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Improved mechanical performance of FeCoNiAlMn films through controlled annealing

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ABSTRACT

As soft magnetic materials continue to attract significant attention, investigating their mechanical properties has become increasingly important. In this study, FeCoNiAlMn alloys with varying elemental concentrations and annealing temperatures were examined to evaluate their mechanical behaviour. Alloys were fabricated using DC magnetron sputtering using three separate targets: FeCoNi, Al, and Mn under an argon atmosphere. All films had an approximate thickness of 600 nm. The alloys were investigated in the as-deposited state and after annealing at 400 °C, 600 °C, and 800 °C for 1 h. X-ray Photoelectron Spectroscopy (XPS) was employed to determine the elemental composition of each alloy, while X-ray Diffraction (XRD) analysis revealed variations in crystal structure associated with changes in elemental ratios and heat treatment conditions. The mechanical properties were evaluated using a nanoindenter. The FeCoNi_{0.8} alloy exhibited a significant improvement in hardness with increasing annealing temperature, reaching approximately 16 GPa when annealed 600 °C, about three times higher than its as-deposited value. In contrast, the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy showed a considerable reduction in hardness, decreasing from around 5 GPa for the as-deposited film to approximately 0.9 GPa after annealing at 600 °C.

1. Introduction

High-entropy alloys (HEAs) represent a novel strategy in metallic materials design. Since the pioneering works of Yeh and Cantor, who first articulated the principles of high-entropy and multi-component alloy systems, these materials have attracted significant scientific attention due to their exceptional structural and functional characteristics [1,2]. With carefully engineered compositions, the HEAs can exhibit outstanding performance across multiple domains, including high strength [3], superior ductility [4], and remarkable resistance to oxidation and irradiation [5]. Additionally, this versatility means that HEAs have exceptional potential for diverse applications, particularly in areas requiring superior mechanical performance [6,7], corrosion resistance [8,9], and high-temperature (refractory) stability [10]. Most HEA systems are predominantly composed of transition metals such as Co, Ni, Fe, Mn, and Cr, and are further tailored with additional elements, including Al, Cu, V, Ti, and Mo, to enhance their structural and functional properties [1,11–14]. In particular, the FeCoNiMnAl alloy system has recently gained attention as a promising candidate for structural and/or magnetic applications owing to its cost efficiency, excellent

corrosion resistance, favourable magnetic characteristics, and, most importantly, its tuneable mechanical properties achievable through microstructural optimisation [15,16].

Nevertheless, the limited mechanical strength of face-centred cubic (FCC) structured alloys remains a major drawback, constraining their practical applicability. The mechanical behaviour of metallic materials can generally be improved through mechanisms such as grain refinement, precipitation strengthening, solid-solution hardening, and the generation of high dislocation densities [17,18]. Numerous investigations have shown that oxide dispersion strengthening (ODS) offers an efficient approach to improving the mechanical performance of alloys by refining the grain structure and restricting dislocation mobility. [19]. Hadraba et al. [20] reported that the addition of 0.3 wt% oxide particles to CoCrFeNiMn resulted in a 50% reduction in grain size (from 0.8 µm to 0.4 µm). Consequently, the yield strength and ultimate tensile strength increased by approximately 30% at room temperature (from 971 to 1269 MPa and from 1010 to 1318 MPa, respectively), while at 800 °C they increased by about 75% and 68% (from 31.5 to 55 MPa and from 40.5 to 68 MPa, respectively). Du et al. [21] reported that the room-temperature mechanical properties of (CoCrFeNi)_{100-x}Gd_x HEAs

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were significantly enhanced through several strengthening mechanisms, including grain refinement, solid-solution strengthening, and second-phase strengthening. Among these, grain refinement was identified as the dominant factor, while the alloy still retained good plasticity. In particular, the Gd3-alloy achieved a yield strength of up to 650 MPa, which is nearly three times higher than that of the CoCrFeNi HEA (235 MPa), while maintaining a fracture strain of 36.4%. Tekin et al. [22] reported that when high-energy mechanical alloying was employed to synthesize Y-additions to (1 and 4 at.%) CoCrFeNi HEAs, the resulting hardness increased progressively from 3.45 GPa for the base HEA to 4.18 GPa for the 1Y-alloy and 4.38 GPa for the 4Y-alloy, thus confirming the strengthening effect of Y addition. Also, Tekin et al. [23] reported that Y_2O_3 -reinforced CoCrFeNi multicomponent HEA exhibited a marked hardness increase, from 371 ± 13 HV_{0.5} in the unreinforced alloy to 592 ± 20 HV_{0.5} and 685 ± 30 HV_{0.5} with 1 wt% and 4 wt% Y_2O_3 additions, respectively. Le Minh Duc et al. [16] report that a single-phase FCC structure was observed in the as-cast condition of FeCoNiAl_{0.25}Mn_{0.75}. During annealing at 700 and 800 °C, a fine needle-shaped body-centred cubic (BCC) phase precipitated within the FCC matrix, resulting in a pronounced improvement in mechanical performance. Specifically, heat treatment at 700 °C for 24 h increased the hardness from 1.34 GPa to 1.90 GPa, while the yield strength and ultimate tensile strength increased by 64% and 61%, respectively. Also, when the Al_{0.5}CoCrFeNi alloy was processed at elevated temperatures, this induces a gradual transformation from a stable FCC structure to a BCC structure, thereby resulting in an increase in hardness [24].

Although related FeCoNi-based alloy systems have been previously reported, limited studies have addressed the effect of heat treatment on their mechanical properties, particularly in thin-film form. In the present work, FeCoNi and FeCoNiAlMn films with different elemental compositions and annealing temperatures were systematically investigated to clarify the combined influence of alloying and annealing on their structural evolution and mechanical response.

The selected annealing temperatures were guided by previous studies on related alloy systems [25–27], in which similar temperature ranges were used to investigate annealing-induced property changes and yielded promising results. In the present study, the same temperature range was adopted to assess its influence on the structural and mechanical behaviour of the films. The annealing duration of 1 h was selected considering the thin-film nature of the samples, where shorter diffusion distances and faster structural response can make shorter annealing times sufficient to induce measurable changes.

2. Experimental procedures

In this work, three series of alloys were fabricated at room temperature using a direct current (DC) magnetron sputtering system equipped with three separate targets: FeCoNi, Al, and Mn. The alloys were grown on oxidized silicon substrates with a (100) crystallographic orientation, each cut to dimensions of 1 cm × 1 cm. Before deposition, the substrates were ultrasonically cleaned in acetone and isopropanol for approximately 10 min and subsequently dried under nitrogen gas. The sputter chamber was evacuated to a base pressure in the low 10^{-7} Torr range before deposition, and the working Ar pressure during sputtering was maintained at 5×10^{-3} Torr.

