



TECHNICAL ARTICLE

Role of Rare-Earth Cerium in Martensitic Transformation and Magnetic Properties of Cu-Al-Mn Alloys

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This study investigates the effects of different cerium additions on the properties of Cu-Al-Mn high-temperature shape memory alloy (HTSMA), such as the characteristic martensitic transformation temperatures, transformational kinetic parameters, and martensitic microstructures which are related to its shape memory mechanism and also to its magnetic behavior. Polycrystalline alloys with a base composition of $\text{Cu}_{77.32}\text{Al}_{21.02}\text{Mn}_{1.67}$ (at.%) were synthesized, and varying concentrations of cerium (Ce-1 to Ce-4) were added for comparison. Differential scanning calorimetry tests revealed notable increments in transformation temperatures with cerium additions. Specifically, the austenite start temperature of the reference alloy increased from 143.75 °C to 194.88 °C by 0.05 at.% of Ce addition (Ce-3 alloy), corresponding to the formation of CeCu_5 and $\text{Mn}_{1.15}\text{Cu}_{3.85}\text{Ce}$ phases. However, excessive Ce addition in Ce-4 led to the over-stabilization of secondary phases, reducing the transformation temperatures. Microstructural analysis indicated that Ce addition of refined grains changed the crystallite size of the martensite structure and reduced lattice strain (from 0.72% to 0.34%). Magnetic characterization demonstrated that Ce addition shifted the alloy towards paramagnetic behavior, with M-H curves showing no significant coercive field or remanent magnetization across the studied alloy samples. These findings suggest that cerium can enhance the high-temperature performance of Cu-Al-Mn HTSMAs, with potential applications in environments requiring both shape memory and magnetic properties.

INTRODUCTION

Shape memory alloys (SMAs) are an extraordinary type of functional material that exhibit the distinctive properties of shape memory effect (SME) and superelasticity.¹ These properties make SMAs highly valuable for a range of applications, including sensors, actuators, pipe fittings, high-damping materials, and intelligent structures. Of the SMA systems exhibiting SME, Ni-Ti, Cu-Al-Ni, and Cu-

Zn-Al alloys have been extensively studied and are widely used in commercial products. Ni-Ti SMAs hold particular significance in engineering and biomedical sectors because of their outstanding performance. Nevertheless, despite their extensive application, these alloys face certain drawbacks, including low transformation temperatures, challenges in manufacturing and processing, and high material costs, which restrict their wider utilization.² SMAs based on copper, such as Cu-Al-Ni and Cu-Zn-Al, are considered promising alternatives due to their reduced production costs and straightforward processing. These materials also offer advantages in electrical and thermal conductivity,

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making them attractive for practical applications. However, the polycrystalline forms of these copper-based SMAs are often hindered by brittleness, which limits their cold workability. This brittleness is primarily due to the high level of atomic order and the pronounced elastic anisotropy in the parent austenitic phase of these alloys. The pronounced ordering in the B2, D0₃, or L2₁ structures of the β -phase in these alloys leads to a tendency for intergranular fracture under stress, posing additional challenges for their use in applications demanding high durability and resistance to fatigue.³ Recent developments in material science have revealed that Cu-Al-Mn alloys, especially those with lower aluminum content, display exceptional ductility. This enhancement in ductility is attributed to the reduced atomic ordering in the parent phase, which has an L2₁ structure. In these alloys, the disordered β -phase remains stable at elevated temperatures and undergoes a transformation into martensite when quenched. The transformation process in these alloys involves ordering reactions from A2 to B2 to L2₁, and the specific type of martensite formed depends on the levels of aluminum and manganese.^{3,4} The addition of manganese to Cu-Al alloys plays a crucial role in stabilizing the body-centered cubic (bcc) β -phase, which lowers the temperature range for the stability of this phase and broadens the composition range over which it exists.⁵ Manganese not only stabilizes this phase but also enhances the ductility of the alloy by reducing the degree of order within the phase. This reduction in structure makes the alloy more suitable for cold working, mitigating one of the primary disadvantages of traditional Cu-based SMAs. The practical use of SMAs depends on their transformation temperatures and the degree of their SME and SE properties. Transformation temperatures are particularly critical as they dictate the operational limits and functionality of SMAs in real-world applications. While most research on Cu-Al-Mn SMAs has focused on alloys with lower aluminum content, comprehensive studies examining the effects of varying aluminum and manganese concentrations on transformation temperatures, martensite morphology, and other associated properties remain limited.⁶ In Cu-based SMAs, it is well known that the recoverable strain, a crucial property for practical applications, is significantly influenced by the grain size of the specimen's dimensions, such as sheet thickness and wire diameter. As the relative grain size increases, the recoverable strain tends to increase, which is attributed to the reduction in grain boundary constraints. However, the increase in grain size also introduces challenges, including increased brittleness and a higher likelihood of intergranular fractures, due to the high level of atomic order and elastic anisotropy in the parent phase.⁷ In polycrystalline Cu-based SMAs, the key challenge lies in optimizing the balance between ductility, fatigue

strength, and the desired SME and SE properties. Attempts to improve these properties through grain refinement have seen limited success, as the mechanical performance of these alloys is closely linked to their grain structure and texture. The orientation and texture of grains within the alloy can significantly influence the recoverable strain, with certain textures enhancing these properties.⁶ For example, recent research has demonstrated that Cu-Al-Mn alloys with aluminum content below 18 at.% can attain excellent cold workability, achieving reductions greater than 60% during cold rolling, while still maintaining significant SME and SE due to the transformation from cubic β_1 (L2₁) to monoclinic β'_1 (18R) martensite. Furthermore, developments in Cu-Al-Mn-Ni alloys have demonstrated that specific recrystallization textures, achieved through processes such as heavy cold rolling followed by solution treatment, can significantly enhance PE (pseudoelasticity) strain. In some cases, a PE strain of about 7% has been achieved in textured sheets, indicating the potential for significant improvements in SMA performance through careful control of grain structure and processing conditions.^{6,8–10}

