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Effect of Nickel on the Structure and Phase Composition of the VCrMnFeCoNi_x High-Entropy Alloy

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Abstract—The effect of the nickel concentration on the phase composition, microstructure, and hardness of VCrMnFeCoNi_x ($x = 0–3$) high-entropy alloys has been studied. The structure of the cast system has been composed of fcc solid solution and σ -phase, and both phases are multicomponent. It has been found that an increase of the nickel concentration decreases the volume fraction of the σ -phase. As a result of the reduction of the amount of the solid σ -phase the microhardness of alloys has been detected to decrease from 12 GPa at $x = 0$ to 4.1 GPa at $x = 3$.

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Keywords: sigma phase, crystal structure, solid solution, microhardness.

1. INTRODUCTION

Recently publications concerning the thermodynamic approach to the development of multicomponent alloys appear in the home and foreign literatures [1, 2]. The essence of them lies in the fact that multicomponent alloy may be obtained as a single-phase substitutional solid solution, which by its nature is simultaneously of a higher strength and more thermodynamically stable than multiphase ones [3]. This is achieved due to a choice of such an amount of components and relationship among their concentrations, which ensure the increased mixing entropy (and according to the Gibbs equation, a decreased melt free energy) and retention of this state of the system not only in the melt state, but after crystallization as well. A decreased free energy of the alloy affords the stability of formed phases at subsequent mechanical and thermal treatment and further operations.

Thus, in particular systems of multicomponent high-entropy alloys (HEA) Fe–Co–Ni–Cr–Cu, Cu–Al–Co–Cr–Fe–Ni–Ti, Cu–Cr–Fe–Ni–Mn, Al–Co–Cr–Fe–Cu–Ni are characterized by increased hardness, wear resistance, and plasticity [4–7]. However, the majority of the structures of the above systems have interdendritic regions, which are highly enriched with copper. This is because of the high positive enthalpy of mixing ($\Delta H_{\text{mix}} \geq 3$ kJ/mol) between copper and other elements. In terms of thermodynamics it is disadvantageously for copper to enter the same lattice with the majority of elements of the Mendeleev periodic table (Cr, Fe, V, Mn, Co, W, Ni, Mo, Ta, Re), therefore, copper is pushed aside by the front of crystallization and later crystallizes in interdendritic regions. These regions enriched with copper have essentially lower hardness and melting temperature, and accordingly the heat resistance of the alloy decreases. Also this microstructure forms a local galvanic cell, which actively facilitates the development of corrosion [4]. To overcome these disadvantages, it was decided to develop a HEA system, which should have an increased hardness without an essential loss of plasticity and have no segregations. To attain this aim, we excluded from consideration elements that have positive mixing enthalpies with majority of metals (Cu, Ag, Sn), which were used in manufacturing HEA.

The bcc structure of HEA is known to be harder than the fcc structure but its plastic properties are much lower [8, 9]. HEA that contain intermetallics with the structure of the Laves phase (C14 and C15 types) and σ -phase (FeCr type) are hard but rather brittle.

The aim of the present study was to choose a system of elements and concentrations of them to produce HEA, whose matrix will be the fcc structure reinforced by a strengthening σ -phase, which will ensure a sufficient plasticity of the alloy. As the model system for investigation the VCrMnFeCo was chosen.

2. EXPERIMENTAL

The VCrMnFeCoNi_x (where $x = 0, 0.5, 1, 2, 3$ in molar ratios) high-entropy alloys were produced by vacuum-arc melting in a MIFI-9-3 modified furnace in a protective argon atmosphere. The initial materials were granules of metals of ~99% purity. The melt was cooled at a rate of ~80–100 K/s. From the samples obtained we prepared thin sections by a sequential grinding with a carborundum paper and polishing. The microstructure and chemical composition of alloys were analyzed using a Superprobe-733 (JEOL, Japan) and REM-1061 (Selmi joint-stock company, Ukraine) scanning electron microscopes. The REM-1061 microscope is equipped with a system of energy dispersive analysis (EDS). The phase composition was analyzed using an Ultima IV X-ray diffractometer (Ridaku, Japan) in a monochromatic CuK α radiation in the Bragg–Brentano geometry. As a monochromator a focusing graphite single crystal placed on a diffracted beam was used. A survey was performed by a step-by-step scanning over the $2\theta = 35\text{--}80^\circ$ angle range, the exposure time at a point was 3 s. The results obtained were analyzed using a PowderCell 2.4 software.

