# The influence of the phase and structural state on the low-temperature elastic properties of molybdenum-alloyed non-equiatomic high-entropy alloys of the Fe-Co-Ni-Cr system

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**Abstract.** The mechanical properties and microstructural evolution of a medium-entropy alloy $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$ (at%) in a low temperature range (including the record low temperatures region down to 0.5 K) were investigated. It has been established that low-temperature plastic deformation initiates martensitic phase transformations in this alloy, and the values of the dynamic modulus of elasticity correlate with the degree of phase transformations.

## Introduction

Over the past two decades, a new class of high-entropy alloys (HEAs) have been designed. Investigation of this materials has grown explosively [1–7]. Among these materials, face-centered cubic (fcc) HEAs stand out as they exhibit excellent mechanical properties at cryogenic temperatures owing to deformation-induced twinning [2, 8] and/or martensitic phase transformations [3, 4, 9]. Specifically, the ‘metastability engineering’ approach to martensitic transformations, whereby phase stability is controlled through chemical composition and deformation temperature, has been widely used [3, 4, 10]. To strengthen HEAs at cryogenic temperatures, Bae *et al.* [4] designed metastable ferrous HEAs ($Fe_x(CoNi)_{90-x}Cr_{10}$, x = 55-60 at%) with excellent strain hardening and tensile strength characteristics at low temperature owing to deformation-induced martensitic transformation from fcc to body-centered cubic (bcc) crystal structure. However, the yield strength of ferrous HEAs is relatively low because the initial microstructures of the alloys contain an fcc single phase [4]. The addition of molybdenum to ferrous HEAs enhances yield strength due to the precipitation strengthening by μ phase in the FCC matrix [6]. Therefore, the strategy of “*metastability engineering*” as applied to Mo-added ferrous HEAs appears very hopeful. It is expected to provide a favorable combination of high strain hardening with excellent yield strength and tensile strength at cryogenic temperatures.

Recent studies have shown that a some of non-equiatomic metastable high-entropy (HEA) and medium-entropy alloys (MEA) have a promising ratio of strength and ductility, especially at cryogenic temperatures [7]. Recently, a metastable nonequiatomic MEA $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$ was developed on the basis of iron and molybdenum additives (the indices correspond to the atomic concentration). In this MEA, a favorable combination of yield strength and ultimate strength is observed due to the action of phase martensitic transformations initiated by plastic deformation (DIMT) [6]. Previous works [6, 8, 9] have studied the structure of this MEA in detail, as well as the effect of plastic deformation at different temperatures on DIMT. It was found [8] that tensile-deformed $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$ alloy, due to DIMT from fcc to bcc structure, has excellent low-temperature mechanical properties. So, for example, at 4.2 K the yield strength is 1043 MPa, and the tensile strength is 1748 MPa, while maintaining high plasticity.

It is known that the elastic characteristics of a material are highly sensitive to various phase and structural changes. Therefore the aim of this work was to study the effect of DIMT on the elastic characteristics of the molybdenum doped alloy.

## Research methods, sample characteristics

In a wide range of temperatures, the acoustic and structural properties of a medium-entropy alloy with the nominal composition of components $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_{5}$ were investigated. Liquid 4He (T=4.2 K) and liquid nitrogen (T=77 K) were used to obtain cryogenic temperatures. Intermediate temperatures in the range of 4.2–77 K were obtained by cooling the samples with helium vapor.

Samples of $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_{5}$ alloy was obtained by the standard procedure described in [8]. To reduce the grain, the ingots were rolled at room temperature until the thickness was reduced by 79% (from 7 to 1.5 mm). The rolled sheets were annealed at a temperature of 900° C for 60 minutes, and then quenched in water.

Samples for further research were cut by electroerosion cutting from larger blanks in the direction of rolling, and then mechanically ground and polished with abrasive powders until the required shape and dimensions were achieved. After that, the alloy $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_{5}$ samples were mechanically deformed. Plastic deformation of the samples was carried out at temperatures of 77 K, 4.2 K, 2.1 K, and 0.5 K by uniaxial tension to fracture (a true strain was about of 30%) at a constant rate $10^{-4}$ $s^{-1}$. Next, samples for acoustic and structural studies were cut from the deformed samples. The test samples for acoustic investigations were cut by electric spark and reduced to the final size of $0.3\times4.4\times20.3$ $mm^3$ by mechanical polishing. After the elastic properties of the undeformed sample were studied, this sample was deformed by bending at a temperature of 77 K (a true strain was about of 10%) and its elastic properties were measured again.