Recently, researchers have turned to investigating the effects of rare-earth (RE) elements and have focused on the effects of these elements added to alloys on thermal and mechanical properties. In a study by Zhang and colleagues, it was found that the addition of RE elements (cerium and lanthanum) increased the strength and reduced the electrical resistivity of Al-3.0 Mg alloys.¹¹ In another study, by Zhang and colleagues, the effects of adding different amounts of ytterbium (Yb) to A356.2 aluminum alloy and the T6 heat treatment were investigated. It was found that the addition of Yb improved the microstructure of the alloy, resulting in increased tensile strength and hardness.¹² In another study, by Xiao and co-researchers, the effects of precipitation hardening, microstructure, and mechanical properties were analyzed for three Al-Cu-Mg-Ag alloys containing different cerium levels (0, 0.20, and 0.45 wt.%). The results showed that increasing the Ce content from 0% to 0.45% enhanced the tensile strength at all test temperatures up to 350 °C.¹³ In a separate study investigating the microstructures and mechanical properties of Al-Cu-Mn-Mg-Fe alloys with varying CeLa additions, it was observed that CeLa addition led to the formation of Al₈Cu₄Ce and Al₆Cu₆La phases. Adding 0.25% CeLa encouraged the development of denser Al₂₀Cu₂Mn₃ and Al₆(Mn, Fe) phases, which enhanced the alloy's mechanical properties. Conversely, a 0.50% CeLa addition promoted the formation of coarse Al₈Cu₄Ce, Al₆Cu₆La, and Al₆(Mn, Fe) phases, leading to a decrease in mechanical properties.¹⁴ In a study by Pozdnyakov and colleagues, the impact of adding Hf, Er, Gd, Y, and Sm to aluminum-based alloys on the structure and properties of Al-0.2 Zr-0.1 Sc

alloys was examined. The introduction of 0.1% Y, Sm, Er, and Gd resulted in the formation of Al_3Y , Al_3Sm , Al_3Er , and Al_3Gd phases, respectively. These additions improved the thermal stability of $\text{Al}_3(\text{Sc}, \text{Zr})$ particles, with enhanced stability observed after 100 h at 250 °C and delayed onset of softening until after 54 h at 370 °C. The highest hardness was recorded with a 0.1% Er addition, reaching 50 HV after 54 h at 370 °C.¹⁵ A study by Dalvand et al. demonstrated that adding 0.04 wt.% misch metal (alloy of Ce and La) to a Cu–12wt.%Al–3wt.%Ni–0.6wt.%Ti high-temperature SMA resulted in a significant grain size reduction, improved ductility, and enhanced thermo-mechanical properties. The alloy's tensile fracture stress increased from 550 MPa to 660 MPa, the tensile fracture strain increased from 4.50% to 5.0%, and the maximum recoverable strain also rose from 1.2% to 1.8%. These improvements were attributed to the extra grain refinement due to the formation of RE-rich precipitates. Additionally, it was noted that the addition of RE lowered the martensite start temperature (M_s) and increased the austenite start temperature (A_s).¹⁶ Research by Lu et al. showed that adding Ce to Cu–Al–Mn SMAs led to a reduction in grain size and affected the martensitic transformation temperature, and an increase in tensile strength and ductility was observed. The damping capacity ($\tan \delta$) of the martensite was found to be dependent on the strain amplitude, and, as the Ce content increased, the damping capacity initially increased and then decreased.¹⁷ In a study by Zhang et al., adding Sm to a Cu–13.0Al–4.0Ni alloy reduced the grain size from millimeters to hundreds of microns. The microstructure of the alloys at room temperature was composed of 18R martensite and a face-centered cubic Sm-rich phase. The addition of Sm resulted in significant improvements in mechanical properties and the SME. With 0.5% Sm content, the compressive fracture stress increased from 580 MPa to 1021 MPa, and the compressive fracture strain increased from 10.5% to 14.8%.¹⁸ Mirghaderi et al. found that adding yttrium (Y) to a Cu–13Al–3.5Ni–0.7Ti alloy, produced by mechanical alloying, sintering, and hot rolling, reduced the grain size and provided better element distribution. The addition of yttrium was found to increase the martensite-to-austenite transformation temperature from 41.5 °C to 58.5 °C. Additionally, the hardness value increased from 158 HV to 187 HV, and a secondary intermetallic phase was formed.¹⁹

This study aims to build on these findings by investigating the effects of the addition of the RE element Ce to Cu–Al–Mn SMA martensite transformation and mechanical and magnetic properties. With this research, we aim to contribute to a better understanding of the factors affecting the addition of Ce to the Cu–Al–Mn high-temperature shape memory alloy (HTSMA), especially in terms of transformation properties. The results of this study

will not only improve the fundamental knowledge of these materials but will also guide the development of more reliable materials for various industrial applications.

EXPERIMENTAL

For this research, a polycrystalline SMA with a base composition of $\text{Cu}_{77.32}\text{Al}_{21.02}\text{Mn}_{1.67}$ (at.%, EDS) was synthesized as the reference sample (Ref). Additionally, a series of alloys, built on this base CuAlMn alloy by incorporating varying concentrations of cerium (Ce-1, Ce-2, Ce-3, Ce-4), were also prepared for comparative analysis. The element's powder-mix mass (wt.%) and corresponding atomic (at.%) percentages and the final atomic (at.%) EDS compositions of all these base and cerium-doped alloys are given in Table I. The samples were created as cast ingots in an argon atmosphere using an arc melter, following the mixing, pressing, and pelletizing of high-purity ($\sim 99.99\%$) structural aluminum, copper, manganese, and cerium powders. They were then cut into 1 mm-thick pieces ($\sim 40\text{--}60$ mg) for analysis. The samples were homogenized at 900 °C for 1 h and rapidly cooled in iced brine water. The transformation temperatures of the samples were determined by a Shimadzu DSC-60A differential scanning calorimeter (DSC). Cu–Al–Mn + Ce series alloys were measured at room temperature up to 200–400 °C at different heating and cooling rates (10, 15, 20, and 25 °C/min). The chemical compositions of the alloys were determined using a LEO Evo 40 Model energy dispersive x-ray (EDX) analyzer. The SEM images and elemental maps of the alloy samples were taken by a Thermo Scientific Scios 2 LoVac Dual Beam System labeled FIB-SEM instrument. XRD measurements were conducted on a Rigaku RadB-DMAX II diffractometer with $\text{CuK}\alpha$ ($k = 1.5405$ Å) radiation. The resulting XRD patterns were analyzed with the Crystallography Open Database. After EDX and x-ray analysis, the surfaces of the samples were first mechanically polished and then etched in a solution of 10 g ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 192 ml methanol, and 40 ml HCl. The microstructures of the samples were examined using an XJP-6A/SDC-313 optical microscope.

