Journal of Materials Science and Chemical Engineering, 2023, 11, 135-141
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

# On the Influence of High Pressures and Boron Nitride on the Processes of Structure Formation and Microhardness of a High-Entropy Equiatomic Composition AlNiCoFeCr Alloy

**Menshikova Svetlana**

The Udmurt Federal Research Center of the Ural Branch of RAS, Izhevsk, Russia
Email: svetlmensh@udman.ru

**How to cite this paper:** Svetlana, M. (2023) On the Influence of High Pressures and Boron Nitride on the Processes of Structure Formation and Microhardness of a High-Entropy Equiatomic Composition AlNiCoFeCr Alloy. *Journal of Materials Science and Chemical Engineering*, **11**, 135-141.
https://doi.org/10.4236/msce.2023.118009

**Received:** August 8, 2023
**Accepted:** August 28, 2023
**Published:** August 31, 2023

## Abstract

The structure of equiatomic high-entropy AlNiCoFeCr alloy obtained by arc melting was investigated. The influence of high pressures (5, 8 and 11 GPa), quenching temperature (1650˚C) and small additions of reinforcing agent-boron nitride (10% of the alloy volume) on the microstructure and microhardness of the alloy after quenching was studied. Depending on the conditions of thermobaric action, structures based on solid solution of the B2 type or mixed phases with structures of the Al, A2 or B2 types are formed in the AlNiCoFeCr alloy, which influences the alloy microhardness that varies in the range of 5 - 12.5 GPa.

## Keywords

Melt, Pressure, Microstructure, Microhardness, Phase

## 1. Introduction

The alloys of the Al-Ni-Co-Fe-Cr system are dispersion-strengthened composites and refer to high-entropic alloys (HEAs). HEAs contain five or more elements; the amount of each element should not exceed 35 at.% and should not be less than 5 at.% [1] [2]. HEAs belong to a special group of alloys because the processes of the structure and phase formation in them, the diffusion mobility of atoms, the mechanism of the mechanical properties formation and thermal stability essentially differ from similar processes in conventional alloys. In contrast

to conventional multi-component alloys, such alloys are characterized by higher values of entropy of mixing. Additions of various chemical compounds, such as carbides, nitrides, borides or oxides having high values of strength, hardness and high chemical stability, are used for strengthening materials. This takes place due to the creation of barriers preventing dislocation displacement similar to that in precipitation-hardened metal alloys. At present, the most commonly used technology for obtaining a dispersion-strengthened composite is powder metallurgy. The main technological processes are the preparation of powder mixtures, powder pressing with subsequent sintering and plastic deformation of the prepared mass. During plastic deformation, the density of a composite increases and its porosity decreases. In composites reinforced by particles of more than 1 mm in size, the most optimal content of the particles is in the range of 20% - 25% (throughout the volume) while dispersion-strengthened composites contain from 1% to 15% (throughout the volume) of particles of sizes in the range of 0.01 - 0.1 mm. The sizes of the particles in the composition of nanocomposites (new class of nanocomposites) are even smaller, in the range of about 10 - 100 nm. The material properties and structure can be changed by not only intensive plastic deformation but also by other extreme actions or their combination such as self-propagating high-temperature synthesis, high pressure and temperatures, etc. Extreme actions permit to obtain unique materials: polymers with high strength, new semiconducting materials, new stable crystalline structures with new unusual physical properties from well-known substances, new superconductors operating at room temperature, and many others.

In the present work, an equiatomic alloy AlNiCoFeCr was chosen as an object for investigation as one of typical model HEAs of this system and a promising alloy for application. Studies of the influence of high pressures on the formation of structures at quenching liquid alloys Al-Ni-Co-Fe-Cr and the influence of reinforcing agents, in particular boron nitride, on the alloy structure and properties are absent in the literature. Therefore, the present investigation is of importance.

