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Mechanochemical synthesis of AlCoCrFeNi powders via high-energy ball milling

AlCoCrFeNi powders in equimolar ratios were synthesized by mechanochemical synthesis on a high-energy ball milling machine (HEBM). The elemental and phase composition of AlCoCrFeNi powders before and after mechanochemical synthesis were investigated by X-ray phase analysis and scanning electron microscopy with EDS analysis. A preliminary mathematical calculation of the physical parameter responsible for the phase stability of the solid solution valence electron concentration (VEC) showed that the fusion of this system should form the FCC phase. However, the result of XRD analysis showed that during the synthesis a solid solution with FCC and BCC phases was formed. The EDS mapping results of AlCoCrFeNi powders after HEBM showed a homogeneous distribution of elements without macro-segregation. The results presented in this work indicate the formation of a high-entropy alloy of AlCoCrFeNi system in a short time of mechanochemical synthesis. Continuous deformation, fracture and cold welding during mechanochemical synthesis leads to increased diffusion of elements and accounts for the formation of the HEA alloy.

Keywords: high-entropy alloy, mechanochemical synthesis, high-energy ball milling, phase analysis, elemental analysis, particle size distribution.

Introduction

During the last decades, the development of technologies in the field of new materials is moving towards the use of multi-element alloys. This class of metallic compounds is called high-entropy alloys (HEA). HEA consist of five or more elements in equiatomic ratios, where the composition of each element varies from 5 to 35 at. % [1]. The main difference of HEA is the formation of stable thermodynamically stable solid substitution solution mainly with FCC and/or BCC lattice [2]. HEA with a BCC lattice have predominantly high strength and low plasticity, while materials with a FCC lattice have low strength and high plasticity. However, this simple combination of solid solution phases is unlikely to provide the desired matching of strength and ductility without adjusting the phase composition and microstructure. Few literatures mention the effect of simultaneous biphasic (BCC + FCC) on material properties and sometimes the formation of solid solution with HCP lattice. It has been shown that dual phase HEA consisting of FCC and BCC phases are considered to be an effective way to balance strength and ductility.

Mechanical alloying is one of the most effective methods to obtain HEA [3, 4]. Varalakshmi S. and co-authors [5] were the first (2008) to obtain HEA of AlCrCuFeTiZn system exhibiting an BCC structure with crystallite size less than 10 nm using ball milling. Since then, ball milling has become one of the most popular methods to obtain HEA. However, a long mechanical alloying process (usually more than 60 h) is required to obtain HEA powder. It should be noted that many of the apparatuses used in mechanochemical synthesis are designed for milling of matter. HEA synthesis requires apparatuses that generate high energy stress, i.e., a large amount of energy that the working body transfers to the processed substance in the course of mechanical processing in the form of creating defects, to which solid-phase reactions are particularly sensitive. The advantage of using a high-energy ball milling machine for HEA synthesis is in its ability to produce bulk quantities of materials in solid state at room temperature in a short time. In addition, an important parameter in the mechanical synthesis of HEA is the change in temperature, which can determine the nature of the final powder product. If the temperature is high, the associated higher elasticity (higher atomic mobility of atoms) leads to processes leading to reduction (and recrystallization). In such a case, a stable phase is formed, for example, as an intermetallic phase. On the other hand, if the temperature is low, the recovery of defects will be less, and an amorphous (or nanocrystalline) phase is formed [6].

The aim of the present work is to investigate the mechanochemical synthesis of AlCoCrFeNi powders in a high-energy ball milling (HEBM) for 2 h under a controlled temperature regime of 23 °C - 33 °C. The

AlCoCrFeNi system is one of the most widely investigated HEBM systems due to its distinctive thermomechanical properties such as high compressive strength and hardness [7-11].

Experimental

Al, Co, Cr, Fe and Ni powders with purity of 99.7 % and particle sizes of 20-40 μm in equimolar portions were used as starting materials. Mechanical alloying of the powders was carried out in an Emax high-energy ball milling machine (Retsch, Germany) with water cooling for 2 hours at a temperature regime of 23 $^{\circ}\text{C}$ - 33 $^{\circ}\text{C}$. The acceleration of the balls was 1500 rpm. The mass ratio of the balls to the mass of the loading (powder) was 10:1. The powders were pre-mixed at a ball mill speed of 300 rpm for 15 minutes.

Phase analysis of the synthesized powders was carried out on an X'Per PRO diffractometer, using $\text{CuK}\alpha$ -radiation. The microstructure and elemental composition of the synthesized powders were investigated on a TESCAN MIRA3 scanning electron microscope. The particle size distribution of the powders before and after mechanical alloying was analyzed using a laser particle size analyzer (Winner 2005 A Laser Particle Size Analyzer).

