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Low temperature elastic properties of $Al_{0.5}CoCrCuFeNi$ high-entropy alloy

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The independent c_{11}, c_{44}, and c_{12} elastic constants of $Al_{0.5}CoCrCuFeNi$ high-entropy alloy with the fcc structure were experimentally determined by the ultrasonic spectroscopy method in temperature region from 77 to 300 K. The results were obtained on samples with an axial [100] and [111] growth textures. Temperature changes in Young modulus, shear modulus, volume modulus, Poisson's ratio, Pugh's index and the elastic anisotropy factor were determined. The Pugh's index values are in the range between 1.26 (77 K) and 1.60 (300 K), which indicates the relatively low alloy ductility at low temperatures. Negative values of the Cauchy pressure $c_{12} - c_{44}$ are possibly caused by the influence of a relatively strong directed interatomic bond in a disordered solid solution, which is a high-entropy alloy.

Keywords: high-entropy alloy, elastic constants, elastic anisotropy, ultrasonic studies.

Низькотемпературні пружні властивості високоентропійного сплава $Al_{0.5}CoCrCuFeNi$. *О.С.Булатов, В.С.Клочко, А.В.Корнієць, І.В.Колодій, О.О.Кондратов, Т.М.Тихоновська*

Незалежні константи пружності c_{11}, c_{44} і c_{12} високоентропійного сплаву $Al_{0.5}CoCrCuFeNi$ з гранецентрованою кубічною структурою експериментально визначено ультразвуковою спектроскопією від 77 до 300 К. Результати отримано на зразках з аксіальною текстурою росту [100] і [111]. Визначено температурні зміни модулів Юнга (E), зсуву (G), об'ємного модуля (B), коефіцієнта Пуасона, індекса Пуха і фактора пружної анізотропії. Індекс Пуха має величину від 1.26 (77 К) до 1.60 (300 К), що припускає відносно низьку пластичність сплаву при низькій температурі. Від'ємне значення параметра Коши $c_{12}-c_{44}$ можливо обумовлене проявом відносно сильного направленого міжатомного зв'язку у невпорядкованому твердому розчині, яким є високоентропійний сплав.

Независимые константы упругости c_{11}, c_{44} и c_{12} высокоэнтропийного сплава $Al_{0.5}CoCrCuFeNi$ с гранецентрированной кубической структурой экспериментально определены ультразвуковой спектроскопией от 77 до 300 К. Результаты получены на образцах с аксиальной текстурой роста [100] и [111]. Определены температурные изменения модулей Юнга (E), сдвига (G), объемного модуля (B), коэффициента Пуассона, индекса Пуха и фактора упругой анизотропии. Индекс Пуха обладает величиной от 1.26 (77 К) до 1.60 (300 К), что предполагает относительно низкую пластичность сплава при низкой температуре. Отрицательные значения параметра Коши $c_{12} - c_{44}$, возможно, вызваны проявлением относительно сильной направленной межатомной связи в неупорядоченном твердом растворе, каким является высокоэнтропийный сплав.

1. Introduction

Multicomponent equiatomic high-entropy alloys (HEAs) containing five or more different elements attract special attention, since the concept of high mixing entropy opens new doors to the development of modern materials with unusual combinations of mechanical and functional characteristics that cannot be achieved by traditional microdoping on the basis of one dominant element. HEAs have excellent physical and chemical properties, such as high specific density and hardness, increased strength and ductility, wear, heat and corrosion resistance. The advantage of HEAs over conventional alloys, along with an abundance of possible stoichiometric compositions, allows not only the creation of unique structural and functional materials, but also makes it possible to discover their new properties. However, the potential of HEAs properties has not been fully disclosed.

Model cast alloys of $Al_xCoCrCuFeNi$ system (x = 0.25 – 6 mol) with a phase composition on the basis of simple fcc and bcc structures are the most studied among the high-entropy materials [1–10]. They demonstrated unique properties of HEAs.