RESULTS AND DISCUSSION

The DSC results as heating/cooling curves of the fabricated $\text{CuAlMn} \pm \text{Ce}$ alloys are presented in Fig. 1(a–e). Based on these figures, each DSC curve for the alloys shows downward endothermic peaks, which indicate the reverse martensitic transformation from the martensite phase to the austenite phase ($M \rightarrow A$) during the heating segment of the curves. As a counter to these peaks, the upward exothermic peaks, indicating forward martensitic transformation from austenite to martensite phase ($A \rightarrow M$), are seen correspondingly on the upper cooling parts of these curves. These coupled

Table I. EDS (at.%) and powder-mix (at.%, wt.%) alloying compositions of the Cu-Al-Mn ± Ce alloys

Alloy ID	EDS results				Alloying elements powder-mix percentages							
	(at.%)				(at.%)				(wt.%)			
	Cu	Al	Mn	Ce	Cu	Al	Mn	Ce	Cu	Al	Mn	Ce
Ref.	77.32	21.02	1.67	—	73.64	23.88	2.48	—	85.70	11.80	2.50	—
Ce-1	77.79	20.56	1.62	0.03	73.62	23.87	2.38	0.12	85.70	11.80	2.40	0.3
Ce-2	76.71	21.35	1.91	0.03	73.61	23.87	2.28	0.23	85.70	11.80	2.30	0.6
Ce-3	77.96	20.97	1.02	0.05	73.60	23.87	2.19	0.35	85.70	11.80	2.20	0.9
Ce-4	78.10	20.26	1.55	0.09	73.64	23.88	2.09	0.39	85.70	11.80	2.10	1.0

reversible martensitic transformation peaks formed on each heating/cooling rate curve imply that the fabricated CuAlMn ± Ce alloys have SME properties. Since the reverse transformation peaks of these alloys all formed above 110 °C, they are all classified as HTSMAs. In the beginning, in the Ref alloy, these peaks, especially the forward transformation peaks on upper cooling curve parts, are scarcely distinguished. However, when only a small amount (0.11 at.% ≈ 0.3 wt.% powder) of cerium is added to the Ce-1 alloy, then the peaks become more apparent, more powerful, sharper, and deeper. Then, with a doubled (0.23 at.% ≈ 0.6 wt.% powder) amount of cerium together with 0.79 at.% (EDS) of more Al and 0.29 at.% (EDS) of more Mn in Ce-2 alloy, they become sharper and deeper, demonstrating that the martensitic transformation or shape memory mechanism is improved by these small cerium additions. However, with more cerium additions in Ce-3 and Ce-4, the peaks again start to weaken. So, it can be said that by adding 0.23 at.% ≈ 0.6 wt.% (powder) of cerium and 0.79 at.% (EDS) of more Al and 0.29 at.% (EDS) of more Mn additions together to the base CuAlMn alloy, the resultant Ce-2 alloy gives the best martensite transformation peaks compared to the base and other cerium-added CuAlMn alloys. The cerium additions in Ce-1 and Ce-2 improved the shape memory capacity in these alloys more than that of the base CuAlMn alloy. Cerium also improved the shape memory capacity in Ce-3 and Ce-4 (at least it did more than that of the base alloy), but the improvements in these alloys cannot be seen obviously nor did it keep going more than occurred in Ce-2, mainly because of the use of lower (at.%, EDS) Mn in Ce-3 and lower (at.%, EDS) Al in Ce-4. Apart from these, secondary smaller endothermic peaks are seen formed at between 300 and 400 °C on the heating segments of the DSC curves of the Ce-1 alloy, due to continuing to heat this alloy sample to ca. 400 °C (the other alloy samples were heated to lower temperatures). These peaks indicate the austenite to B2 (metastable) phase transitions which are also seen in the DTA curves of other alloy samples. The DTA curves of the alloys are shown in Fig. 1f. According to the downside heating segments of these curves, the common high-temperature behavior of copper-based SMAs showing itself as a

multi-stage phase transition chain was observed on the heating baselines of all these DTA curves, and, from far left to the far right, these transitions are $\beta_1'(18R, \text{martensite}) \rightarrow \beta_1(\text{DO}_3 \text{ or } L2_1, \text{austenite}) \rightarrow \text{B2 (metastable cubic)} \rightarrow \text{precipitations} \rightarrow \text{eutectoid dissolution (of precipitations)} \rightarrow \text{B2 (ordered cubic)} \rightarrow \text{A2 (disordered cubic)}$.^{20–23} Here, the most powerful reverse (martensite → austenite) transformation peak appears on the DTA curve of the Ce–2 alloy, and the most prominent eutectoid peak indicates the high alloying quality of this alloy. The characteristic martensitic phase transformation temperatures, hysteresis gap (A_s – M_f) values, enthalpy, and entropy change values obtained from the DSC measurements at different heating/cooling rates for each sample are shown in Table II. Here, the equilibrium temperature (T_0), which is the temperature generally between the M_s and A_s temperatures, is the temperature where the chemical Gibbs free energies of the two interconverting phases are equal, which means that no driving force exists at this point to trigger a martensitic transformation. The T_0 , typically falling between the M_s and A_s temperatures, is the point at which the chemical Gibbs free energies of the two interconverting phases are equal. At this temperature, there is no driving force to initiate a martensitic transformation/ The T_0 equilibrium temperature parameter was calculated using:²⁴

$$T_0 = \frac{A_f + M_s}{2} \quad (1)$$

Also, the lattice entropy change ΔS values for the reverse ($M \rightarrow A$) transformations were calculated by using:²²

$$\Delta S_{M \rightarrow A} = \frac{\Delta H_{M \rightarrow A}}{T_0} \quad (2)$$

Additionally, the increase in Mn content observed in the Ce-1 and Ce-2 samples lowers the transformation temperatures. Although the Mn content is lower in Ce-1, the A_s and A_f temperatures are higher than in Ce-2. In addition to reducing the phase transformation energy and leading to