Three sputtering targets were utilised: a ternary FeCoNi alloy containing equal atomic ratios of Fe, Co, and Ni (33.3% each), high-purity aluminium (99.999%), and manganese with 99.9% purity. The first composition was only the FeCoNi target operating at 70 W. For the second and third compositions, the FeCoNi target was sputtered at 70 W together with the Al target at 30 W, while the Mn target was sputtered at 70 W for the second composition and at 105 W for the third composition. All alloys were deposited to a total thickness of approximately 600 nm. From each composition, four samples were prepared; one was kept as-deposited while the remaining three were annealed at 400 °C, 600 °C, and 800 °C, respectively, for 1 h. The annealing process was performed

under flowing Ar gas with a heating rate of 2 °C/min and followed by natural slow cooling inside the furnace.

The structural properties of the thin films were examined using X-ray diffraction (XRD). Measurements were conducted on a Bruker D2 Phaser diffractometer equipped with a Cu K α radiation source ($\lambda = 1.54184$ Å) operating at 40 kV and 40 mA. Conventional θ – 2θ geometry was employed, and diffraction scans were collected over the 25°–65° range with a step size of 0.020°, enabling analysis of the film structure while avoiding the intense Si substrate peak near 69°. To evaluate the chemical composition, X-ray photoelectron spectroscopy (XPS) analyses were carried out using a Kratos Supra instrument with a monochromated Al K α source (photon energy 1486.6 eV). Two analysis locations were selected on each film within a 700 $\mu\text{m} \times 300 \mu\text{m}$ area. Survey spectra were recorded between 0 and 1200 eV at a pass energy of 160 eV and a step size of 1 eV, with each scan acquired in a single 300-s sweep. Mechanical characterisation was performed using nanoindentation. A standard Berkovich diamond indenter (142°) was employed, with a tip Poisson's ratio of 0.07 and a tip modulus of 1.14×10^3 N mm^{−2}. Each sample was tested with a 10 × 10 indentation matrix (100 indents total) spaced 5 μm apart, and the target indentation depth was approximately 50 nm.

3. XPS and XRD results

Fig. 1(a) presents the X-ray photoelectron spectroscopy (XPS) spectra of Mn for the as-deposited alloys, illustrating an increase in peak intensity with increasing Mn content in the respective compositions. This trend is consistent with the increase in the Mn target power used during sputtering. From the XPS spectra, the elemental compositions of each alloy were quantified using CasaXPS software and are listed in Table 1.

Using these compositions, the thermodynamic prediction equations [28] can be used to predict the phases present in the films and whether the films will be solid-solutions. The average valence electron concentration (VEC) provides a prediction as to whether the alloys will be FCC (VEC >8) or BCC (VEC <6.87) or both FCC and BCC ($8 > \text{VEC} > 6.87$). For these FeCoNiMnAl films, it is predicted that the FeCoNi_{0.8} film will be FCC (VEC = 8.9), while both the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} films having VEC ~ 7, which means they are predicted to contain both BCC and FCC phases. This is due to the Al (VEC = 3) and Mn (VEC = 7) additions having smaller VECs compared to Fe, Ni and Co. Another thermodynamic parameter used to predict solid-solutions is the average enthalpy of mixing, ΔH , which if it is between −22 kJ/mol and 7.5 kJ/mol, the alloy is predicted to be a solid-solution. The FeCoNi_{0.8} film ΔH is −1.33 kJ/mol, while the two films with the addition of Mn and Al: Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} film $\Delta H = -14.3$ kJ/mol and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} film $\Delta H = -12.3$ kJ/mol. Thus all three films should be solid-solutions, with no intermetallics present.

Fig. 1(b) shows the XRD spectra of the FeCoNi_{0.8} films. For the as-deposited film, a single diffraction peak characteristic of the FCC structure appears at approximately 44° [14,29]. After annealing at 400 °C and 600 °C, this peak shifts due to the thermal treatment. At 400 °C, the diffraction peak shifts slightly to higher angles, indicating a reduction in the interplanar spacing d , as described by Bragg's law ($2d \sin \theta = n\lambda$). This behaviour can be attributed to lattice contraction resulting from stress relaxation and local atomic rearrangement within the metallic FCC structure. In contrast, at 600 °C, the peak moves to a lower angle, corresponding to a decrease in θ and consequently an

Table 1
Elemental Composition of the alloys determined by XPS.

Alloy	Co (at %)(± 4)	Fe (at %)(± 4)	Ni (at %)(± 4)	Mn (at %)(± 4)	Al (at %)(± 4)
FeCoNi _{0.8}	35.5	35.9	28.6	0	0
Fe _{1.3} CoNiAl _{1.5} Mn _{2.5}	13.5	17.6	13.9	34.5	20.5
Fe _{1.1} CoNiAl _{1.5} Mn _{5.4}	10	10.9	10.1	54	15