In [11], using an example of the $Al_{0.5}CoCrCuFeNi$ composition, for the first time, the qualitative nature of the relationship between low-temperature (0.5 – 300 K) acoustic properties and structural state was observed. The results were obtained using the method of resonant mechanical spectroscopy at a bending vibration frequency of 310 Hz. The authors point to the heterogeneity of the dendritic microstructure due to the segregation of elements, but do not take into account the crystallographic texture, which is inevitably formed when creating alloy blanks by the argon-arc method with directed heat removal. Texture leads to anisotropy of properties, including elastic properties, which are some of the most important mechanical properties that reflect the nature of the internal bond forces in the crystal.

In this regard, it became necessary to study the low-temperature (between 77 and 300 K) properties of the $Al_{0.5}CoCrCuFeNi$ alloy, using the resource of pulsed ultrasonic technology, which includes high frequencies (50 MHz), orientation and polarization of ultrasonic waves.

2. Experimental

Multicomponent $Al_{0.5}CoCrCuFeNi$ alloy with the composition Al-4.46, Co-13.48, Cr-17.18, Cu-21.01, Fe-18.46, Ni-19.4 (wt.%) was obtained by alloying the elements (~ 99.9 % purity) on a water-cooled copper hearth in an arc furnace using a non-consumable tungsten electrode in an atmosphere of high-purity argon. The density of the alloy determined by hydrostatic weighing was 7.979 g/cm^3. Two rectangular samples 5.5×4×4 mm^3 in size were cut out by electrospark cutting from adjacent sections of the initial cast billet (7×7×30 mm^3). For acoustic measurements, plane-parallel faces oriented perpendicular HEA^{perp} and parallel HEA ^{parallel} to the direction of heat removal were ground. Metallography showed a coarse-grained dendritic structure consisting of a dendritic matrix and an interdendritic phase. The grain size was in the range of 10–20 microns. The morphology of the dendritic structure has a pronounced columnar character. The microhardness of the alloy was 2500 MPa (HEA^{perp}) and 2300 MPa (HEA^{parallel}). X-ray diffractometry showed the cast alloy with two fcc phases with lattice parameters a_{fcc1} = 0.3599 (dendritic matrix) and a_{fcc2} = 0.3594 ± 0.0005 nm (interdendritic phase). For both samples, the predominant orientation of the dendrites by the crystallographic axes [001] (HEA^{perp}) and [111] (HEA^{parallel}) is perpendicular and parallel to the direction of heat removal, respectively. Hereinafter, the designations of the samples are accepted as HEA$_{(001)}$ and HEA$_{(111)}$.

By the time of our measurements, the microstructure data for the alloy were obtained using a scanning electron microscope with an X-ray microanalyzer. The elemental compositions of the dendritic matrix and the interdendritic phase were found to be significantly different. The composition of dendrites is enriched in Fe, Cr and Co by more than 20 at.% of each element and depleted in Cu and Al by less than 10 at.%. The interdendritic regions are enriched in Cu up to ~ 65 at.% and practically do not contain (less than 4 at.%) Fe, Cr and Co. In addition, the Laves phase with an ordered B2 structure and a different element composition is present at the boundary between dendrites and interdendritic regions. Thus, the cast alloy $Al_{0.5}CoCrCuFeNi$ is formed inhomogeneously due to spinoidal decomposition.

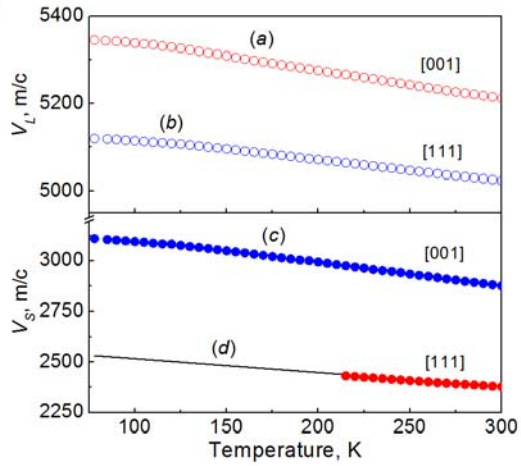

Fig. 1. Temperature dependences of the propagation velocity of longitudinal V_L and shear V_S ultrasonic waves at 50 MHz frequency in $HEA_{(001)}$ (*a*, *c*) and $HEA_{(111)}$ (*b*, *d*) samples.