Mechanical characteristics of the material were defined by microindentation on a Micron-gamma device [10] with a Berkovich diamond pyramid having a re-sharpening angle of 65° under a load up to $F = 0.3$ N. The loading and unloading were performed automatically for 30 s. At the same time diagrams of loading, exposure, and unloading were recorded in the F – h coordinates. The device automatically calculates the material characteristics like hardness, H , and contact elastic modulus (Young modulus), E_{exp} , according to the ISO 14577-1:2002(E) standard.

3. RESULTS AND DISCUSSION

The authors of a number of papers [11–15] concerning studies of HEAs observed the formation of the σ -phase but did not explain the reason for its appearance. Besides, no paper mentions a HEA, which was 100% crystallized to form the structure of the σ -phase.

It has been established in our studies that the VCrMnFeCo alloy is single-phased with the σ -phase structure of the FeCr type. By analyzing this system, one may conclude that the necessary prerequisites to the formation of a high-entropy σ -phase are the following:

- each element of the alloy should form a σ -phase in a two-component system with any other element of the alloy (for this system the σ -phase is present in the following double diagrams Cr–Fe, Fe–V, Cr–Co, Cr–Mn, Mn–V, Co–V);

- the difference between atomic radii of the alloy elements (Table 1) should not exceed 6%.

Table 1. Atomic radii, number of valence electrons at an outer level, types of crystalline structures and Young moduli of elements that enter into the composition of the VCrMnFeCoNi_x HEA system [13]

Element	V	Cr	Mn	Fe	Co	Ni
R , nm	0.1314	0.1246	0.1300	0.1239	0.1250	0.1245
N , el/at	5	6	7	8	9	10
Structure	bcc	bcc	bcc	bcc	hcp	fcc
E , GPa	140	250	194	210	200	200

It is known that the σ -phase in two-component systems based on metals (compounds AlTa₂ and Co₂W₃) forms at mean electronic concentration within $C = 4.33\text{--}7.2$ el/at, ($C = \sum_{i=1}^n c_i N_i$, where n is the number of components of the alloy, c_i is the concentration of the i th element in at %, N_i is the number of valence electrons of the i th element), the fcc phase starts to form in HEA, which have $C \geq 7.2$ el/at [9]. The mean electronic concentration of the initial VCrMnFeCo alloy is 7.0 el/at (Table 2). Therefore, to increase the mean electronic concentration (and accordingly, a coexistence of the σ - and fcc phases), it was decided to add the element, which contained a large number of valence electrons in the outer level. Such an element is nickel, which contains in the outer level $N = 10$ el/at valence electrons (copper with $N = 11$ el/at, as it was mentioned above, we excluded because of its high liquation in the alloy).

Table 2. Mean electron concentration, phase composition and mechanical properties of VCrMnFeCoNi_x HEA

Alloy	Mean electronic concentration, el/at	Phase composition, at %		Mechanical properties		
		σ	fcc	Hardness, GPa	Young modulus, E_{exp}	Young modulus, E_{theor}
VCrMnFeCo	7	100	0	12 ± 0,5	145 ± 4.35	198.80
VCrMnFeCoNi _{0,5}	7.27	100	0	11 ± 0,5	148 ± 4.44	198.85
VCrMnFeCoNi	7.47	68	32	9.1 ± 0.5	140 ± 4.2	198.90
VCrMnFeCoNi _{1,5}	7.69	16	84	5.4 ± 0.3	134 ± 4.02	199.0
VCrMnFeCoNi ₂	7.85	0	100	3.6 ± 0,2	131 ± 3.93	199.10
VCrMnFeCoNi _{2,5}	7.99	0	100	3.7 ± 0,2	130 ± 3.90	199.20
VCrMnFeCoNi ₃	8.13	0	100	4.1 ± 0,3	144 ± 4.32	199.25