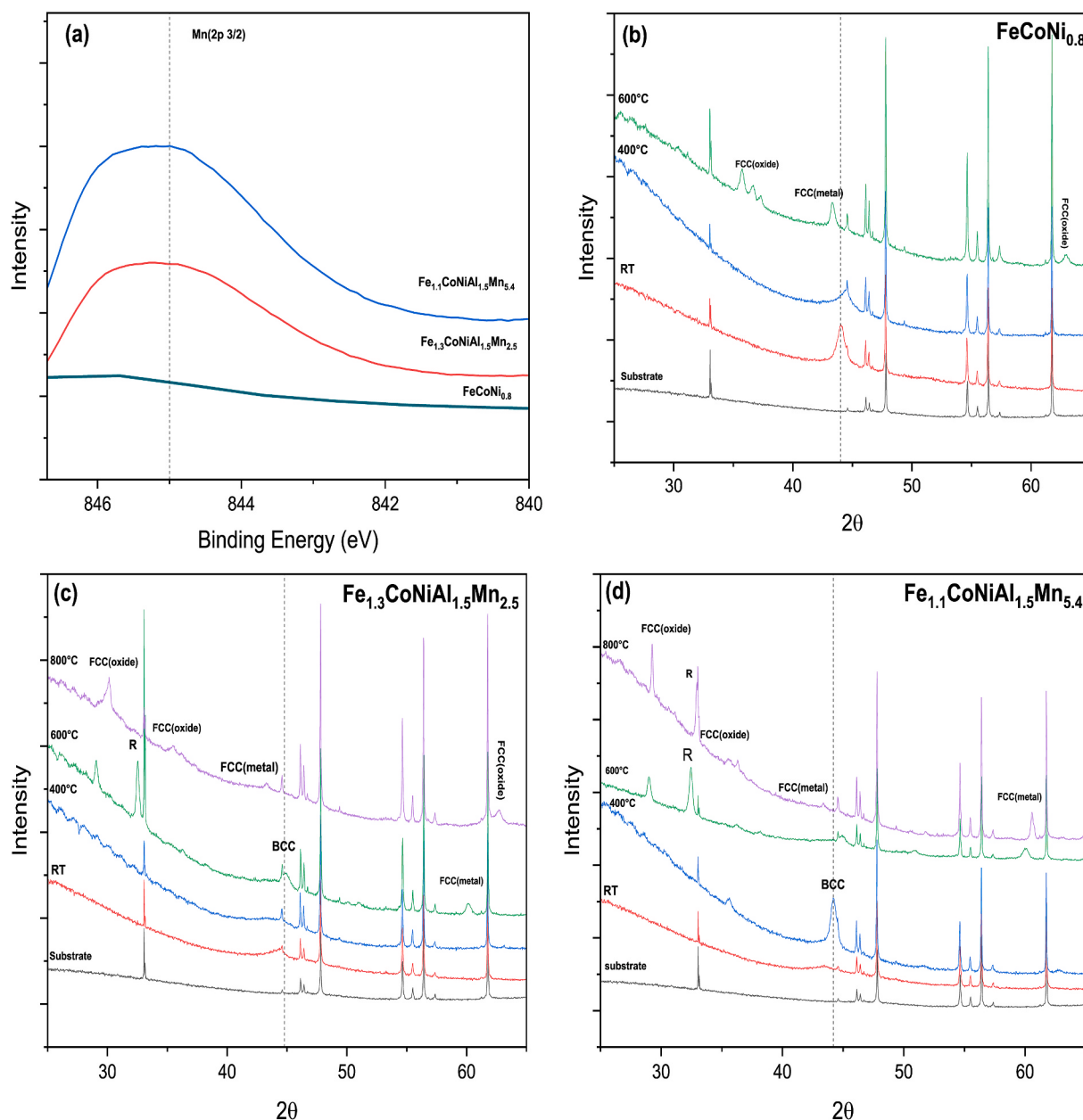


Fig. 1. (a) XPS spectra corresponding to the Mn (2p 1/2) for FeCoNi_{0.8}, Fe_{1.3}CoNiAl_{1.5}Mn_{2.5}, and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4}. (b), (c), and (d) X-ray diffraction (XRD) measurements for FeCoNi_{0.8}, Fe_{1.3}CoNiAl_{1.5}Mn_{2.5}, and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloys, respectively, at different annealing temperatures.

increase in *d*-spacing. This expansion is consistent with the appearance of additional FCC-type oxide reflections (FeCo-rich oxide and FeSi-rich oxide) [29] (PDF No. 04-026-0037), as FCC oxides generally possess slightly larger lattice spacings compared with the metallic FCC phase. Although the difference could also be due to element separation between the FCC-oxide phase and the metallic FCC phase, where the FCC-oxide is say Fe rich and the metallic FCC phase is say Ni or Co rich. Fig. 1(c) presents the XRD patterns of the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at different annealing temperatures. The as-deposited film exhibits body-centred cubic (BCC) reflection, which is expected due to the incorporation of Al and Mn into the FeCoNi and is also predicted to form from the average VEC calculations [30]. Upon annealing to 400 °C, the alloy retains its BCC structure. However, at 600 °C, the alloy evolves into a multi-phase structure. The BCC peak is still present; while additional peaks corresponding to FCC-type oxides emerge along with peaks associated with the trigonal phase of Fe₂O₃ (R). This demonstrates that oxidation becomes more significant at this temperature, driven by

enhanced atomic mobility that allows oxygen incorporation into the lattice. At the highest annealing temperature of 800 °C, the BCC peak completely disappears. The diffraction pattern becomes dominated by FCC oxide peaks together with FCC metallic reflections. Fig. 1(d) illustrates the XRD patterns of the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy. In the as-deposited state, the alloy exhibits a weak and broad FCC diffraction peak, which is most likely attributed to the high Mn content. After annealing at 400 °C, a pronounced BCC peak emerges alongside a FCC oxide peak, clearly demonstrating the influence of thermal treatment on phase formation and crystallisation. Upon annealing at 600 °C, the BCC peak shifts toward a higher diffraction angle while its intensity decreases. This shift corresponds to a reduction in the interplanar spacing and suggests lattice contraction due to further atomic rearrangement. Moreover, the diffraction pattern reveals the presence of FCC metallic and FCC oxide peaks, accompanied by the trigonal Fe₂O₃ phase (R). After annealing at 800 °C, the BCC peak disappears, and only an FCC metal and oxide peak remains. This behaviour is similar to that observed

for the previous alloy at 800 °C and indicates that the BCC phase is no longer stable at such high annealing temperatures. Previous work on HEAs, have shown that Fe will phase separate after annealing from Ni, Mn and Al [31,32], the appearance of a FCC oxide with lattice constants similar to Fe₃O₄ and a metallic FCC phase with lattice constant similar to FCC phases measured in FeCoMnAl alloys, suggests this may have happen within these films.

Although annealing was carried out under Ar atmosphere, the presence of FCC oxide reflections suggests that limited oxidation still occurred, most likely due to trace residual oxygen in the annealing chamber, incomplete removal of atmospheric gases, or oxygen exposure of the film surface during cooling or post-annealing handling. Fig. 2 shows a schematic representation of the phase transformations induced by heat treatment, providing a visual guide for the structural analysis in Fig. 1 (b), (c), and (d). Table 2 provides an overview of the lattice constants and grain size for each of the films, determined from the XRD. It is observed that the results indicate that both the crystal structure and microstructure of the films are strongly affected by annealing. The lattice parameter also changes with phase type, with much larger values recorded for the oxide-related phases than for the metallic FCC and BCC phases. Additionally, the grain size shows a noticeable increase after annealing at higher temperatures, indicating grain growth and microstructural coarsening, especially in the oxide phases, where larger crystallite sizes are recorded compared to the as-deposited state.

4. Mechanical properties

Fig. 3 (a) shows the load–displacement curves of the FeCoNi_{0.8} alloy at different annealing temperatures. The as-deposited and 400 °C-annealed samples exhibit comparable behaviour, indicating similar mechanical responses. In contrast, the film annealed at 600 °C requires a higher load to achieve a 50 nm indentation depth, suggesting structural modifications during annealing enhanced the hardness and resistance to deformation. However, it appears that increasing the annealing temperature does not affect all composites equally, as shown in Fig. 3(b) and (c). Those samples with a higher Mn content exhibit a different response, which can be attributed to the presence of Mn, a brittle element known to reduce ductility [33], as well as to the changes in phase constitution

and annealing-induced microstructural evolution associated with the emergence of a multiphase structure. We can extract from Fig. 3 (a), (b), and (c) the ratio between the final indentation depth (h_f) and the maximum indentation depth under peak load (h_{max}). This ratio is bounded between 0 and 1 ($0 \leq h_f/h_{max} \leq 1$) and serves as an indicator of the material's deformation behaviour, i.e. whether it is predominantly elastic or plastic. A value of $h_f/h_{max} = 0$ corresponds to completely elastic recovery, whereas $h_f/h_{max} = 1$ indicates fully plastic deformation [34]. Fig. 3(d) presents this factor and shows a general decrease as the annealing temperature increases, which is consistent with the observed increase in hardness and indicates improved resistance to plastic deformation with heat treatment. However, the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} composition, which contains the highest Mn content, exhibits a consistently higher h_f/h_{max} ratio at all annealing temperatures compared with the other composites, which indicates that this alloy undergoes predominantly plastic deformation.