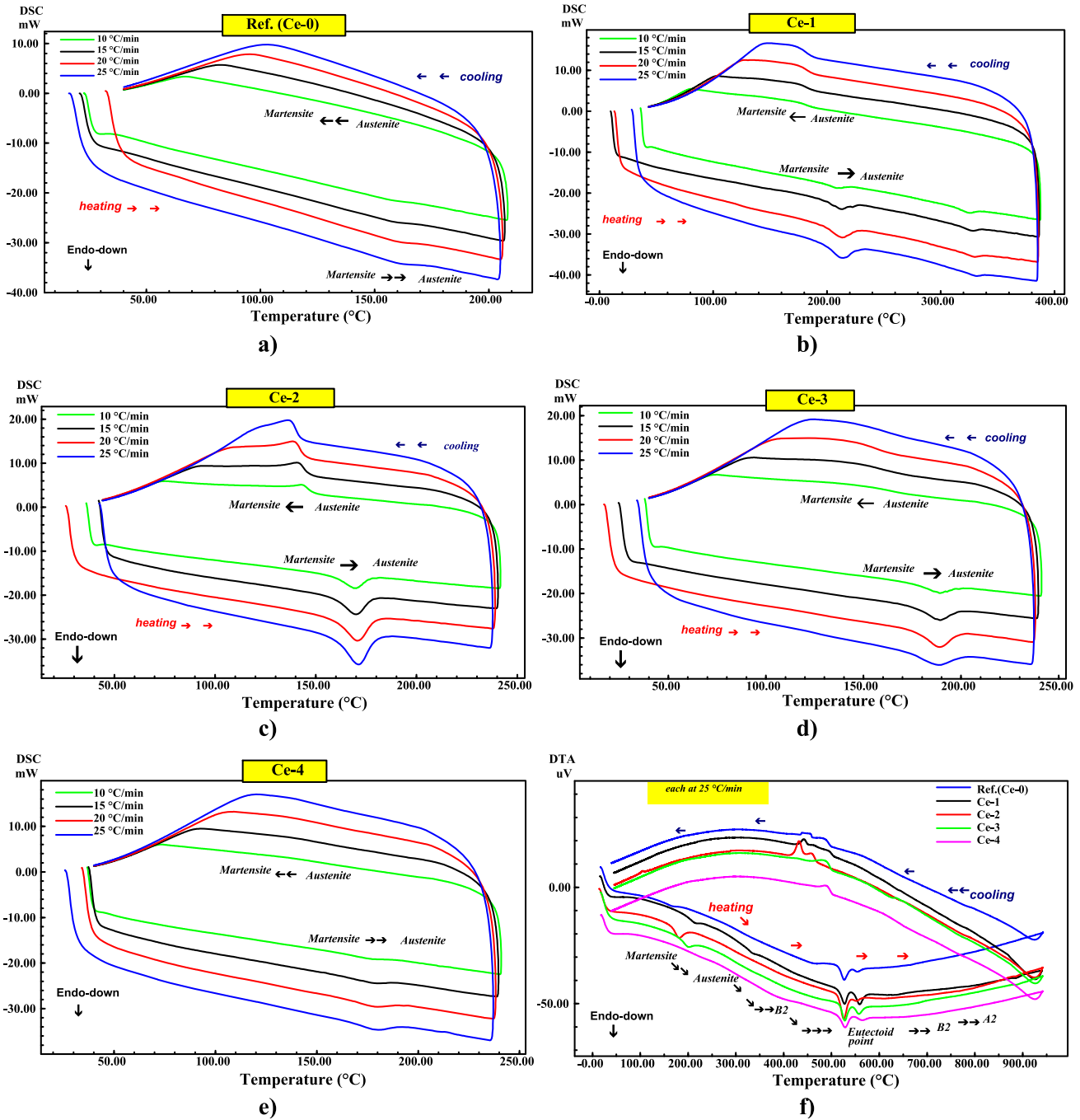


Fig. 1. (a–e) DSC curves, and (f) DTA curves of the fabricated CuAlMn ± Ce alloys. It is well known that the transformation temperatures (especially M_s) of CuAlMn SMAs increase with the decrease of the aluminum and/or manganese ratio.²⁵ According to this knowledge, and also to the average M_s change plot drawn versus both percentage changes of Al and Mn (at.%, EDS), which is given in Fig. 2a, the average M_s temperature of the Ref alloy with 21.02 at.% Al (EDS) and 1.67 at.% Mn (EDS) increases at the introduction of the first Ce addition in Ce-1 alloy due to the slightly lower use of Al (at.%, EDS) in Ce-1. This means that even a small Al decrement increases the M_s temperature. Similar increasing and decreasing trends in the average M_s due to changes in the Al and/or Mn percentages continue in other Ce alloys. However, in Fig. 2b and c, it can be seen that all the other average martensitic transformation temperatures (A_s , A_f , M_f , and T_0) and hysteresis gap ($A_s - M_f$) values are generally increased due to the gradually increasing use of Ce additions, even in the Ce-2 alloy (despite both higher Al and Mn used in this alloy). Also, as seen in Fig. 2d, the corresponding average enthalpy ($\Delta H_{M \rightarrow A}$) and entropy ($\Delta S_{M \rightarrow A}$) change values also obey this trend, and, among these, the highest values are seen exhibited by the Ce-2 alloy, which, once again, shows that this alloy has the most powerful SME. All in all, it can be said that the characteristic martensitic transformation temperatures and related thermodynamic parameters and shape memory capacity of the fabricated CuAlMn ± Ce HTSMAs are found to be the extremely sensitive to the alloying composition ratios of Al, Mn, and Ce components, and minor Ce additions generally increase or improve these features.