## 2. Materials and Investigation Methods

An alloy of the equiatomic composition AlNiCoFeCr was produced in the atmosphere of high-purity argon by arc melting with a nonconsumable electrode from components with purity of 99.999%. To improve the chemical homogeneity, an ingot was remelted five times. The structure of the ingot was studied in the as-obtained state, after its melting and subsequent solidification under high pressure of 5 and 11 GPa. The samples were obtained in a high-pressure chamber of the "toroid" type [3] (**Figure 1**). As a pressure transmitter, catlinite was used. The sample, placed into a crucible from hexagonal boron nitride, was heated and melted by passing alternating current through it. The value of the temperature was calculated based on the indications of a thyristor with calibration according to the alternating current power. The melts were cooled at the

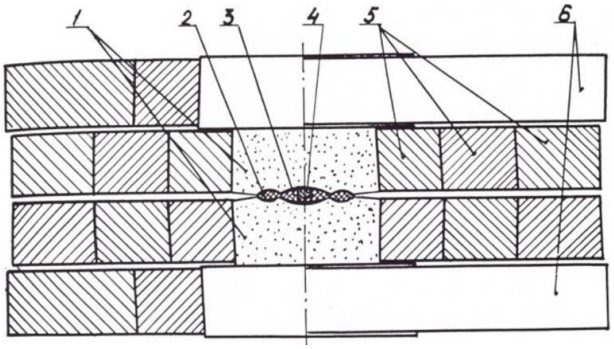


**Figure 1.** Chamber "toroid". 1—solid substance, 2—torus, 3—central part in the form of a lentil, 4—heater and sample, 5—steel rings, 6—support plate.

rate of 1000 deg/sec; the melt temperature before quenching was 1650˚C. The scheme of the experiment was as follows: pressure setting → pulse heating → holding at the set pressure and temperature-cooling to room temperature without pressure release-high pressure decrease to atmospheric pressure. The phase composition of the samples was determined by X-ray diffraction analysis on a device DRON-6 at $CoK_a$-monochromatic radiation. The investigation of the structure and the determination of the chemical and elemental composition, morphology and dimensions of the structural components of each sample were performed using a system Quatro S-scanning electron microscope (SEM) equipped with a standard detector DBS (direct backscattering) ABS/CBS. The error in the determination of the percentage content of elements in the samples was no more than 5%. Durametric measurements (Vickers hardness) were performed on a microhardness tester PMT-3M. A load of 100 g was applied on the indenter for a period of 10 s. The $H_v$ values were averaged over 20 measurements.

## 3. Results and Discussion

An initial ingot has a submicrocrystalline structure with the average grain size of 120 nm (**Figure 2(a)**). All the alloy elements are present in the grains and intergranular space, though, in different amounts (**Table 1**). The ingot has packing with components corresponding to the B2 structure based on the distorted bcc-lattice of nickel monoaluminide NiAl with the lattice period of 0.2870 - 0.2883 nm and the space group Pm3m (**Figure 3**).

In the sample obtained under the pressure of 5 GPa, the decomposition of the initial solid solution takes place; separate phases with different morphology and eutectic can be seen (**Figure 2(b)**). Initially, a phase of a regular geometric shape is formed, which are hexagons in the section in **Figure 2(b)** that are denoted by 1. The phase is rich in chromium (**Table 2**). After that the rest of phases and eutectic are formed. All the phases are multicomponent. As can be seen from **Table 2**, all elements of the alloy are present in the eutectic composition (denoted by 2 in **Figure 2(b)**). According to the X-ray diffraction analysis data, a mixed structure of two types: A1 type and A2 type is formed in the alloy (**Figure 3**). In

the chosen conditions of the investigation, the exact stoichiometric composition of all the phases cannot be determined. The analysis of the concentration maps of the element distribution for this sample shows that aluminum is distributed homogeneously, iron and cobalt-quasi-homogeneously and nickel and chromium-heterogeneously. Solidification under pressure of 8 GPa is preformed similarly. The X-ray diffraction patterns of the samples obtained under 5 and 8 GPa do not practically differ (**Figure 3**).

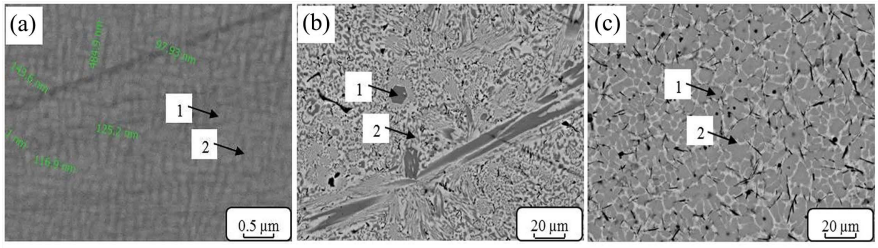


**Figure 2.** Microstructure of the initial ingot (a); the sample 1650˚C, 1000 deg/sec, 5 GPa (b) and the sample 1650˚C, 1000 deg/sec, 11 GPa with the addition of BN (c).