The temperature dependences of the dynamic Young modulus $E$ were measured at temperatures of 80-280 K. The rate of change of the temperature was ≈1 K/min and the accuracy of the temperature measurements was ≈50 mK.

The elastic characteristics of the alloy were investigated in the temperature range of 80-280 K by mechanical resonance spectroscopy [10]. This method is based on the study of linear bending vibrations of a cantilever-fixed sample - a thin plate at small values of the acoustic deformation amplitude $\varepsilon_0 \approx 10^{-7}$. Forced flexural oscillations of sample with a frequency of $f_r = 530$ Hz in the amplitude independent deformation region were excited and detected electrostatically. A resonance occurs as the frequency $f$ of the external electrostatic driver force approaches the characteristic frequency $f_r$ of the mechanical oscillations of the sample. Then the elastic modulus $E$ of the cantilever mounted sample of given thickness $h$ and length $l$ depends on the experimentally measured resonance frequency $f_r$ of the mechanical oscillations of the test sample and is given by [10-12]:

$$E = 38.3\frac{f_r^2 \rho l^4}{h^2}, \quad (1)$$

where $\rho$ is the density of the sample and 38.3118 is a correction factor that depends on the shape of the sample and the Poisson coefficient (taken to be ≈ 0.3).

## Results and discussion

It was shown [6] that the structure of the annealed $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_{5}$ alloy in the undeformed state is fully recrystallized and randomly oriented. The inverse pole figure (IPF) map shows that the annealed alloy is fully recrystallized and randomly oriented. The average grain size of the annealed alloy is 3.82 ± 1.82 μm. The X-ray diffraction (XRD) pattern reveals that the annealed alloy comprises an fcc matrix with submicron μ precipitates. The backscattered electron

(BSE) image also shows that fine μ precipitates are dispersed in the matrix. The average size and the area fraction of the μ precipitates are 177.16±62.53 nm and 3.21±0.26%, respectively [8].

The phase composition of both undeformed and deformed samples was investigated. Phase images of electron backscatter diffraction (EBSD) for alloy deformed at cryogenic temperatures show that DIMT from fcc to hexagonal close packed (hcp) and bcc phase occurs. At true deformation of 10%, the fcc phase begins to transform in the hcp and bcc phase (see Fig. 1). With further deformation, DIMT continues and the proportion of bcc phase increases significantly, while the proportion of hcp phase remains below 10%. The deformation-induced martensitic transition of the fcc phase to bcc is almost complete with a true deformation of 30% at a temperature of 77 K, when the proportion of bcc phase is 98.2% (Table 1). Interestingly, the proportion of bcc at 30% strain decreased to 68.8% when the alloy deformed at 4.2 K, but increased to 80.3% and 87.7% when the strain temperature was reduced to 2.1 K and 0.5 K (see Table 1). The course of the temperature dependence of the dynamic Young's modulus of both undeformed and deformed samples coincides with the notions of the additive contribution of the phonon and electron components. An increase in temperature leads to a monotonic decrease in the dynamic modulus of elasticity by 8%.

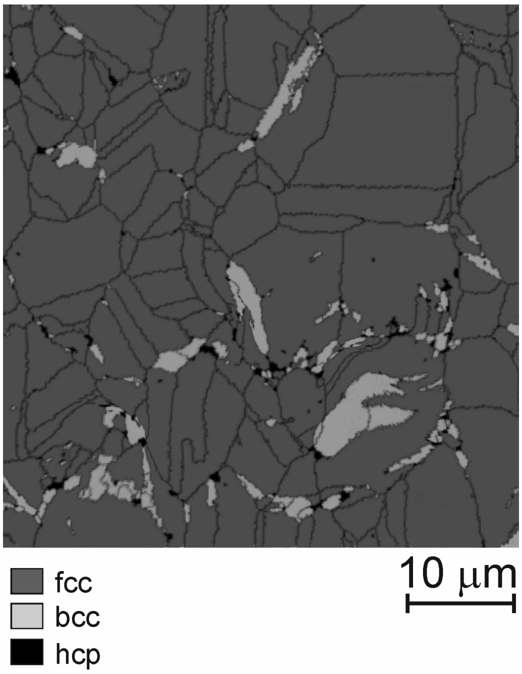


Fig. 1 EBSD phase map; bending deformation 10% at a temperature of 77 K.