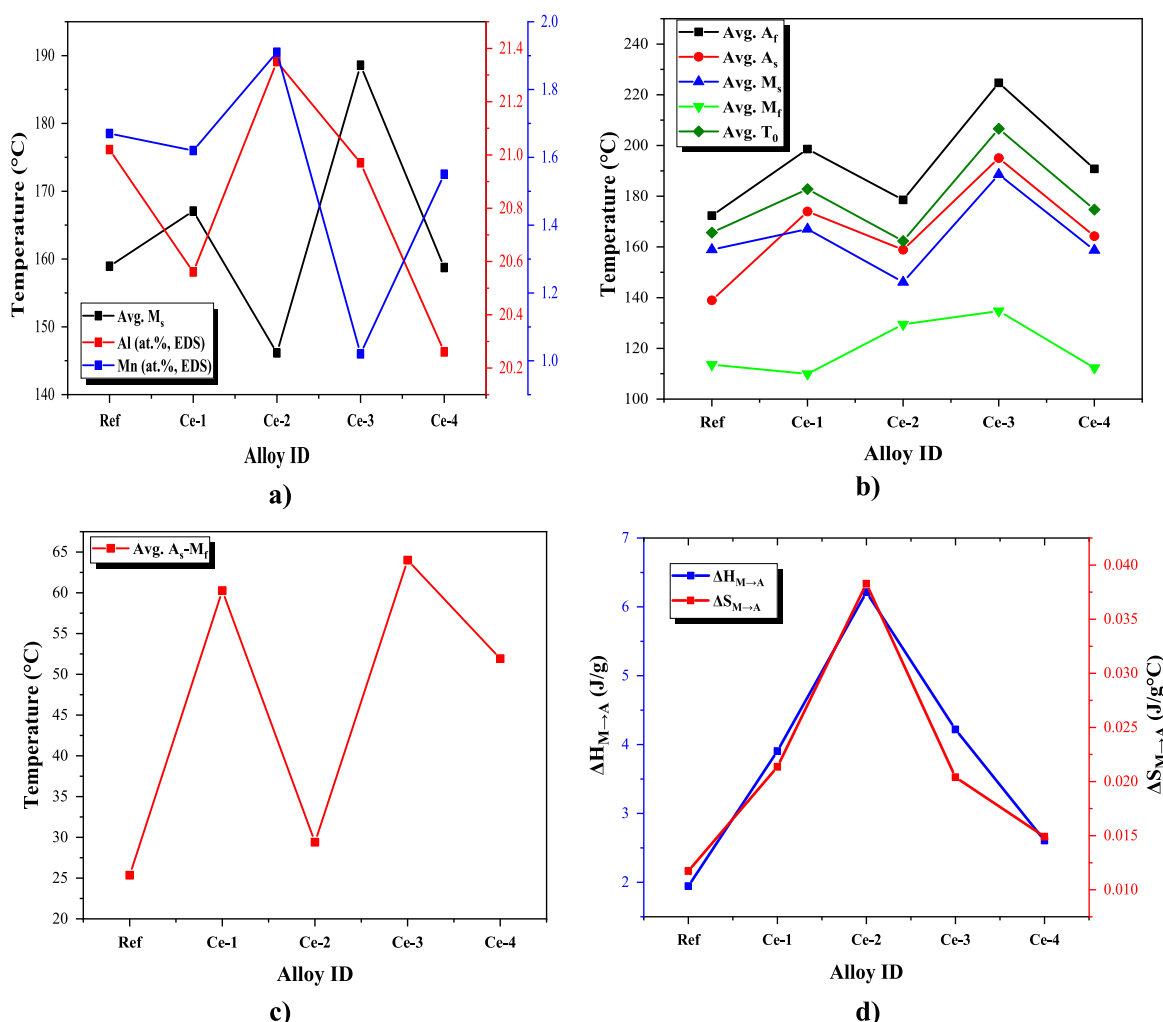


Fig. 2. (a) The change in the average M_s temperature depending on Al and Mn at.% (EDS) percentages, and the changes in the average, (b) transformation temperatures, (c) hysteresis gap ($A_s - M_f$) values, and (d) enthalpy ($\Delta H_{M \rightarrow A}$) and entropy ($\Delta S_{M \rightarrow A}$) change values between the fabricated CuAlMn $\pm$ Ce HTSMAs. The transformation temperatures of the Ce-3 and Ce-4 alloys are generally higher compared to the Ce-1 and Ce-2 alloys. This increase is attributed to the RE element cerium either forming new phases in the alloy or stabilizing existing phases.¹⁷ Cerium causes distortions in the crystal structure of the alloy, leading to the formation of internal stresses affecting the phase transformations, and the transformation temperatures generally tended to increase as the heating/cooling rate increases (from 10 °C/min to 25 °C/min). The addition of cerium to CuAlMn alloy changed the Gibbs free energy and affected the phase transformations.

transformations at lower temperatures, the restriction of dislocation motion by Mn also contributes to this temperature decrease.

Excessive addition of cerium in the Ce-4 sample caused over-stabilization of the secondary phases and would increase the transformation temperatures if the Al and Mn EDS ratios were somewhat higher, the same as with the ratios in the Ref alloy. It also caused solid-solution strengthening which restricted dislocation movement in the alloy and created new dislocations which are good for increasing the shape memory capacity. We see that this occurred optimally in Ce-2 because lower use of Al and Mn in Ce-4 reduced the improvement of shape memory capacity in Ce-4, indicating that exceeding a certain cerium concentration disrupts phase coherence and increases structural distortion at the phase boundaries.^{14,17}

The average valence or conduction electron concentration per atom ratio (e/a) parameter values of the alloys were calculated by using the $e/a = \sum f_i v_i$ formula,³ where f_i refers to the atomic (at.%, EDS) fractions of the alloying elements and v_i represents the corresponding valence electron numbers of the alloying elements. The e/a ratio values of the fabricated CuAlMn $\pm$ Ce HTSMAs were found to be 1.44, 1.43, 1.45, 1.43, and 1.42 for the Ref, Ce-1, Ce-2, Ce-3, and Ce-4 alloys, respectively. The Cu-based SMAs generally need to have an e/a ratio between 1.45 and 1.51 to have a SME property,²² and, in this range, both 18R (β_1') and 2H (γ_1') types of martensite are formed together, when 18R becomes dominant over 2H for the e/a ratio values below this range close to 1.45, and vice versa for the values above this range. Since the e/a ratio values of the CuAlMn $\pm$ Ce HTSMAs were found at 1.45 (for

Table II. The martensitic transformation temperatures and thermodynamic parameters of the Cu-Al-Mn $\pm$ Ce high-temperature shape memory alloys

Alloy ID	Heating/cooling rate (°C/min)	A _s (°C)	A _f (°C)	A _{max} (°C)	M _s (°C)	M _f (°C)	A _s -M _f (°C)	T ₀ (°C)	$\Delta H_{M \rightarrow A}$ (J/g)	$\Delta S_{M \rightarrow A}$ (J/g °C)
Ref.	10	143.75	172.88	157.45	153.31	111.20	32.55	163.10	1.66	0.01018
	15	129.50	170.04	158.94	152.26	116.15	13.35	161.15	1.87	0.01160
	20	142.29	172.17	160.71	161.43	109.72	32.57	166.80	2.07	0.01241
	25	140.33	174.30	161.29	168.77	117.37	22.96	171.54	2.18	0.01271
Ce-1	10	171.19	200.75	189.10	171.36	112.13	73.01	186.06	3.95	0.02123
	15	174.37	198.64	189.31	166.20	110.05	51.41	182.42	3.99	0.02187
	20	176.05	202.64	189.10	164.88	103.82	57.74	183.76	3.94	0.02144
	25	174.36	192.31	189.32	165.84	113.95	58.94	179.08	3.74	0.02089
Ce-2	10	158.64	176.93	169.96	149.46	134.81	23.83	163.20	5.57	0.03413
	15	158.59	178.33	170.01	146.98	131.65	26.94	162.66	6.38	0.03922
	20	159.21	179.01	170.70	145.14	131.76	27.45	162.08	6.29	0.03881
	25	159.20	179.99	171.04	143.00	119.81	39.39	161.50	6.61	0.04093
Ce-3	10	194.88	218.15	208.31	189.02	121.87	59.06	203.59	3.31	0.01626
	15	196.34	225.32	213.22	188.03	144.93	64.32	206.68	3.95	0.01911
	20	194.74	227.73	213.24	188.47	137.00	72.23	208.10	4.65	0.02235
	25	194.13	227.61	213.80	188.78	135.19	60.41	208.20	4.97	0.02387
Ce-4	10	159.02	188.74	175.42	155.71	116.48	42.54	172.23	1.72	0.00999
	15	164.90	191.80	176.74	158.86	112.40	52.50	175.33	2.81	0.01603
	20	166.58	191.54	178.55	160.46	105.97	60.61	176.00	2.74	0.01557
	25	166.60	191.00	179.80	159.87	114.57	52.03	175.44	3.16	0.01801

Ce-2) and below this value, these alloys should have dominant β_1' martensite and secondary γ_1' martensite together. From this, one can easily understand why Ce-2 showed the best SME among the others, because, among the fabricated CuAlMn $\pm$ Ce HTSMAs only the e/a ratio value of this alloy falls in the above-mentioned e/a ratio value range. The presence of the β_1' and secondary γ_1' martensite phases expected to be formed in CuAlMn $\pm$ Ce HTSMAs depending on their e/a ratio values were confirmed by the XRD results and optical micrographs of these alloys.