The data presented in Fig. 3, was also fitted by Oliver and Pharr Method [35,36], followed by extracting the hardness, H , and reduced modulus of elasticity, E_r . Both properties are derived from the equations below [37,38].

$$H = \frac{P_{max}}{A_c} \quad (1)$$

$$E_r = \frac{\sqrt{\pi}}{2} \beta \frac{S}{\sqrt{A_c}} \quad (2)$$

where P_{max} represents the maximum applied load, A_c denotes the projected contact area of the indentation, β is a correction factor, and S represents the contact stiffness.

The determination of E_r allows the estimation of the Young's modulus (E_s) of the sample under test, which is expressed as [37]:

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \quad (3)$$

Where ν_s is the Poisson's ratio of the film, E_s is the Young's modulus of the film, ν_i is the Poisson's ratio of the indenter (0.07), and E_i is the Young's modulus of the indenter (1140 GPa).

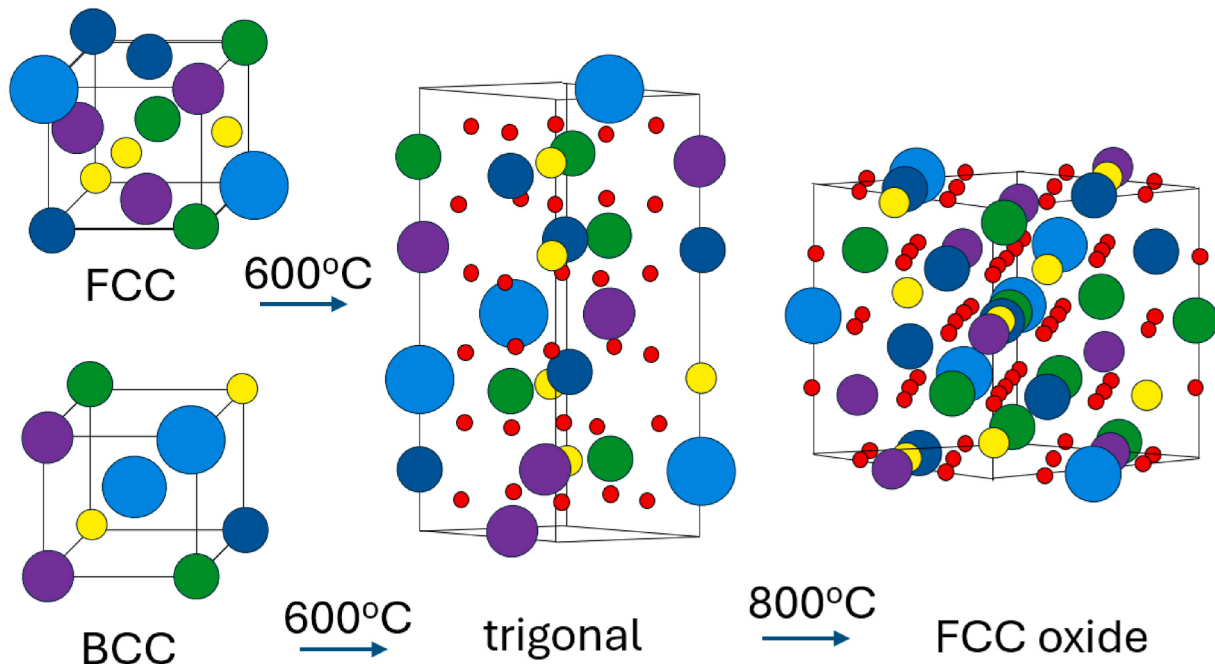


Fig. 2. shows the structural evolution of the films during annealing. The coloured atoms represent the metallic elements (Co, Fe, Ni, Mn, and Al), while the red atoms represent oxygen ions.

Table 2

Lattice constants and grain sizes of FeCoNiAlMn films obtained from XRD patterns at different annealing temperatures (RT, 400 °C, 600 °C, and 800 °C). The lattice parameters were calculated using the cubic lattice-spacing formula, and the grain sizes were estimated using the Scherrer equation.

samples	Annealing	2 θ	Miller Indices	Lattice parameter (Å)	Grain Size D (Å)
FeCoNi _{0.8}	RT	44.06	FCC (111)	3.55	102
	400	44.43	FCC (111)	3.52	78
	600	43.36	FCC (111)	3.61	178
		35.71	FCC Oxide (311)	8.33	173
		36.62	FCC oxide (222)	8.5	134
		37.27	FCC oxide (222)	8.3	279
		62.97	FCC Oxide (440)	8.34	150
Fe _{1.3} CoNiAl _{1.5} Mn _{2.5}	RT	44.36	BCC (110)	2.88	74
	400	43.93	BCC (110)	2.91	60
	600	44.91	BCC (110)	2.85	91
		29.06	FCC Oxide (220)	8.68	241
		32.74	R (104)	11.27	318
		60.21	FCC oxide (511)	8	176
	800	43.29	FCC (111)	3.62	237
		30.05	FCC Oxide (220)	8.40	228
		35.5	FCC Oxide (311)	8.38	173
		62.74	FCC Oxide (440)	8.37	132
Fe _{1.1} CoNiAl _{1.5} Mn _{5.4}	RT	43.42	FCC (111)	3.6	66
	400	44.21	BCC (110)	2.89	142
		35.57	FCC Oxide (311)	8.36	173
	600	44.91	BCC (110)	2.85	153
		28.97	FCC Oxide (220)	8.71	256
		32.42	R (104)	11.38	258
		60.06	FCC oxide (511)	8	170
	800	43.35	FCC (111)	3.61	194
		29.25	FCC Oxide (220)	8.63	684
		32.94	R (104)	11.20	276
		35.6	FCC Oxide (311)	8.36	174

Table 2 (continued)

samples	Annealing	2 θ	Miller Indices	Lattice parameter (Å)	Grain Size D (Å)
		36.3	FCC oxide (222)	8.6	279
		60.6	FCC oxide (511)	8	354

Fig. 4 shows that the as-deposited FeCoNi_{0.8} alloy exhibits a hardness of approximately 6.5 GPa. This value increases by about 10% upon annealing at 400 °C. However, after annealing at 600 °C, the hardness shows a significant rise, reaching more than double its initial value, approximately 16 GPa. This behaviour is evident in Fig. 3 (a), where a pronounced change appears in the load-displacement curve. For previous hardness measurements on thin films, Baco et al. [37] found that for 600 nm polycrystalline FeCo films, the hardness was 14.8 nm, while Abbas et al. [34] reported hardness values of about 6 GPa for amorphous FeSiB thin films with a thickness of 668 nm and about 5 GPa for amorphous FeGaSiB thin films with a thickness of 640 nm. Therefore, the present polycrystalline FeCoNi_{0.8} film annealed at 600 °C exhibits competitive mechanical performance.