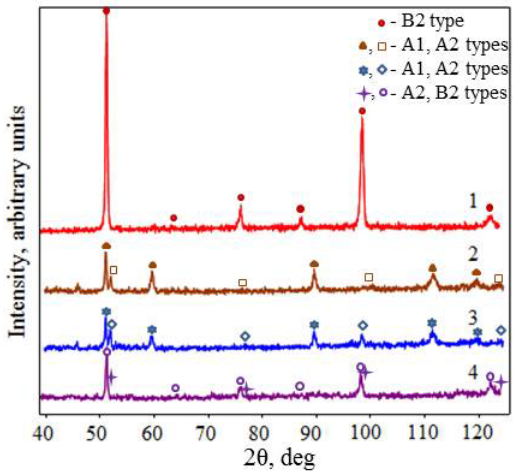


**Figure 3.** X-ray diffraction patterns of the samles alloy. 1—initial alloy, 2—alloy obtained under 5 GPa, 3—8 GPa, and 4—11 GPa.

**Table 1.** Elemental composition of the selected areas of the initial alloy.

| No. of area | Al, at.% | Ni, at.% | Co, at.% | Fe, at.% | Cr, at.% |
|---|---|---|---|---|---|
| 1 | 20 | 20 | 20 | 20 | 20 |
| 2 | 22 | 17 | 19 | 20 | 22 |

**Table 2.** Elemental composition of the selected areas of the alloy (1650˚C, 1000 deg/sec, 5 GPa).

| No. of area | Al, at.% | Ni, at.% | Co, at.% | Fe, at.% | Cr, at.% |
|---|---|---|---|---|---|
| 1 | - | 6 | 14 | 20 | 60 |
| 2 | 21 | 18 | 18 | 22 | 21 |

Then, the initial sample was ground to chips; a small amount (10% of the sample volume) of the powder of hexagonal boron nitride (BN)[1] [4] was added to the metal chips (**Figure 4**) and the mixture was blended. The mixture obtained was melted and cooled under pressure of 11 GPa according to the above-mentioned scheme. The microstructure of the obtained sample considerably differs from those considered above. In the structure, there are dendrites denoted by 1 in **Figure 2(c)**. In the interdendritic space (denoted by 2 in **Figure 2(c)**), mainly along the dendrite boundaries, a needle-like phase with branches and ball-shaped inclusions is located (shown in black color in **Figure 2(c)**). The elemental composition of the selected areas in **Figure 2(c)** is given in **Table 3**. As seen from **Table 3**, in the points chosen for analysis, practically all the alloy elements are present in different amounts. Dendrites are aluminum-rich, and in the interdendritic space, the amount of chromium is larger than that of other elements. As the investigations have shown, the needle-like phase of black color with inclusions represents aluminum nitride and boron. According to the X-ray diffraction data, a mixed structure consisting of A2 and B2 types (**Figure 3**) is formed in the sample. The analysis of the concentration maps of element distribution in the sample shows that in dendrites the elements are heterogeneously distributed.

**Figure 5** shows the microhardness of all the samples under study. From **Figure 5** it follows that the sample obtained under pressure of 11 GPa has the largest microhardness value 12.5 GPa. The average microhardness of this sample is 2.5 times higher than that of the initial sample, and almost 2.3 times higher than

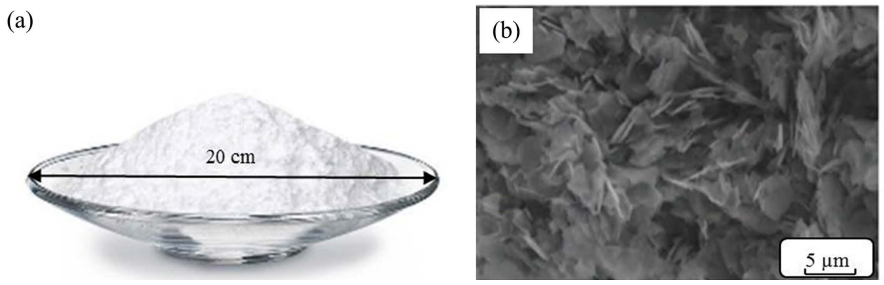


**Figure 4.** Boron nitride powder (a) and the powder particles (b).

**Table 3.** Elemental composition of the selected areas of the alloy (1650˚C, 100 deg/min, 11 GPa with BN addition).

| No. of area | Al, at.% | Ni, at.% | Co, at.% | Fe, at.% | Cr, at.% |
|---|---|---|---|---|---|
| 1 | 53 | 20 | 16 | 7 | 4 |
| 2 | 27 | 6 | 10 | 18 | 39 |

[1]Owing to chemical inertness and thermal stability, boron nitride is widely used in many branches of industry. Hexagonal (*α*)—h-BN form of boron nitride has the largest number of applications owing to low friction coefficient, electric conduction and thermal stability (the compound withstand temperatures up to 3000˚C). The material represents fine powder of pure white color resembling talc (**Figure 4(a)**); 90% of its particles are no more than 20 μm in diameter.