Table 1. Dependence of the conversion rate of partial fcc – bcc DIMT on the deformation temperature: * - uniaxial tension to fracture, true strain 30%; ** - bending, true strain 10%.

| Deformation temperature, K | Part of the fcc phase, % | Part of the bcc phase, % | Part of the hcp phase, % |
|---|---|---|---|
| undeformed | 100.0 | 0 | 0 |
| 77.0** | 89.8 | 5.0 | 5.2 |
| 4.2* | 30.7 | 68.8 | 0.5 |
| 2.1* | 13.4 | 80.3 | 6.3 |
| 0.5* | 8.8 | 87.7 | 3.5 |
| 77.0* | 1.3 | 98.2 | 0.5 |

## Summary

The values of the dynamic modulus of elasticity in deformed samples of $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$ alloy differ from the undeformed state and correlate with the degree of DIMT (fraction of bcc phase) - increases linearly as the proportion of the bcc phase increases (see Fig. 2).

Thus, comparison of the two research methods confirms the effect of DIMT on the physical and mechanical properties of MEA $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$.

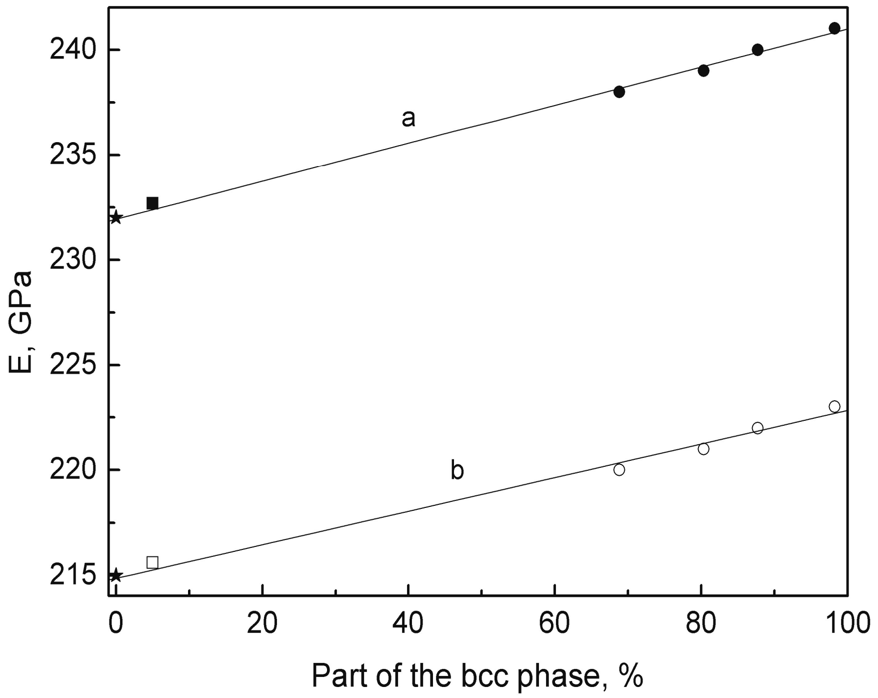


Fig. 2 Dependence of the dynamic Young's modulus $E$ of the $Co_{17.5}Cr_{12.5}Fe_{55}Ni_{10}Mo_5$ alloy on the part of the bcc phase (★ - undeformed sample; ●, ○ - uniaxial tension to fracture, true strain 30%; ■, □ - bending, true strain 10%): a) - dynamic Young's modulus $E$ at the 80 K; b) - dynamic Young's modulus $E$ at the 280 K.

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