfaces with the use of a Vickers diamond pyramid with an angle of 136° under a load of 250 g for 15 sec.

Results and Discussion

The X-ray diffraction patterns of MnFeCoNiCuCr_x cast alloys are shown in Fig. 1. The initial MnFeCoNiCu alloy contained solely the FCC phase with a lattice constant $a = 3.6322$ (Fig. 1). After the addition of 0.5 mole

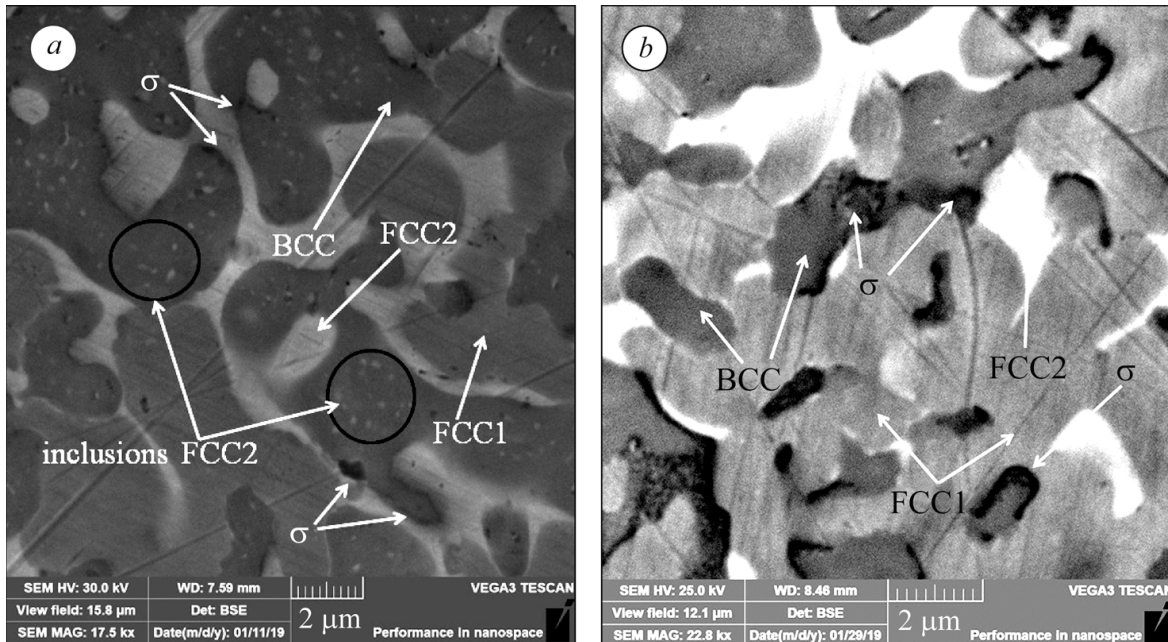


Fig. 2. Back-scattered electron images of the microstructures of as-cast MnFeCoNiCuCr_x alloys with different chromium contents: (a) $x = 2.0$; (b) $x = 3.0$.

Table 1
Contents of Phases in the MnFeCoNiCuCr_2 and MnFeCoNiCuCr_3 Alloys

Alloy	Content of phases, wt.%			
	FCC1	FCC2	BCC	-phase
MnFeCoNiCuCr_2	56.0	20.0	7.0	17
MnFeCoNiCuCr_3	23.0	29.0	19	29

of chromium, two phases FCC1 and FCC2 with lattice constants $a = 3.6021$ and $a = 3.6632$, respectively, were formed in the alloy (Fig. 1b). According to the results of the XRD analysis, the FCC1 phase whose content constitutes 72 wt.% is predominant. In the X-ray diffraction pattern of the equimolar alloy, we recorded the same phases as in the $\text{MnFeCoNiCuCr}_{0.5}$ alloy. The ratio of these phases does not change but their lattice constants are equal to $a_{\text{FCC1}} = 3.6087$ and $a_{\text{FCC2}} = 3.6744$.

With subsequent increase in the chromium content, the phase compositions of the alloys change substantially (Table 1). In particular, in the cast MnFeCoNiCuCr_2 alloy, three solid solutions (FCC1, FCC2, and BCC) and the FeCr-type σ -phase were recorded by the X-ray phase diffraction analysis (Fig. 1). The specimen was additionally investigated with the use of electron microscopy (Fig. 2). Since the σ - and BCC phases have similar chemical compositions and high hardness [6], they manifest themselves as dark areas (without polishing-induced scratches). At this chromium concentration, the average atomic numbers of the phases are close, and thus, they are similar in color in the image of the microstructure, but the area with the chromium-enriched

Table 2
Electron Concentration and the Entropy of Mixing of MnFeCoNiCuCr_x Alloys [7]

Chromium content in alloys, mole	0	0.5	1.0	2.0	3.0
Electron concentration, el/atom	9.0	8.7	8.5	8.1	7.9
Entropy of mixing, J/(mole K)	13.30	14.60	14.90	14.53	13.85

Table 3
Enthalpy of Mixing of the Atomic Pairs Used for the Preparation of HEA, kJ/mole [8]

Element	Cr	Fe	Co	Ni	Cu	Mn
Cr	0	-1	-4	-7	+12	2
Fe		0	-1	-2	+13	0
Co			0	0	+6	-5
Ni				0	+4	-8
Cu					0	4
Mn						0

-phase is the darkest. The light and gray phases are associated with the FCC1 and FCC2 phases. It should also be noted that microscopic inclusions of the light phase (FCC2, which is obviously enriched in copper) with a mean size of 0.25 μm were detected over the whole dark area.