Results and Discussion

To predict the formation of solid solutions in the AlCoCrFeNi system, we used the basic parameters of the HEA calculation [6] based on the Hume-Rothery rules, i.e., taking into account the composition-weighted terms for differences in atomic radii (δr) and average valence electron concentration (VEC), using data from Table.

The calculation formulas for the parameters are as follows:

$$\delta r = 100\% \sqrt{\sum c_i (1 - r_i/\bar{r})^2}, \quad (1)$$

where c_i – content (at. %) i - th element in the alloy, r_i – atomic radius of the i - th element in the alloy, $\bar{r} = \sum c_i r_i$ – average atomic radius of the alloy.

$$VEC = \sum_{i=1}^n c_i (VEC)_i, \quad (2)$$

where $(VEC)_i$ is a valence electron concentration.

Table

Properties of the elements under consideration [7]

Elements	Atomic number	Structure	Radius, pm	T_m , K	VEC	Pauling EN
Al	13	FCC	143.70	933	13	1.61
Co	27	FCC	125.10	1768	9	1.88
Cr	24	BCC	124.91	2180	6	1.66
Fe	26	BCC	124.12	1811	8	1.83
Ni	28	FCC	124.59	1728	10	1.91

The atomic size difference (δr) for our composition is 5.9 %, which is within the accepted range of $0 \leq \delta r \leq 8.5$ % [7]. $VEC = 9.2$ enters the range of $VEC \geq 8$, hence a single FCC phase is predicted [12].

X-ray diffraction patterns of equiatomic AlCoCrFeNi powder before and after mechanical alloying are presented in Figure 1. In the initial state (stirred for 15 minutes), diffraction lines corresponding to the elemental composition of AlCoCrFeNi powder are visible. According to X-ray phase analysis after 2 h HEBM, BCC and FCC phases are formed after 2 h HEBM. The diffraction peak of Al at $2\theta = 38.46^{\circ}$ disappears. The dissolution of Co and Ni in each other results in the formation of FCC phase. According to the results of [13-16] over 10 hours mechanical alloying at 200-300 rpm, the BCC phase prevails in the AlCoCrFeNi system. Also, in [14] it is reported that after 20 hours treatment B2 phase is formed and complete amorphization of the structure occurs at 84 hours treatment.

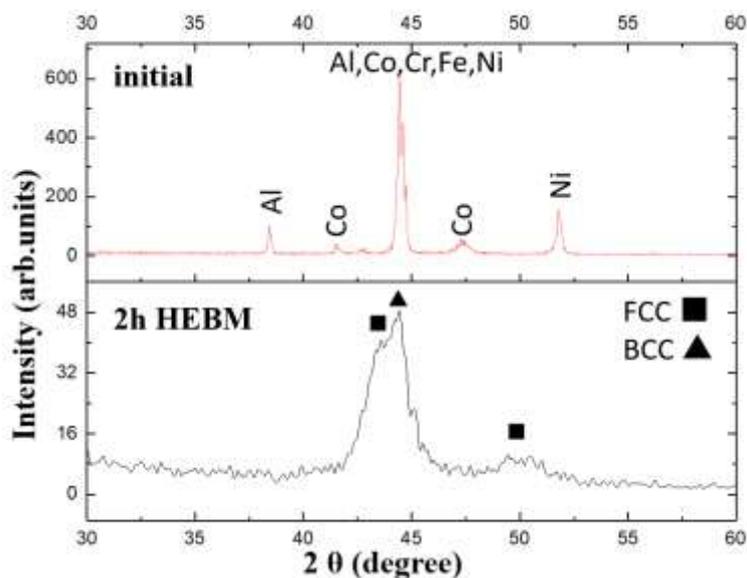


Figure 1. X-ray diffraction patterns of equiatomic AlCoCrFeNi powder before and after HEBM

The chemical composition of the powder before and after HEBM was analyzed by EDS mapping (Fig. 2). The EDS mapping results of AlCoCrFeNi powders after HEBM showed a homogeneous distribution of elements without macrosegregation (Fig. 3). This indicates that the initial powders have completely reacted with each other, and the BCC and FCC phases were successfully synthesized in the process. Probably, in the process of mechanical alloying, continuous deformation, fracture and cold-welding lead to increased diffusion of elements, which accounts for the formation of the HEA.