The modest increase in hardness after annealing at 400 °C can be correlated with the structural refinement of the metallic phase, as evidenced by the decrease in grain size and the slight reduction in lattice parameter, as shown in Table 2. At 600 °C, however, the XRD pattern changes markedly, with the appearance of multiple diffraction peaks that indicate substantial phase evolution and the formation of oxide-related phases. Therefore, the larger increase in hardness at 600 °C is likely governed not only by refinement effects but also by multiphase and oxide-assisted strengthening mechanisms. Moreover, the reduced modulus and Young's modulus follow a different trend. Both attain their highest values in the as-deposited film, decrease by ~30% after annealing at 400 °C, and recover at 600 °C to levels comparable to the as-deposited state. This non-monotonic behaviour is likely related to annealing-induced structural changes. In particular, the 400 °C sample shows a slight reduction in lattice parameter together with a decrease in grain size, indicating modification of the FCC metallic phase. In contrast, the 600 °C sample exhibits multiple diffraction peaks, suggesting significant phase evolution and the development of a more complex structure, which may contribute to restoring the elastic response.

Fig. 5 shows the variation in hardness of the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at different annealing temperatures. At room temperature, the hardness is approximately 5.7 GPa, which is about 15% (1 GPa) lower than that of FeCoNi_{0.8}. This decrease is most likely attributed to the addition of Al and Mn, as Mn is relatively brittle element that tend to reduce the overall hardness of the alloy [33], and the lower hardness is also could influenced by the resulting changes in phase constitution and annealing-induced microstructural evolution associated with the emergence of a multiphase structure. Upon annealing at 400 °C, the hardness increases by nearly 50%, possibly due to crystal structure reordering and the relaxation of internal stresses. However, at 600 °C, the hardness decreases from 8.4 GPa to 4.8 GPa, likely because of the formation of a multi-phase structure composed of both BCC and FCC phases. At 800 °C, the measured hardness drops further to around 3 GPa, most likely because the surface has become non-uniform, as indicated by the large experimental error. This non-uniformity may arise from grain coarsening, surface oxidation, and elemental segregation. The reduced modulus and Young's modulus follow a similar trend to that of the hardness, suggesting that they share the same underlying interpretation.

Fig. 6 gives the hardness, reduced modulus, and Young's modulus of the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy. The hardness of the as-deposited remains lower than that of the FeCoNi_{0.8} and Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} as-deposited alloys. This reduction is mainly attributed to the higher Mn content in

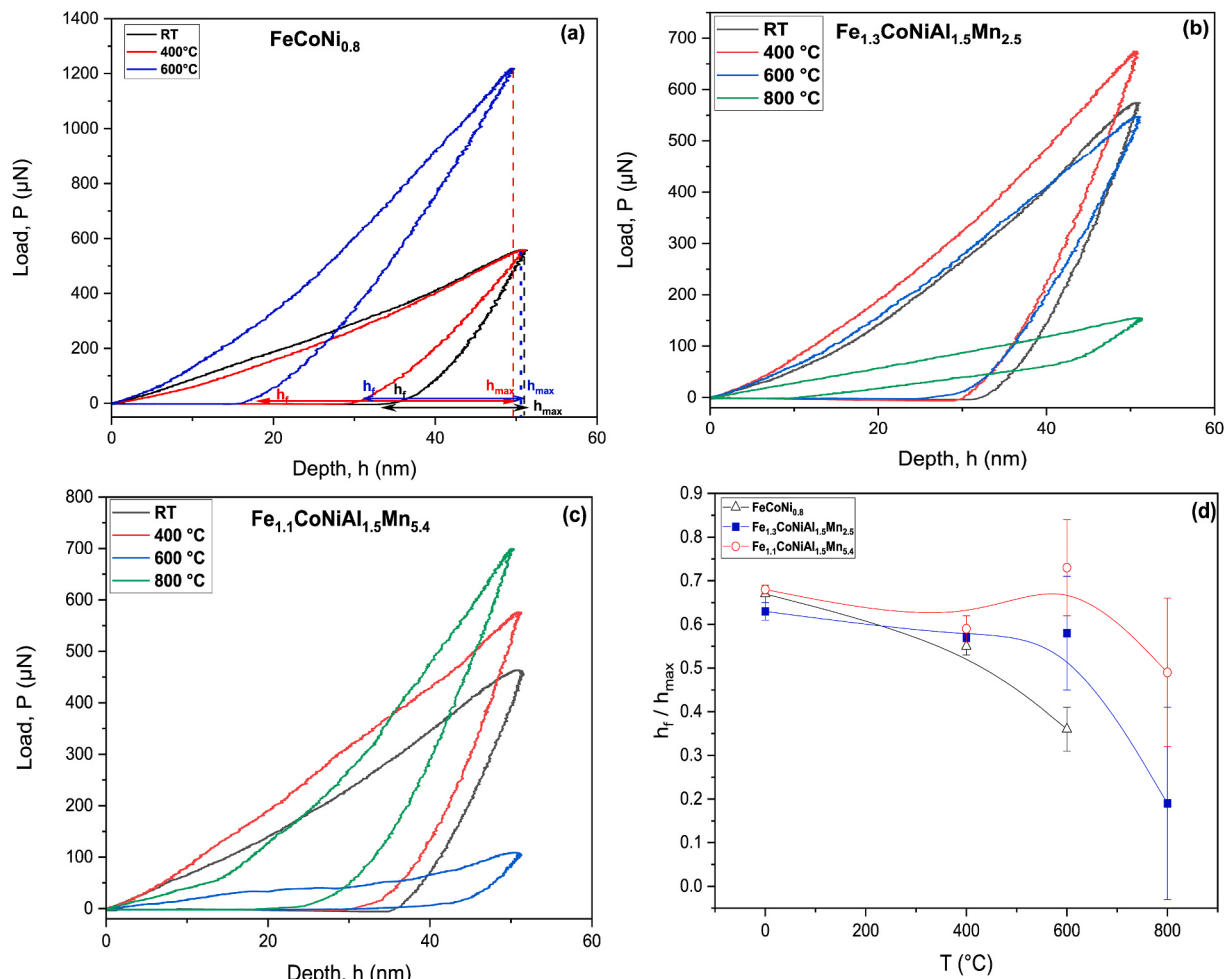


Fig. 3. Comparison of load–depth curves for FeCoNi_{0.8}, Fe_{1.3}CoNiAl_{1.5}Mn_{2.5}, and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloys (600 nm) at different annealing temperatures: room temperature (RT), 400 °C, 600 °C, and 800 °C. The curves also indicate the maximum indentation depth (h_{max}) and the final depth (h_f) during unloading. (d) The ratio of h_f/h_{max} for FeCoNi_{0.8}, Fe_{1.3}CoNiAl_{1.5}Mn_{2.5}, and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloys as a function of annealing temperature. The lines are a guide for the eye.