The XRD patterns of the CuAlMn $\pm$ Ce HTSMAs given in Fig. 3 reveal that the addition of cerium in varying amounts resulted in the formation of new phases in the alloy. Notably, phases such as CeCu₅, Mn_{1.15}Cu_{3.85}Ce, and Cu₃Al₂Ce directly influenced the alloy's microstructure and, consequently, its mechanical and thermal properties. The peaks indicating β_1' and secondary γ_1' martensite phases can be seen formed on these patterns. Therefore, the presence of these phases expected from the e/a ratio values of these alloys is confirmed. The crystallographic data for these phases is provided in Table III. In the literature, it is known that RE elements stabilize such phases in alloys and alter internal stresses by increasing dislocation density in the matrix structure.¹⁴ These phases have led to changes in the elastic moduli within the matrix, resulting in either an increase or decrease in the martensitic transformation temperatures. For example, in the Ce-3 sample, the transformation temperatures increased significantly, with the start of transformation temperature (A_s) rising to

194.88 °C. This increase is attributed to the cerium atoms positioning themselves at the phase boundaries within the matrix, thereby increasing the phase transition energy.

Additionally, it has been observed that heating and cooling rates significantly influence the transformation temperatures. Experiments conducted at various heating/cooling rates (10, 15, 20, 25 °C/min) demonstrate that both martensitic and austenitic transformations vary with the applied rates. Conversely, slower heating/cooling rates allow for more homogeneous phase transformations, resulting in lower transformation temperatures. In this study, a slight increase in transformation temperatures was also observed with increasing rates. The average crystallite size values and the values of crystallite size of the highest martensite peak for the CuAlMn $\pm$ Ce HTSMAs and the corresponding lattice strain values are given in Table IV, from which it can be seen that the addition of cerium to CuAlMn alloy significantly affects both the crystallite size and lattice strain values. In the Ref alloy, the average crystallite size is 17.34 nm with a lattice strain of 0.72%. The addition of Ce initially increases the average crystallite size to 24.84 nm (Ce-1) but reduces the martensite crystal size from 58.8 nm to 31.1 nm, while reducing the lattice strain from 0.72% to 0.34%, indicating grain growth and a reduction in internal stresses, because a slightly lower Al (but much more than 0.03 at.% Ce) was used in Ce-1 than in the Ref. These suggestions support that Ce induces localized lattice distortions, refining the microstructure and potentially enhancing mechanical properties.^{15,17} Similarly, in the

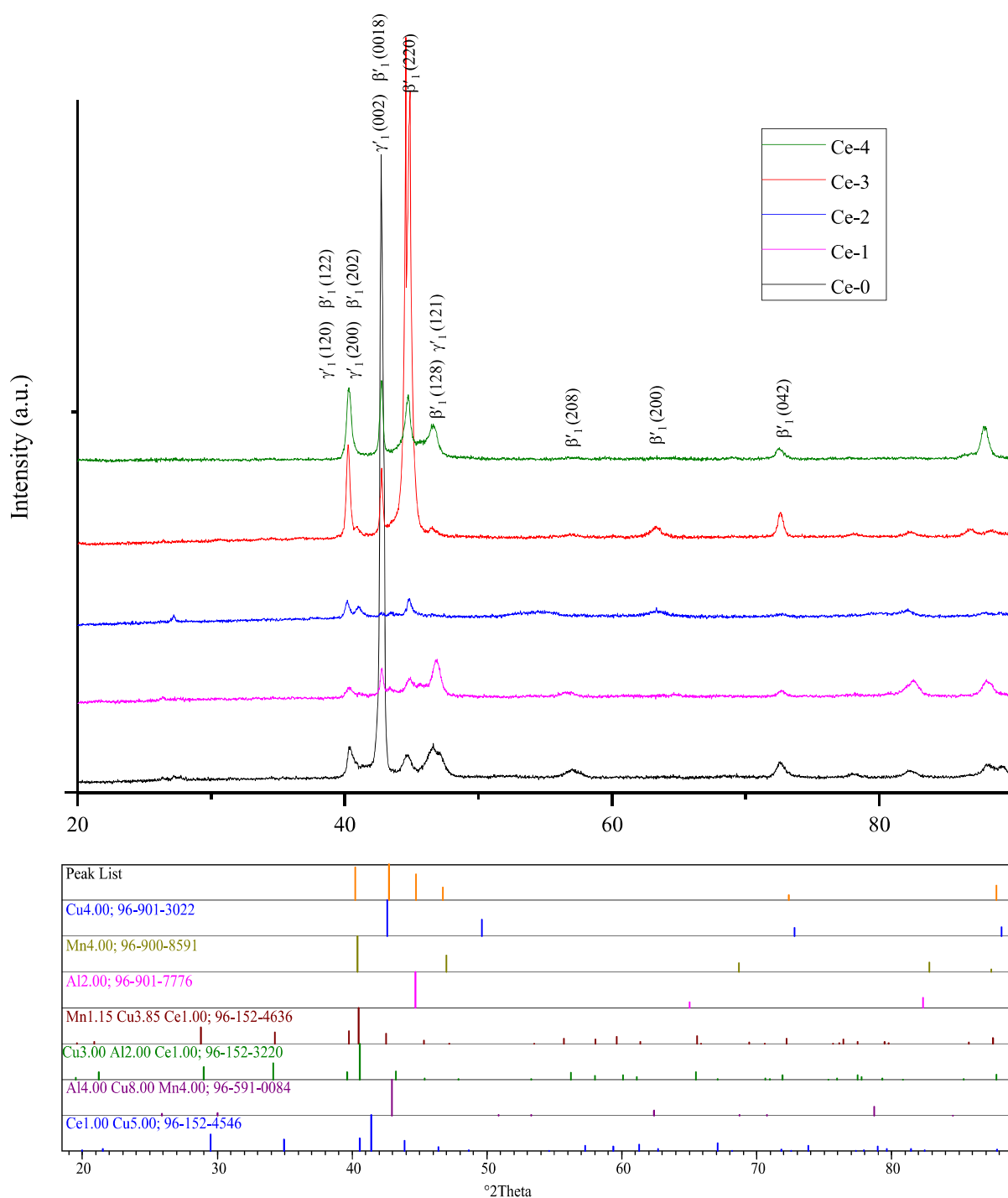


Fig. 3. XRD diffraction patterns of Cu-Al-Mn alloys before and after the additions of Ce.