With subsequent increase in the chromium content up to 3 mole, according to the results of the X-ray diffraction analysis, only the content of these phases changes (Table 2). The electron microscopy data agree well with the results of the X-ray diffraction analysis. At a chromium concentration of 3 mole, four phases were clearly recorded in the microstructure. We think that dendrites of the BCC phase (dark gray), along the contour of which dark spots of the δ phase are located, are the first to crystallize, then dendrites of the FCC1 phase (light gray) crystallize, and the interdendritic space is filled by the FCC2 phase (light). Inclusions of the light phase (FCC2) were not detected in the body of dendrite (BCC). On the BCC and δ -phases, polishing-induced scratches were absent.

This radical change in the phase composition and structure depends on the chromium concentration in the MnFeCoNiCuCr_x alloys and is connected with the fact that its atoms in the melt realize three main functions: change the electron concentration of the melt (Table 2) and, hence, the phase composition [7]; cause liquation of copper because this pair of elements (Cr-Cu) has one of the highest enthalpies of mixing (Table 3) [8]; promote the formation of the δ -phase (Cr-Fe, Cr-Co, etc.), moreover, at high chromium concentrations, the formation of the δ -phase is thermodynamically more favorable than the formation of the BCC solid solution.

In the MnFeCoNiCu alloy with an electron concentration of 9 el/atom, we observe the formation of FCC phase (whose region of stability does not exceed 8.2 el/atom [6]). For the MnFeCoNiCuCr_{0.5} alloy, the electron concentration changes insignificantly (8.7 el/atom), but, as chromium atoms appear in the lattice, the Gibbs energy

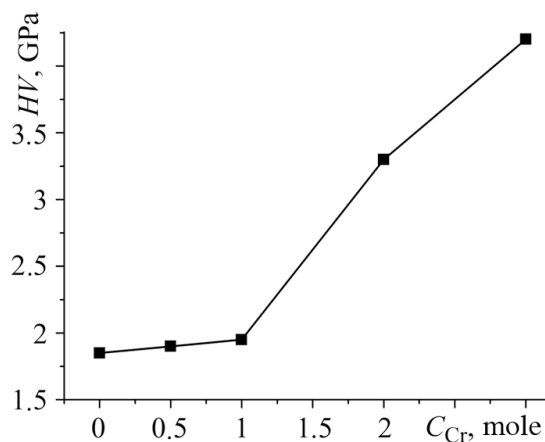


Fig. 3. Concentration dependence of the Vickers hardness for alloys of the MnFeCoNiCuCr_x system.

increases due to their closeness to copper atoms with a positive enthalpy of mixing, and thus, during crystallization of the high-entropy phase FCC1, the liquation of copper occurs, and the individual FCC2 phase is formed.

For the MnFeCoNiCuCr equiatomic composition, the above-mentioned trends are preserved because an electron concentration of 8.5 e/atom still promotes the stabilization of the FCC phase and the entropy of the alloy is maximum (Table 2). In the MnFeCoNiCuCr₂ alloy, the mean concentration is equal to 8.1 e/atom and this is already the region of simultaneous crystallization of the BCC and FCC phases [6]. Thus, the BCC phase crystallizes in the form of gray dendrites on whose surface we observe the precipitation of the γ -phase due to the partial liquation of chromium and the remaining part of the melt crystallizes with formation of the FCC1 and FCC2 phases. As the chromium concentration increases further, the phase composition remains invariable but the ratios of the phases undergo certain changes (Table 1). The presence of a large number of phases is explained by the sharp decrease in the entropy of the melt (Table 2).

It was also established (Fig. 3) that, in the initial stage of increase in the chromium content, the level of solid-solution hardening of the system gradually increases, as well as the level of hardness (within the range from 0 to 1.0 mole of chromium). For higher concentrations of chromium, the level of hardness abruptly increases as a result of precipitation of the BCC and γ -phases.

CONCLUSIONS

In alloys of the MnFeCoNiCuCr_x system, their phase composition changes as the chromium concentration increases, from a one-phase (FCC) composition into a four-phase (FCC1, FCC2, BCC, γ) composition. The formation of the BCC and γ -phases was recorded for chromium concentrations higher than the equiatomic concentration. The γ -phase precipitates along the contour of the BCC phase. The composition of the MnFeCoNiCuCr₂ alloy is characterized by the presence of finely divided inclusions of the interdendritic area (FCC2) in the body of the dendrite (BCC). The BCC and γ -phases have a much higher hardness than the FCC1 and FCC2 phases and, hence, cause an abrupt increase in the hardness of alloys.

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