the alloy. Moreover, Mn may influence phase stability and alter the stacking fault energy in HEAs, thereby affecting the active deformation mechanisms and the resulting hardness. Consequently, the lower hardness is likely related to the combined effects of higher Mn content, phase stability, and stacking-fault-energy-controlled deformation behaviour [33]. Upon annealing at 400 °C, the hardness increases by approximately 30%, similar to the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy, which exhibits a ~50% increase at the same temperature. This enhancement is likely associated with crystal structure reordering and the relaxation of internal stresses. When annealed at 600 °C, the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy shows a significant decrease of about 85% in hardness, compared with the ~50% reduction observed for the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at the same temperature. This pronounced drop is attributed to the formation of a multi-phase structure composed of both BCC and FCC phases, which weakens the overall mechanical strength and may also be associated with oxidation-related changes and stress relaxation during annealing, which together may contribute to the reduced hardness. At 800 °C, the alloy exhibits the presence of FCC metallic and oxide phases, which partially restore the hardness to approximately 6.8 GPa; however, this partial recovery is more likely associated with the FCC metallic phase rather than the oxide phase itself. The Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} samples annealed at 600 °C and 800 °C show remarkable large experimental errors, similar to those observed in the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at the same annealing conditions. This behaviour suggests that the surface becomes non-uniform, as indicated by the large data scatter. Such non-uniformity may result from grain coarsening, surface oxidation, and

elemental segregation, which collectively produce local variations in composition and hardness. The variations in the reduced modulus and Young's modulus exhibit a trend consistent with that of the hardness, indicating that these properties are governed by similar underlying microstructural mechanisms.

The yield strength (σ_y) was calculated [39] and plotted for all samples in Fig. 7 (a). The as-deposited FeCoNi_{0.8} alloy, along with the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} and Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy, exhibits very similar values of approximately 900 MPa, with less than 10% variation among the samples. Upon the onset of heat treatment, the variation in yield strength diverges, as the annealing temperature affects each composition differently. For the FeCoNi_{0.8} alloy annealed at 400 °C, the yield strength increases by about 80%, from 910 MPa to 1610 MPa, which correlates with the observed shift of the peak toward higher diffraction angles. However, when the annealing temperature is further increased to 600 °C, the yield strength rises sharply to approximately 6750 MPa. Although this value appears unusually high, it is consistent with Tabor's method [40], which relates the yield strength to the hardness through the empirical correlation $\sigma_y \approx H/3$. Given that the measured hardness is 16 ± 3 GPa, the calculated yield strength is in reasonable agreement with this relation. The unusually high value observed only for the 600 °C sample may also be influenced by thin-film confinement effects or indentation size effects during nanoindentation.

The Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy exhibits behaviour similar to that of the FeCoNi_{0.8} alloy at both room temperature and after annealing at 400 °C. Upon annealing at 400 °C, the yield strength increases by

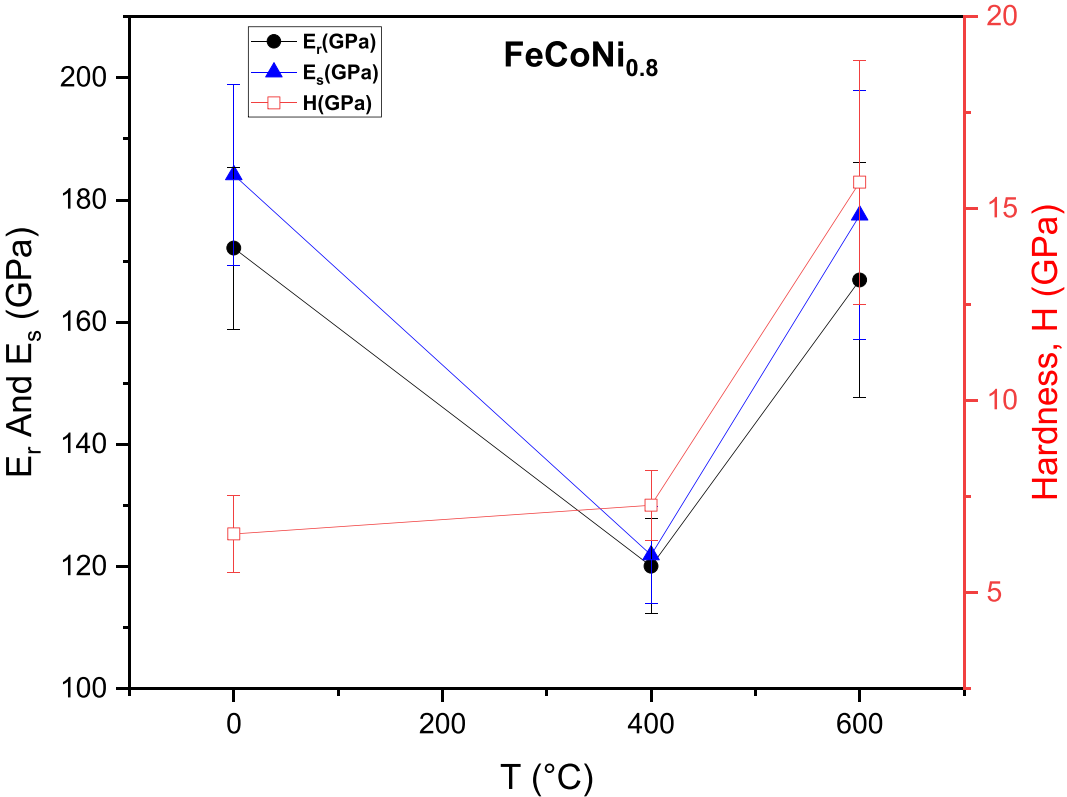


Fig. 4. Comparison of hardness (H), Young's modulus (E_s), and reduced modulus (E_r) of FeCoNi_{0.8} thin films at different annealing temperatures. The lines are a guide for the eye.