For a primary assessment of plastic properties after melting the samples were tested using a dynamic loading (hammer probe). The material ability for plastic deformation was visually assessed from the value of the impression. The VCrMnFeCo and VCrMnFeCoNi_{0,5} samples cleaved (the fracture was similar to that of the gray cast iron), impressions almost did not remain in the samples of VCrMnFeCoNi₁ and VCrMnFeCoNi_{1,5} alloys, the rest showed a high ability to plastic deformation. Grinding and polishing of VCrMnFeCoNi_x (where $x = 0, 0.5, 1, 1.5$) samples were rather complicated, after a long polishing the VCrMnFeCo and VCrMnFeCoNi_{0,5} alloys exhibited the mat surfaces. From alloys having $x \geq 2$ thin sections were produced without complications.

Figure 1 shows X-ray patterns of the VCrMnFeCoNi_x HEA system with various nickel contents. The phase compositions of this HEA changes essentially with an addition of nickel. With $x = 0$ and 0.5 the system completely crystallizes to form the structures of the σ -phase (of the FeCr type) with the lattice parameters $a = 0.8844$, $c = 0.4570$ and $a = 0.8853$, $c = 0.4582$, respectively. The c/a ratios for these structures are in the range of 0.517–0.518, which virtually coincides with the c/a ratio (~ 0.516) for a double and triple σ -phases. The coexistence of the σ -phase and fcc solid solution is observed in X-ray patterns of samples with $x = 1.0$ and $x = 1.5$ (see Fig. 1). The amount of the fcc solid solution in these samples is proportional to nickel content (see Table 2). According to the diffractometer experiment, at $x \geq 2$ the system crystallizes completely to form a solid solution with the fcc structure.

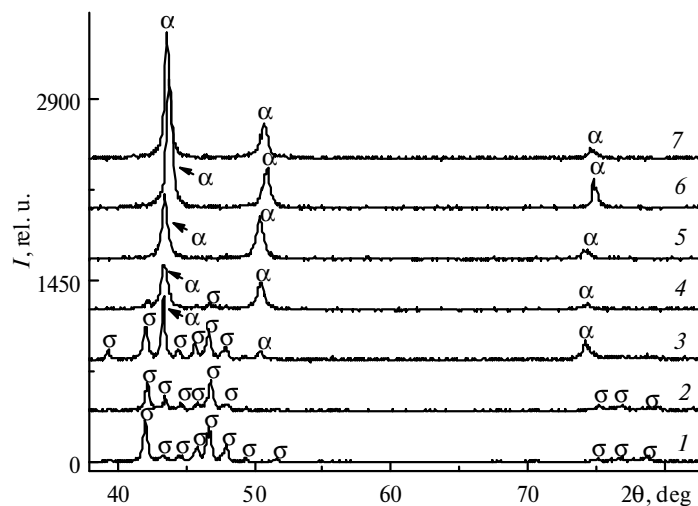


Fig. 1. Diffraction patterns of alloys of the VCrMnFeCoNi_x system depending on the Ni content: $x = 0$ (1), 0.5 (2), 1.0 (3), 1.5 (4), 2.0 (5), 2.5 (6), 3 (7) (CuK α monochromatic radiation): α is the fcc phase, σ is the σ -phase.

The kinetics of the variations of the weight ratio of phases in cast alloys of the VCrMnFeCoNi_x system is shown in Fig. 2. It is seen that in a change of the nickel content from $x = 0.5$ to $x = 2.0$ the amount of the σ -

phase decreases from 100% to zero. Then, just the range of the coexistence of the fcc and σ -phases is the most interesting for developing a material having the required plastic, strength, and wear resistant properties.