literature, it has been reported that NTE contributions accumulate at grain boundaries, inhibiting grain growth and promoting the formation of new grains.¹⁶ The SEM-EDS and XRD analyses in our study also confirm that the Ce additive exhibits this effect. In Ce-2 with the use of more Al, Mn, and Ce (at.%, EDS), the average crystallite size decreased to the lowest 14.6 nm value among the others due to the formation of new phases as a result of more Ce

use, but the martensite crystallite size increased by 44.3 nm, which is higher than those of other Ce-added alloys, and the most interesting here is that the lattice strain of Ce-2 became the highest at 0.99%, among all the other alloys, which indicates that the highest shape memory capacity is in this alloy. The reason for this is because, in Ce-2, more Al and Mn (at.%, EDS) were used besides Ce, and more or more than enough Al and Mn resulted in

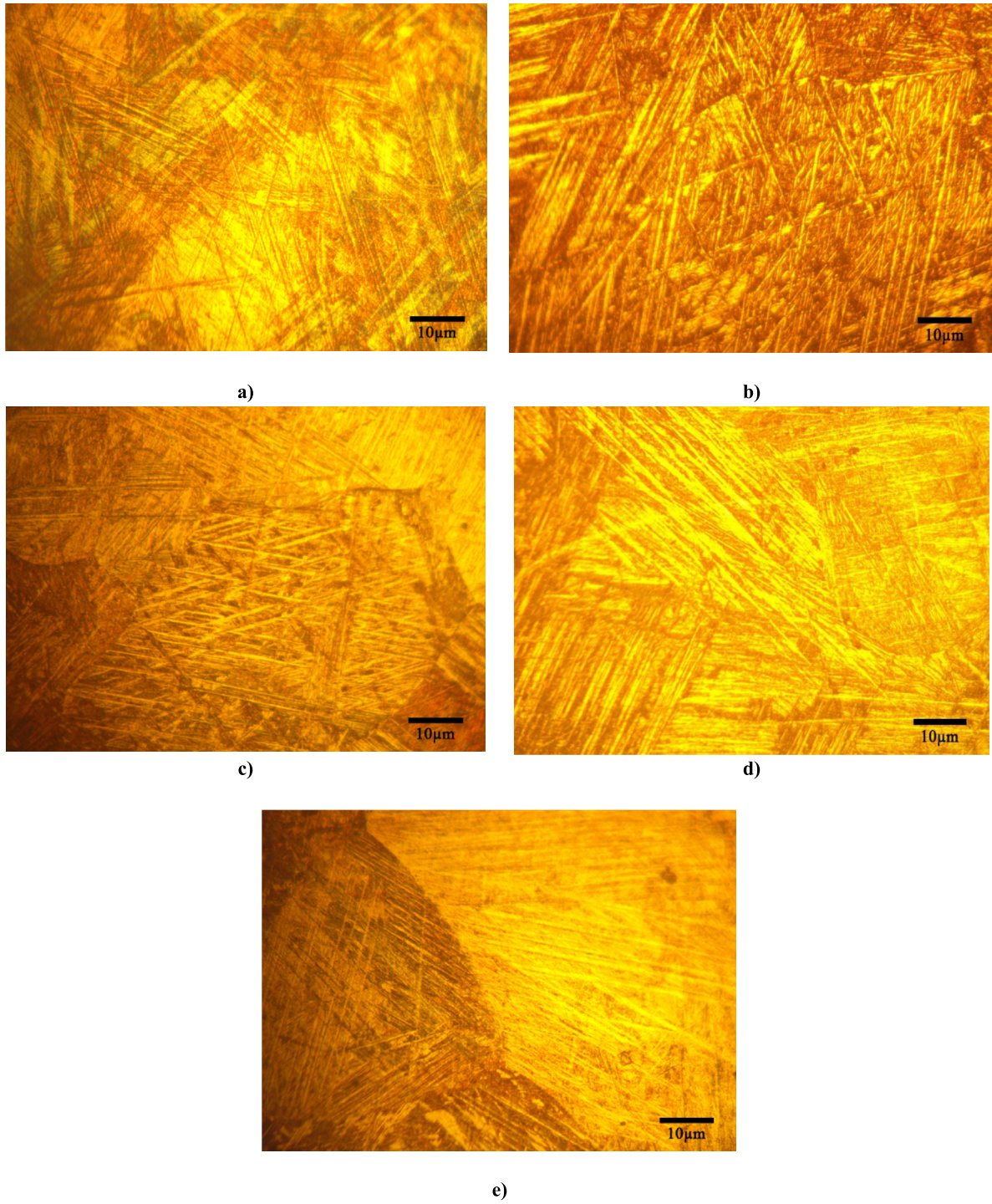


Fig. 4. Optical micrographs of CuAlMn $\pm$ Ce HTSMAs: (a) Ce-1 sample, (b) Ce-2 sample, (c) Ce-3 sample, (d) Ce-4 sample, (e) Ref sample.

the formation of more or better $L2_1$ austenite or β_1' martensite, thus the best crystallographic base mechanism for martensite transformation or shape memory among the others. It is noted that the e/a

ratio value of this alloy only falls in the e/a ratio range that gives the best shape memory properties in general.

Table III. Crystallographic data and some structural lattice parameters of the produced CuAlMn $\pm$ Ce HTSMAs

Crystal system	Cubic	Hexagonal	Hexagonal	Hexagonal
Space group	F m $\bar{3}$ m	P 6/m m m	P 6/m m m	P 6/m m m
a ($\text{\AA}$)	5.95	5.2490	5.2300	5.1310
b ($\text{\AA}$)	5.95	5.2490	5.2300	5.1310
c ($\text{\AA}$)	5.95	4.1800	4.2500	4.1240
Volume of cell ($\text{\AA}^3$)	210.64	99.74	100.68	94.03
Density (g/cm^3)	6.59	7.73	7.39	7.55
Reference Code ^a	96-591-0083	96-152-3220	96-152-4636	96-152-4546

^aBy Crystallography Open Database.**Table 4. Variations in crystal size and lattice strain parameters of the CuAlMn $\pm$ Ce HTSMAs**

Alloys ID	Avg. crystallite size	Crystallite size (of the highest martensite peak)	Lattice strain (%)
Ref.	17.34	58.8	0.72
Ce-1	24.84	31.1	0.34
Ce-2	14.6	44.3	0.99
Ce-3	15.66	12.7	0.61
Ce-4	19.1	36.8	0.45

The optical micrographs showing the surface morphologies of the CuAlMn $\pm$ Ce HTSMAs obtained under room-temperature conditions are given in Fig. 4. In these surface images, the thinner needle-like or V-like β_1' -type martensite and the fewer, thicker, and lath-like secondary γ_1' -martensite (shown with their labels in the Fig. 5) are clearly seen formed on each alloy surface in the grains and mostly grain boundaries.