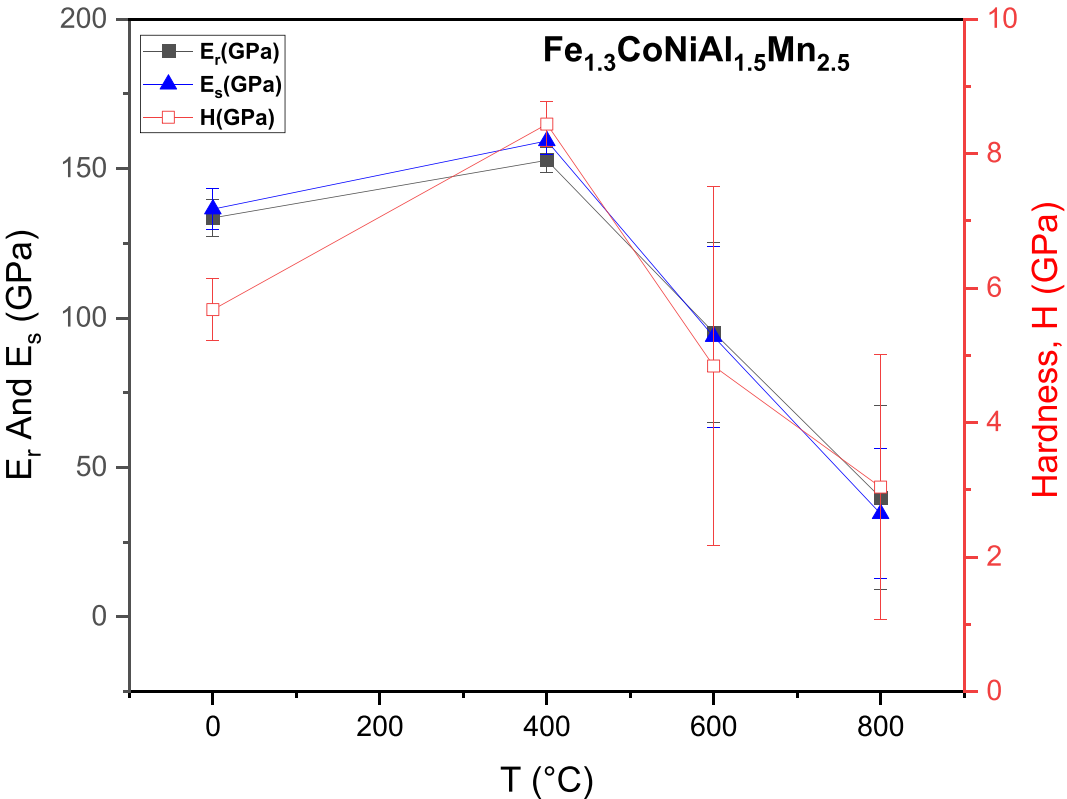


Fig. 5. Comparison of hardness (H), Young's modulus (E_s), and reduced modulus (E_r) of Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at different annealing temperatures. The lines are a guide for the eye.

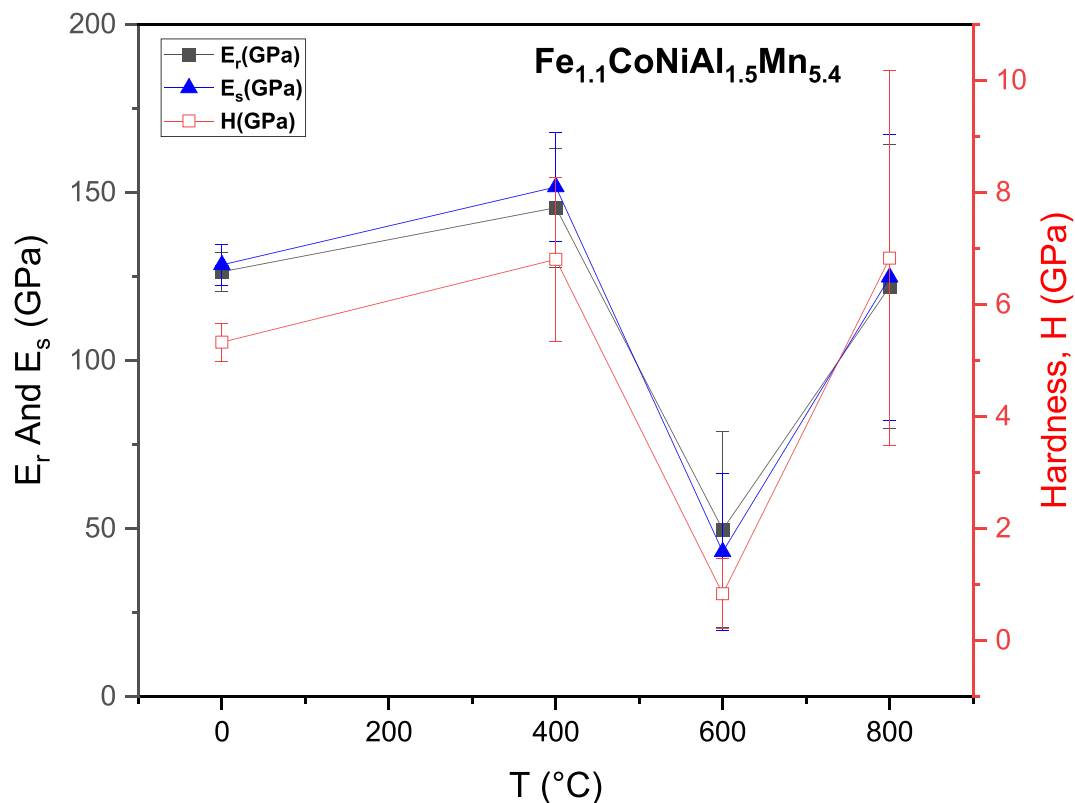


Fig. 6. Comparison of hardness (H), Young's modulus (E_s), and reduced modulus (E_r) of $\text{Fe}_{1.1}\text{CoNiAl}_{1.5}\text{Mn}_{5.4}$ alloy at different annealing temperatures. The lines are a guide for the eye.