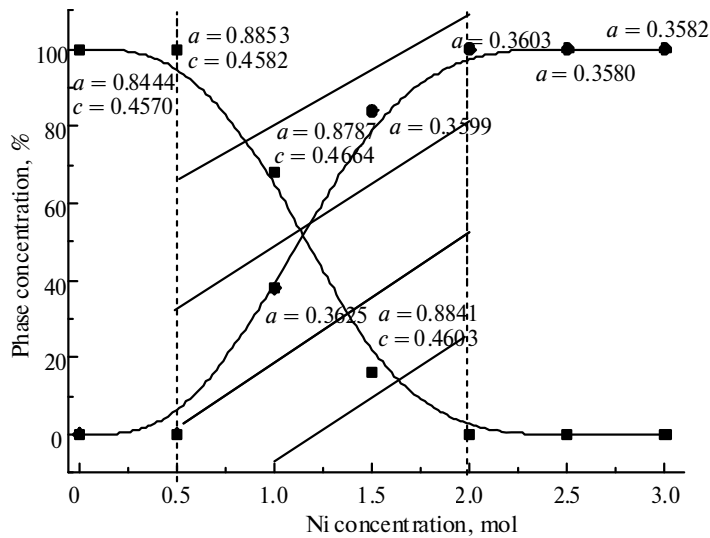


Fig. 2. Variations of the weight ratios of σ (■) and fcc (●) phases depending on the Ni content of cast alloys VCrMnFeCoNi_x (near the points the lattice constants of the phases are indicated in nm).

Figure 3 illustrates the microstructures of alloys with nickel content of 0–0.5 mol in a cast state. The VCrMnFeCo and VCrMnFeCoNi_{0.5} alloys have a usual crystallization patterns and have no dendritic structures, which are characteristic of casting. Although diffractometer analysis showed the formation of the σ -phase in these samples, no liquation and inhomogeneities are observed in the presented microstructures. This suggests that at these concentrations all elements of the alloys with the nickel content from 0 to 0.5 mol well dissolve in the σ -phase. At 300 \times magnification sites of chipping are well observed in these microstructures (as it was mentioned above, these samples are hard and brittle).