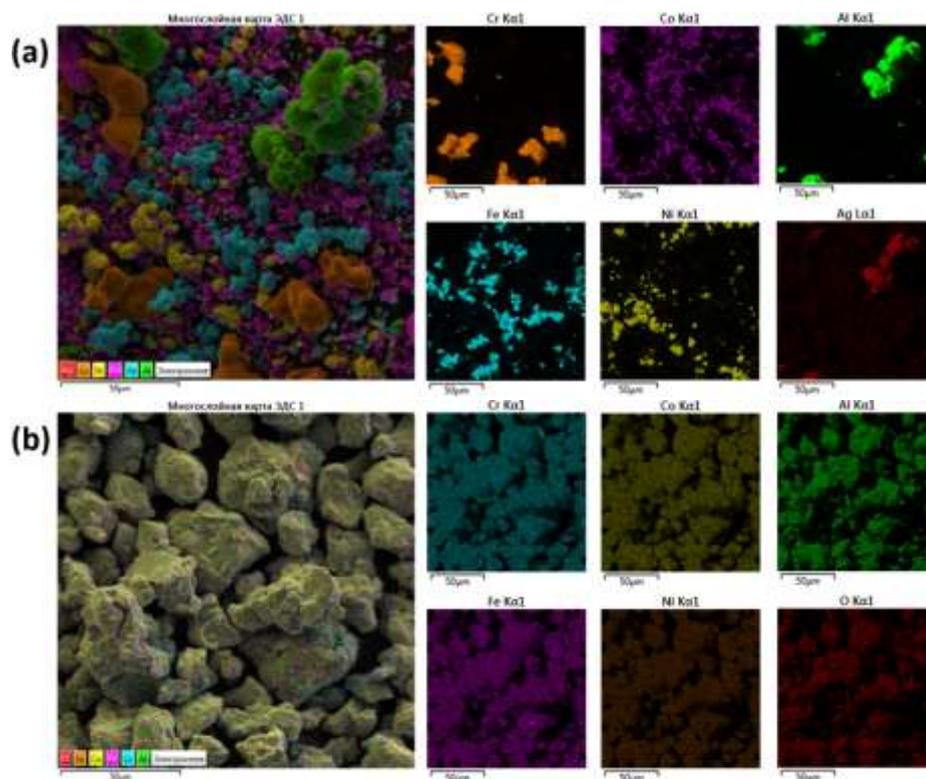


Figure 2. Elemental mapping results of AlCoCrFeNi powders (a) mixed state; (b) after HEBM for 2 hours.

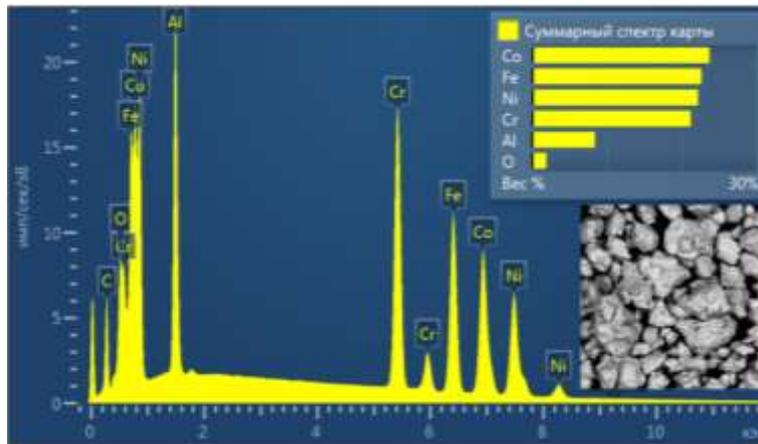


Figure 3. Total EDS spectrum mapping of AlCoCrFeNi powder after HEBM for a time of 2 hours

Figure 4 shows the results of the particle size distribution of the powders before and after HEBM. The initial powder size ranges from 13 μm to 36 μm , and after HEBM the powder size varies from 27 μm to 49 μm . The increase in the average particle size is due to the predominance of the agglomeration process over the fracture process. The particle size distribution data coincide with the results obtained using electron microscopy (Fig. 2).

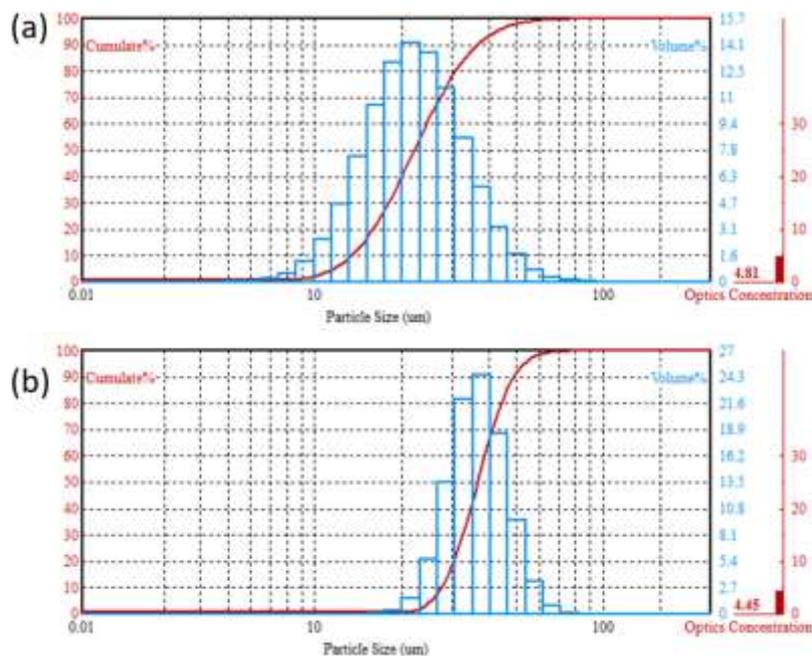


Figure 4. Particle size distribution of AlCoCrFeNi HEA particles (a) mixed state; (b) after HEBM for 2 h.