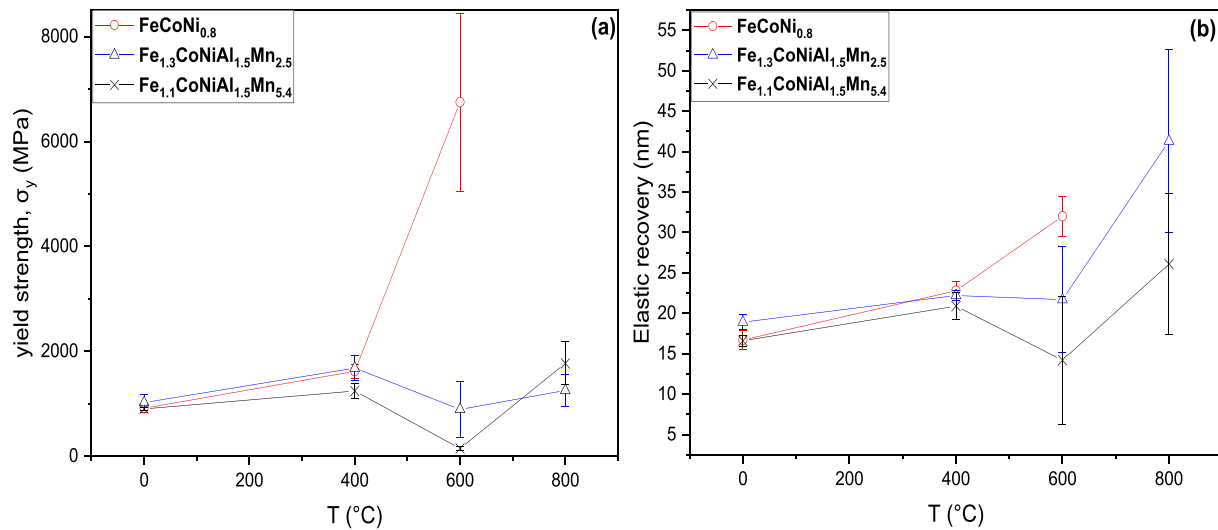


Fig. 7. (a) Comparison of yield strength (σ_y), (b) elastic recovery for $\text{FeCoNi}_{0.8}$, $\text{Fe}_{1.3}\text{CoNiAl}_{1.5}\text{Mn}_{2.5}$, and $\text{Fe}_{1.1}\text{CoNiAl}_{1.5}\text{Mn}_{5.4}$ alloys as a function of annealing temperature. The lines are a guide for the eye.

approximately 70%, which can be attributed to changes in the film morphology, as evidenced by the XRD peak characteristics. In particular, the peak broadening suggests a reduction in grain size, which may contribute to the observed strengthening. At room temperature, the XRD pattern shows a distinct BCC peak; however, after annealing at 400 °C, this peak becomes broader and less intense, suggesting lattice distortion accompanied by a decrease in grain size within the film from approximately 74 Å to 60 Å (calculated using Scherrer equation), as well as possible overlapping BCC reflections. When the annealing temperature is raised to 600 °C, the yield strength decreases noticeably, most likely

owing to the formation of a dual-phase structure (FCC + BCC), as confirmed by the XRD results. At 800 °C, only minor changes are observed, as the alloy still exhibits a mixed FCC phase composed of both metallic and oxide components.

The $\text{Fe}_{1.1}\text{CoNiAl}_{1.5}\text{Mn}_{5.4}$ alloy shows a similar initial trend, with an increase in yield strength after annealing at 400 °C. However, further annealing at 600 °C results in a sharp decrease to approximately 145 MPa. This substantial drop can be attributed to several factors: the high Mn content, which introduces severe lattice distortion due to its larger atomic radius compared with Fe, Co, and Ni [41]; and the presence of

multiple crystalline phases (trigonal, FCC-oxide, FCC-metal, and BCC), which collectively increase brittleness and reduce cohesive strength. Upon annealing at 800 °C, the yield strength partially recovers to a value comparable to that of the Fe_{1.3}CoNiAl_{1.5}Mn_{2.5} alloy at the same temperature, likely due to partial recrystallisation and the stabilisation of the FCC-oxide phase.

Another parameter that can be derived from Fig. 3 (a, b, and c) is the elastic recovery of the material. This represents the portion of the film that elastically returns to its original position after the indenter tip is withdrawn. The elastic recovery is quantified as the difference between the maximum indentation depth ($h_{\max}$) and the final indentation depth (h_f) following unloading [34]. Fig. 7 (b) illustrates the elastic recovery, which increases with the rise in annealing temperature. However, the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy at 600 °C does not follow this trend, most likely due to its lower hardness and yield strength values, which can be attributed to the factors mentioned earlier.

Taking account of these findings, the investigated FeCoNi-based alloys demonstrate excellent mechanical stability and tunability through controlled annealing. The ability to optimise hardness, elastic recovery, and yield strength with heat treatment highlights their potential for advanced structural and functional applications. In particular, the balanced combination of strength and ductility observed in the FeCoNi_{0.8} alloy at 600 °C makes it a promising candidate for use in microelectromechanical systems (MEMS), magnetic sensors, and wear-resistant coatings, where high hardness, resistance to deformation, and structural integrity are important [42]. Moreover, the Fe_{1.1}CoNiAl_{1.5}Mn_{5.4} alloy annealed at 600 °C exhibits relatively low hardness (≈ 0.85 GPa) and reduced yield strength, which makes it a potential candidate for soft magnetic applications or flexible substrate layers where high ductility, low residual stress, and minimal pinning are advantageous for improving magnetic permeability and mechanical compliance. These properties indicate that the investigated films may be promising for MEMS-related thin-film components and wear-resistant coatings, where resistance to deformation and structural integrity are important [42].

5. Conclusion

In conclusion, FeCoNiAl-based alloys with varying Mn contents were successfully fabricated using DC magnetron sputtering and systematically investigated to elucidate the combined effects of elemental composition and annealing temperature on their structural and mechanical properties. The as-deposited FeCoNi alloy exhibited a predominantly FCC crystal structure, while the incorporation of Al and Mn promoted the formation of a BCC structure, with higher Mn contents leading to weaker and less stable BCC reflections. Upon annealing, pronounced phase transformations were observed, including the formation of FCC oxide phases and the emergence of trigonal Fe₂O₃ in alloys containing Al and Mn at elevated temperatures.

The nanoindentation results demonstrated a strong correlation between phase evolution and mechanical response. The FeCoNi_{0.8} alloy showed a remarkable enhancement in hardness with increasing annealing temperature, reaching a maximum value of approximately 16 GPa at 600 °C, which is attributed to phase transformation and oxide-related strengthening mechanisms. In contrast, alloys containing higher Mn content exhibited reduced hardness and yield strength at elevated temperatures due to multiphase formation, oxidation, and increased brittleness. The evolution of elastic recovery and yield strength further highlighted the sensitivity of mechanical performance to both composition and heat treatment. Overall, these findings provide scientific insight into how composition-dependent phase stability and annealing-induced structural evolution govern the mechanical tuning of sputtered FeCoNi-based thin films, thereby establishing a clear composition–structure–property relationship in these alloy systems.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dkhillallah Alsebaie reports equipment, drugs, or supplies was provided by Henry Royce Institute. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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