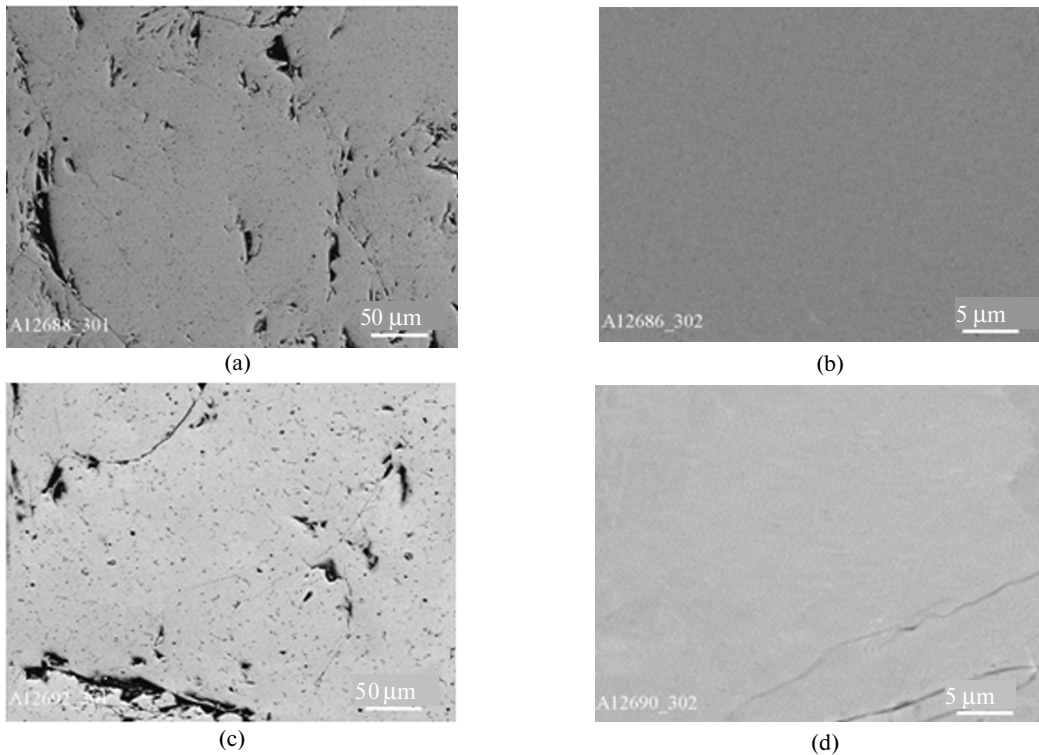


Fig. 3. Microstructures of the VCrMnFeCo (a, b), and VCrMnFeCoNi_{0.5} (c, d) alloys taken in reflected electrons; 300 \times (a, c), 3000 \times (b, d).

According to the X-ray diffraction analysis, the VCrMnFeCoNi alloy has two components. To define the nature of the distribution of elements between phases, we studied the alloy microstructure in an X-ray radiation. However, in any microstructure the difference between these phases is not seen (Fig. 4). The X-ray pattern showed that all elements are uniformly distributed in the thin section plane. An additional EDS analysis, which was carried out in different sites using the energy analyzer of the REM-1061 microscope, confirmed the aforesaid, i.e., sample is uniform over the whole plane of the section and its chemical composition corresponds to the declared. The solid solution with the fcc structure and σ -phase have different crystalline structures. Despite this fact, atoms of all elements of this alloy in a cast state are uniformly distributed among lattices of these structures. In the microstructure of VCrMnFeCoNi_{1.5} (Fig. 5) a barely perceptible contrast appears between liberations of the σ -phase and matrix, which is associated with a solid solution having the fcc structure. The liberations of the σ -phase are uniformly distributed in the alloy matrix and their mean diameter is about 5 nm. These structures are characteristic for wear-resistant materials. The EDS analysis showed that the σ -phase is somewhat enriched with Cr, while the fcc solid solution is enriched with nickel (Table 3). This verifies our assumption that it is just nickel due to a great number of electrons at the outer level contributes to the formation of fcc solid solution in this system. At the grain boundaries black inclusions are seen. As the EDS analysis did not reveal the difference between these inclusions and matrix in the chemical composition, therefore, these inclusions are probably pores. Microstructures of all following samples are uniform and equal (Fig. 6).