Acoustic studies in the temperature range between 77 and 300 K were performed using the ultrasonic spectroscopy technique, which includes a phase-sensitive pulse bridge with frequency compensation. The relative error in the speed sound measurements was 10^{-6}. In this work, the excitation and detection of longitudinal (*L*) and shear (*S*) waves at 50 MHz frequency was carried out by broadband lithium niobate resonant piezoelectric transducers with 50±2 MHz intrinsic resonance frequency. The "piezoelectric transducer – sample" acoustic contact was created with silicone oil and honey. The studies were carried out in the heating mode at a rate of 40 K/h and a temperature step of 2 K.

3. Results and discussion

Fig. 1 shows the temperature dependences (77 – 300 K) of the propagation velocities of longitudinal V_L and shear V_S waves at 50 MHz frequency for $HEA_{(001)}$ (Fig. 1*a*, *c*) and $HEA_{(111)}$ (Fig. 1*b*, *d*) samples with the sound propagation vector oriented in [001] and [111] directions, respectively. When measuring $V_{S[111]}(T)$, an extremely small amplitude of the ultrasonic wave was noted (due to the scattering of sound on structural inhomogeneities) comparable to the wavelengths, which were observed in this sample according to electron microscopy data. At $T < 215$ K, the amplitude value became critical for further measurements due to a slight deterioration in the acoustic contact. The dependence $V_L(T)$ and $V_S(T)$ is represented by linear functions within the experimental error. It should be noted that the angular velocity dispersion $V_{S[001]}$ was not detected, which indicates a high degree of the axial texture perfection in the sample volume.

Table 1. Low temperature elastic properties of $Al_{0.5}CoCrCuFeNi$ high-entropy alloy

T, K	c_{11}, GPa	c_{44}, GPa	c_{12}, GPa	A_z
80	227.9	77.2	45.4	0.845
100	227.4	76.4	46.5	0.845
120	226.6	75.7	47.7	0.846
140	225.5	74.8	49.1	0.847
160	224.3	73.7	50.7	0.849
180	223.2	72.5	52.3	0.849
200	222.1	71.5	53.7	0.849
220	221.1	70.4	55.4	0.850
240	219.9	69.3	56.9	0.850
260	218.8	58.5	58.5	0.850
280	217.8	67.0	60.2	0.851
300	216.8	66.0	61.6	0.851

Based on the $V_L(T)$ and $V_S(T)$ data, an estimated calculation of the constants and moduli of elasticity of the alloy was carried out using the known relations for cubic crystals. The values of c_{11}, c_{44}, c_{12} independent elastic constants were calculated by the formulas:

$$c_{11} = \rho V^2_{L[001]}, \quad c_{44} = \rho V^2_{S[001]}$$

and

$$c_{11} + 2c_{12} + 4c_{44} = 3\rho V^2_{L[111]}.$$

The results are summarized in Table.

The elastic constants made it possible to determine the averaged polycrystalline B (bulk modulus), G (shear modulus), E (Young's modulus) elastic moduli and σ (Poisson's ratio) using the Voigt-Reuss-Hill approximation [12]:

$$B = \frac{B_V + B_R}{2}, \quad B_V = B_R = \frac{c_{11} + 2c_{12}}{3}$$

$$G = \frac{G_V + G_R}{2}, \quad G_V = \frac{c_{11} - c_{12} + 6c_{44}}{5}$$

$$G_R = \frac{5(c_{11} - c_{12})c_{44}}{4c_{44} + 3c_{11} - 3c_{12}},$$

$$E = \frac{9BG}{(3B + G)}, \quad \sigma = \frac{3B - 2G}{2(3B + G)}.$$

The subscripts "V" and "R" represent the Voigt and Reuss approximations, respectively.