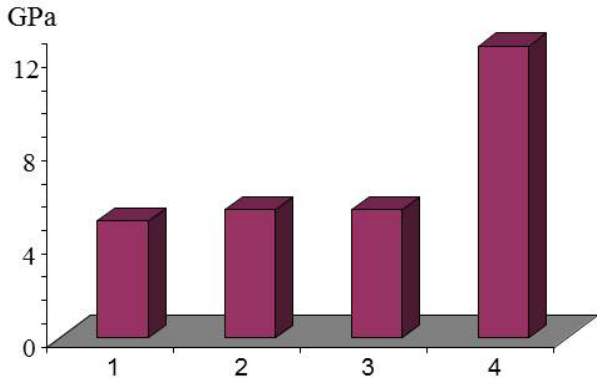


**Figure 5.** Microhardness of the samples: 1—initial, 2—5 GPa, 3—8 GPa, 4—11 GPa.

that of the samples obtained under pressure of 5 and 8 GPa. This is explained by the morphological features of the structure and the presence of reinforcing agents. In the studied alloy, under the action of high pressure and temperatures hexagonal boron nitride turns into hard aluminum nitride and boron [5].

## 4. Conclusions

Thus, the alloy of the AlNiCoFeCr can have a structure based on a solid solution, complex structure and mixed phases.

Depending on the composition, microstructure and corresponding properties, high-entropy alloys, for example, the alloy considered in the present work, have a great potential for the application as heat-resistant materials; coatings requiring high hardness and high wear-resistance; and corrosion-resistant materials with high strength. At present, many different HEAs have been studied. Despite the fact that some investigations are of purely scientific character and directed to the establishment of the regularities of the influence of different factors such as atomic size, enthalpy of solution, electron concentration, etc. on the properties of obtained HEAs, among the studied alloy there are materials that can compete with the best conventional alloys of special purpose in hardness, high-temperature strength, heat-resistance, corrosion resistance, wear-resistance and thermal stability.

## Acknowledgements

The work is performed within the framework of the Project of RNF (No. 22-22-00674). The electron-microscopic investigations were performed with the use of the equipment of the Center for Collective Usage "The Center of physical and physical-chemical methods of analysis, investigation of properties and surface characteristics, nanostructures, materials and items". UdmFITs UrO RAS, Izhevsk. The samples under high pressure were obtained in IFVD RAS, the city of Troitsk, Moscow Region. The author expresses her sincere appreciation to Doctor of Physics and Mathematics, Academician of RAS V. V. Brazhkin for his assistance in obtaining samples in the chamber of the type "toroid".

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

## References

[1] Yue, Su., Shuncun, L. and Zemin, W. (2020) Microstructure Evolution and Cracking Behaviors of Additively Manufactured $Al_xCrCuFeNi_2$ High Entropy Alloys via Selective Laser Melting. *Journal of Alloys and Compounds*, **842**, Article ID: 155823. https://doi.org/10.1016/j.jallcom.2020.155823

[2] Sistla, H.R., Newkirk, J.W. and Liou, F.F. (2015) Effect of Al/Ni Ratio, Heat Treatment on Phase Transformations and Microstructure of $Al_xFeCoCrNi_{2-x}$ (x = 0.3, 1) High Entropy Alloys. *Materials and Design*, **81**, 113-121. https://doi.org/10.1016/j.matdes.2015.05.027

[3] Brazhkin, V.V. (1987) Influence of High Pressure on the Solidification of Metal Melts (Pb, In, Cu, Copper-Based Binary Alloys). Ph.D. Thesis, MIPT, Moscow.

[4] Perevislov, S.N. (2019) Structure, Properties and Fields of Application of Graphite-Like Hexagonal Boron Nitride. *Novue Ogneupory*, **6**, 35-40. https://doi.org/10.17073/1683-4518-2019-6-35-40

[5] Kurdyumov, A.V., Malogolovets, V.G. and Novikov, N.V. (1994) Polymorphic Modifications of Carbon and Boron Nitride, Moscow, Metallurgiya.