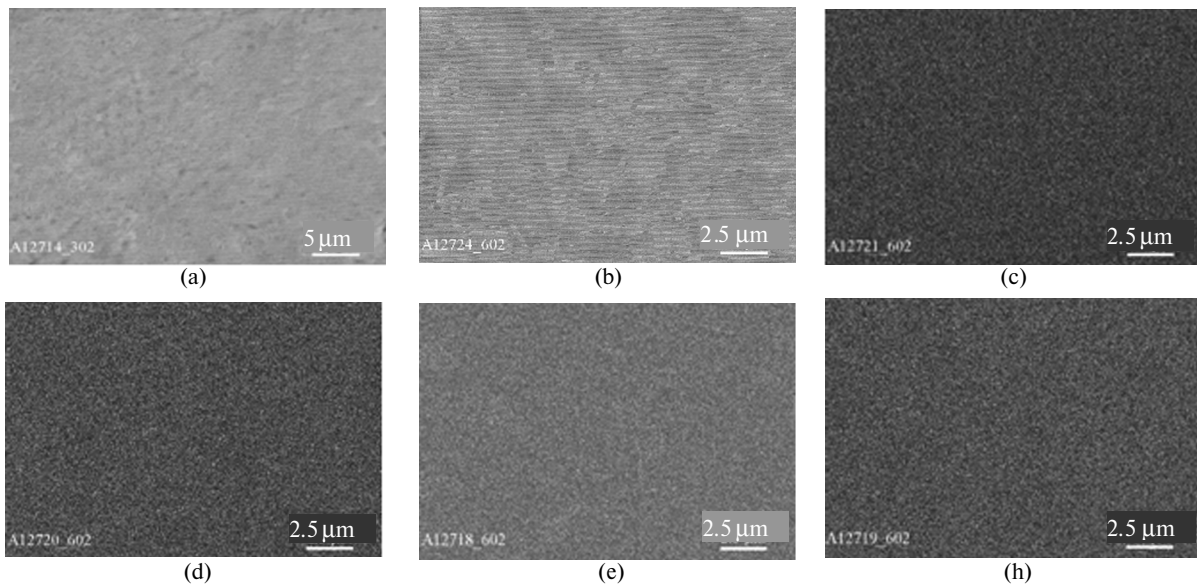


Fig. 4. Structures of the VCrMnFeCoNi₁ cast alloy in reflected electrons (a, b) and in the characteristic radiation Co (c), Cr (d), Ni (e), Mn (h), 3000× (a), 6000× (b–h).

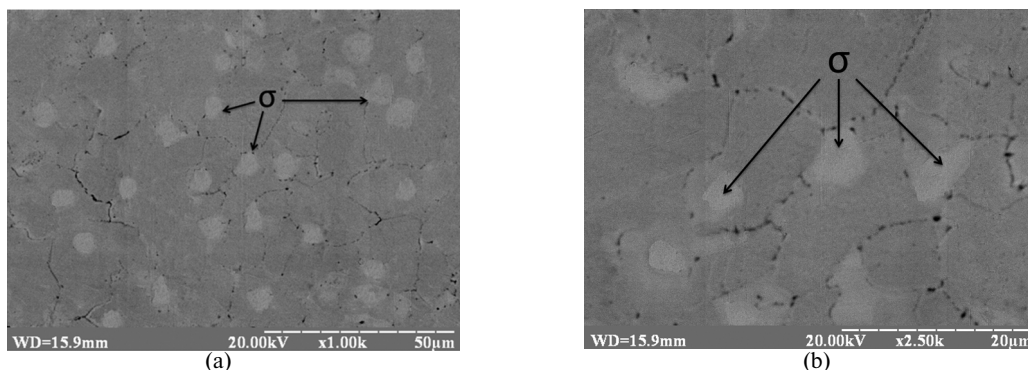


Fig. 5. Microstructures of the VCrMnFeCoNi_{1.5} alloy in the cast state taken in reflected electrons, 1000× (a), 2500× (b).

Values of the microhardness, H , and Young modulus, E_{exp} , of the studied alloys over the whole range of variations of the nickel concentration are presented in Fig. 7. The microhardness decreases as the nickel content increases up to $x = 2$, and then remains almost constant at $\sim 3.5\text{--}4$ GPa. Variation of the experimental

Young modulus is not monotonic and has maximum and minimum at nickel concentrations 0.5 and 2.5 mol. It is worth to note a large (about by a factor of 1.5) difference between experimental value of the Young modulus, E_{exp} , and theoretical, E_{theor} (see Table 2), calculated using the mixture law (Vegard law)

$$E_{\text{theor}} = \sum_{i=1}^n c_i N_i, \text{ where } n \text{ is the number of elements, } c_i \text{ is the concentration of the } i\text{th element in at } \%, E_i \text{ is}$$

the Young modulus of the i th element.