Conclusion

The elemental, phase and particle size distribution of AlCoCrFeNi powders before and after mechanochemical synthesis in a high-energy ball mill (HEBM) for 2 h under a controlled temperature regime of 23 $^{\circ}\text{C}$ - 33 $^{\circ}\text{C}$ were investigated. According to the results of XRD analysis, a solid solution with BCC and FCC structure is formed after mechanochemical synthesis. The formation of intermetallic and oxide compounds was not detected. EDS mapping results of AlCoCrFeNi powders after HEBM showed homogeneous distribution of elements without macro-segregation. The particle size distribution of the powder after HEBM ranged from 27 μm to 49 μm .

The conducted study is the first step in the development of a method for obtaining HEBM of the AlCoCrFeNi system mechanically activated in an Emax high-energy ball milling machine. The results presented

in this work indicate the possibility of synthesizing AlCoCrFeNi HEA in a short time of mechanochemical synthesis.

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Жоғары энергиялы шарлы диірменде AlCoCrFeNi ұнтақтарының механохимиялық синтезі

Эквимоллярлы катынастағы AlCoCrFeNi ұнтақтары жоғары энергетикалық шарлы диірменнің (ЖЭШД) көмегімен механохимиялық синтез арқылы синтезделді. Рентгендік фазалық талдау және ЭҚК талдауы бар сканерлеуші электронды микроскопия әдістерімен механохимиялық синтезге дейінгі және одан

кейінгі AlCoCrFeNi ұнтақтарының элементтік және фазалық құрамы зерттелді. Валенттік электрондар концентрациясындағы (ВКЭ) қатты ерітіндінің фазалық тұрақтылығына жауап беретін физикалық параметрге алдын-ала математикалық есеп жүргізілді, яғни бұл жүйе балқытылған кезде ЦҚТ (ГЦК) фазасының пайда болуы керек екенін көрсетті. Алайда рентгенфазалық талдау нәтижесі синтез кезінде ЦҚТ және КЦТ фазалары бар қатты ерітінді түзілгені берілген. ЖЭШД-ден кейін AlCoCrFeNi ұнтағын картаға түсіргенде EDS нәтижелері макро сегрегациясыз элементтердің біркелкі таралғанын көрсетті. Бұл жұмыста ұсынылған нәтижелерде механохимиялық синтездің қысқа уақытында AlCoCrFeNi жоғары энтропиялық қорытпа жүйесінің түзілгені айтылған. Механохимиялық синтез кезінде үздіксіз деформация, деструкция және суық дәнекерлеу элементтердің диффузиясының жоғарылауына және ЖЭҚ түзілуіне әкеледі.

Кілт сөздер: жоғары энтропиялық қорытпа, механохимиялық синтез, жоғары энергетикалық шарлы диірмен, фазалық талдау, элементтік талдау, гранулометриялық құрамы.

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Механохимический синтез порошков AlCoCrFeNi на высокоэнергетической шаровой мельнице

Порошки AlCoCrFeNi в эквимолярном соотношении были синтезированы методом механохимического синтеза на высокоэнергетической шаровой мельнице (ВЭШМ). Методами рентгенофазового анализа и сканирующей электронной микроскопии с ЭДС анализом были исследованы элементный и фазовый составы порошков AlCoCrFeNi до и после механохимического синтеза. Проведен предварительный математический расчет физического параметра, отвечающий за фазовую стабильность твердого раствора концентрации валентных электронов, который показал, что при сплавлении данной системы должна образоваться фаза ГЦК. Однако результат рентгенофазового анализа свидетельствует о том, что во время синтеза образовался твердый раствор с ГЦК и ОЦК фазами. Результаты EDS картирования порошков AlCoCrFeNi после ВЭШМ показали однородное распределение элементов без макросегрегации. Представленные в данной работе результаты свидетельствуют об образовании высокоэнтропийного сплава системы AlCoCrFeNi за короткое время механохимического синтеза. Непрерывная деформация, разрушение и холодная сварка при механохимическом синтезе приводят к повышению диффузии элементов и обуславливают образование сплава ВЭС.

Ключевые слова: высокоэнтропийный сплав, механохимический синтез, высокоэнергетическая шаровая мельница, фазовый и элементный анализ, гранулометрический состав.