Fig. 2 shows the temperature changes in the elastic moduli B, G, E and Poisson's ratio σ. As a rule, taking into account the elastic properties of a material, it is customary to discuss its plasticity. In this case, the Pugh's index B/G and the Cauchy pressure $c_{12} - c_{44}$ are used. This is due to the fact that the bulk modulus B and shear modulus G represent the total energy of the binding forces and the energy of shear dislocations. The parameter $c_{12} - c_{44} = CP$ is used to determine the angular character of the atomic bond in crystals. It is generally accepted that the critical value of the ratio $(B/G)^* \approx 1.75$ (or $\sigma^* \approx 0.26$, respectively) separates materials into plastic and brittle [13]. If $B/G >$ ($\sigma > 0.26$), the plastic behavior of the material is predicted, otherwise the material behaves rather rigidly. On the other hand, the parameter $c_{12} - c_{44} = CP$ reflects the nature of the bond forces in crystals. At $CP > 0$, the bond is metallic, and at $CP < 0$, the covalent bond predominates and, thus, responds to the elasticity of the solid.

From the temperature dependences of $B(T)$, $G(T)$ and $\sigma(T)$, it follows that Pugh's index B/G and Poisson's ratio σ have 1.26–1.60 and 0.16–0.22 ranges of values, respectively; they are well below the critical values of 1.75 and 0.26. This result unambiguously indicates that in the low-temperature region, this entropy alloy will not have acceptable ductility. This conclusion is also confirmed by the presence of a negative sign in the difference between the elastic constants $c_{12} - c_{44}$, which indicates a noticeable role of the more rigid interatomic covalent bond in the fcc alloy. Its formation is the result of overlapping of the valence electron shells of interacting atoms; and such overlap is possible only with a specific orientation of the electron shells, at the same time, the overlap region is located in a specific direction with respect to the interacting atoms.

Using the example of single-crystal elastic constants of high-entropy Cr–Mn–Fe–Ni and Mn–Fe–Co–Ni alloys with an fcc structure [14, 15], it was suggested that the elastic properties of HEA are similar to intermetallic compounds, although they are disordered solid solutions. Thus, it is possible that strong directed interatomic bonds dominate in high-entropy alloys.

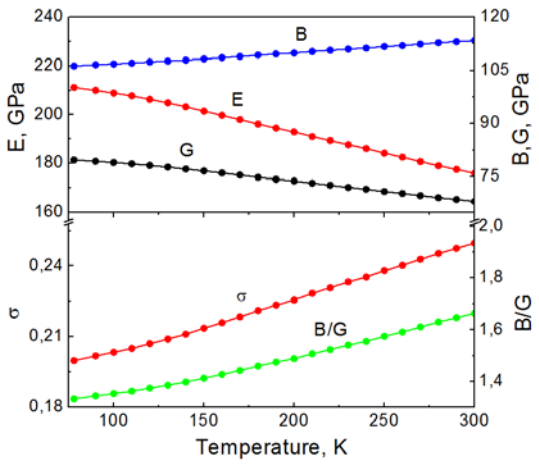

Fig. 2. Temperature dependences of Young's modulus (E), shear modulus (G), bulk modulus (B), Poisson's ratio (σ) and Puch's index (B/G) in the $Al_{0.5}CoCrCuFeNi$ high-entropy alloy.

4. Conclusions

The temperature dependence (77 to 300 K) of the longitudinal and shear sound velocity in the $Al_{0.5}CoCrCuFeNi$ alloy measured by the method of ultrasonic spectroscopy makes it possible to draw the following conclusions.

Temperature changes in the $c_{11}(T)$, $c_{44}(T)$ and $c_{12}(T)$ elastic constants and the Young's modulus, shear modulus, bulk modulus, Poisson's ratio and elastic anisotropy factor have been determined.

The Pugh's index was found to have the value from 1.26 (77 K) to 1.60 (300 K), which indicated a possible low ductility of the high-entropy alloy in the low-temperature region.

It is suggested that the negative values of the Cauchy parameter $c_{12} - c_{44}$ are due to the manifestation of a strong directed interatomic bond in a disordered solid solution of the $Al_{0.5}CoCrCuFeNi$ alloy.

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