Table 3. Elemental composition of the VCrMnFeCoNi_{1.5} sample and EDS analysis of its phases

Elements	Elemental composition of the mixture	Phase composition, at %	
		fcc	s
V	15.4	14.1	14
Cr	15.4	15	21
Mn	15.4	15	15,8
Fe	15.4	15	15
Co	15.4	15.9	15.2
Ni	23	25	19

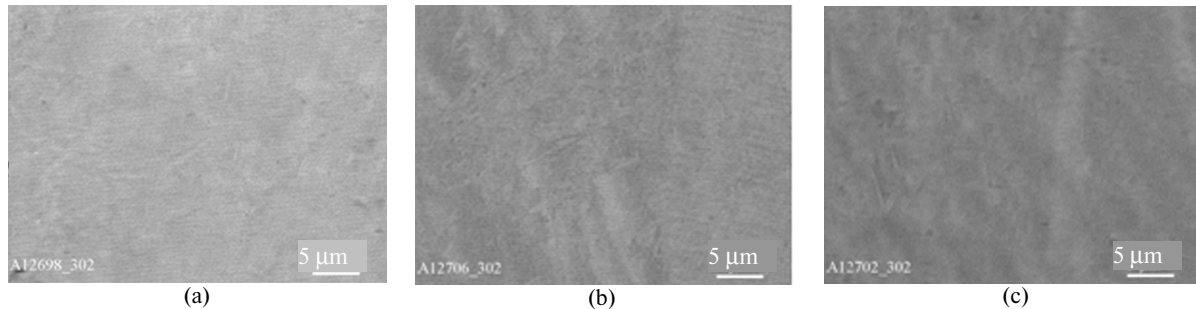


Fig. 6. Microstructures of the VCrMnFeCoNi₂ (a), VCrMnFeCoNi_{2.5} (b), and VCrMnFeCoNi₃ (c) alloys taken in reflected electrons, 3000 \times .

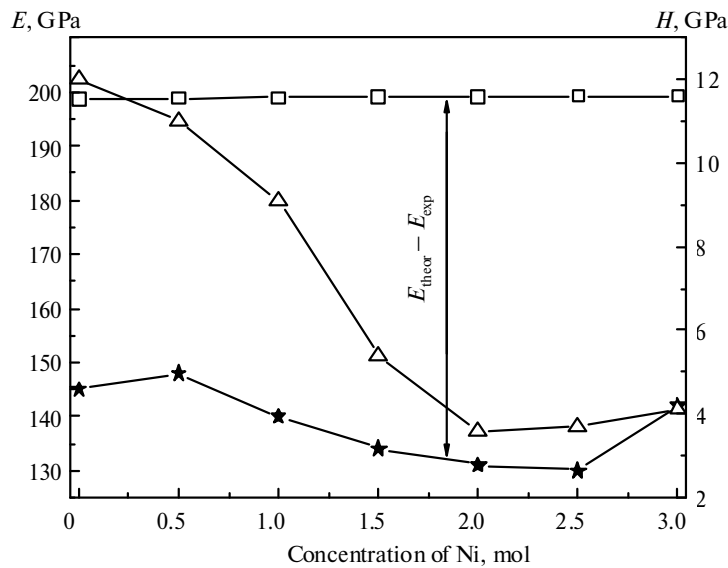


Fig. 7. Concentration dependence of microhardness, H , (1) and Young modulus, E_{exp} (2), E_{theor} (3) for VCrMnFeCoNi_x alloys.

4. CONCLUSIONS

Nickel that has been introduced into the VCrMnFeCoNi_x system in the amount of 0.5 mol enters the crystalline lattice of the σ -phase and in this case the alloy hardness somewhat decreases and Young modulus increases. With further increase of the nickel content the VCrMnFeCoNi_x system benefits more in terms of energy from crystallization with a simultaneous formation of the σ -phase and solid solution having the fcc structure. In this case a composite material is formed with a plastic matrix (the phase with the fcc structure) and hard reinforcing substance (σ -phase), which is uniformly distributed over the matrix volume.

By varying the nickel content of the VCrMnFeCoNi_x system one may achieve any relation between the matrix and reinforcing phase, which will make it possible to choose the optimal combination of properties and wear resistance for the predetermined conditions. In this case all phases of the VCrMnFeCoNi_x system are chemically homogeneous, each element enters the composition of the matrix and reinforcing phase, which ensures a high heat resistance and corrosion stability of the alloy.

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