The SEM images of the CuAlMn $\pm$ Ce alloy samples and elemental maps in these images are given in Fig. 5. The β_1' (18R) and γ_1' (2H) types of martensite structures formed in these alloys are clearly seen on these surface images of the alloy, and demonstrate the base crystallographic mechanism for the martensitic phase transformation or shape memory property in these alloys which have been built. The elemental maps show the homogeneous distributions of Cu, Al, and Mn with small and very few Al- or Mn-rich precipitates of less than 1 μm in size. These maps also show the homogeneous distribution of the Ce contents, but mostly it is the distribution of small Ce-rich particles in changing sizes changing from nano-scale up to 1 μm . This becomes more evident in the map of Ce-4 which shows a larger Ce-rich precipitation (which is labeled as Spectrum 30) due to the use of the largest Ce content in this alloy. These impurity-like Ce particles play a role called the “pinning

effect”. They slow the heat transfer speed in these alloys and block the martensitic transformations a bit like pins. As a result of this, the martensitic transformation temperatures increase.

The magnetic properties of the Cu-Al-Mn alloys with varying Ce content are illustrated in the M-H curves in Fig. 6. A significant change in magnetization is observed with Ce addition, which indicates a shift toward paramagnetic behavior in the doped samples. This shift is particularly evident when comparing the slope of the M-H curve in the Ce-doped samples with that of the Ref alloy. The addition of Ce introduces localized magnetic moments into the alloy matrix due to the unpaired f-electrons of Ce. These magnetic moments contribute to the overall magnetization of the material; however, the lack of a strong coercive field and remanent magnetization in the Ce-containing alloys suggests that the magnetic ordering is largely dominated by paramagnetic contributions. This is consistent with the expected behavior for RE elements like Ce, which typically exhibit paramagnetism due to the partially filled f-orbitals.²⁶ Moreover, the temperature dependence of the magnetic susceptibility indicates that the Ce-doped alloys retain their paramagnetic character across the measured temperature range. This observation suggests that Ce does not induce any ferromagnetic ordering at the concentrations studied. Instead, the

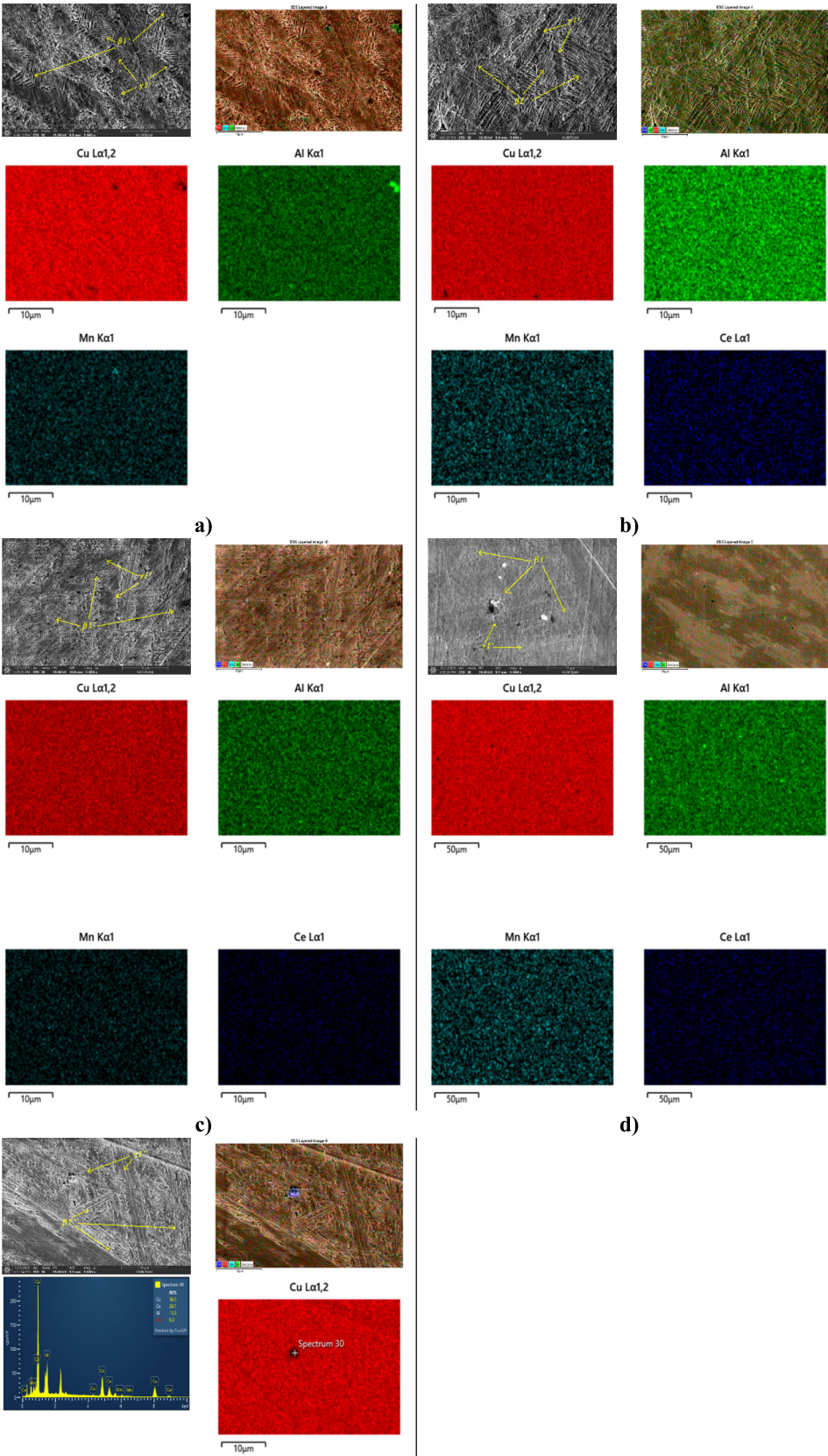


Fig. 5. The morphological SEM and elemental maps of (a) Ce-0 (Ref), (b) Ce-1, (c) Ce-2, (d) Ce-3, and (e) Ce-4 alloy samples.

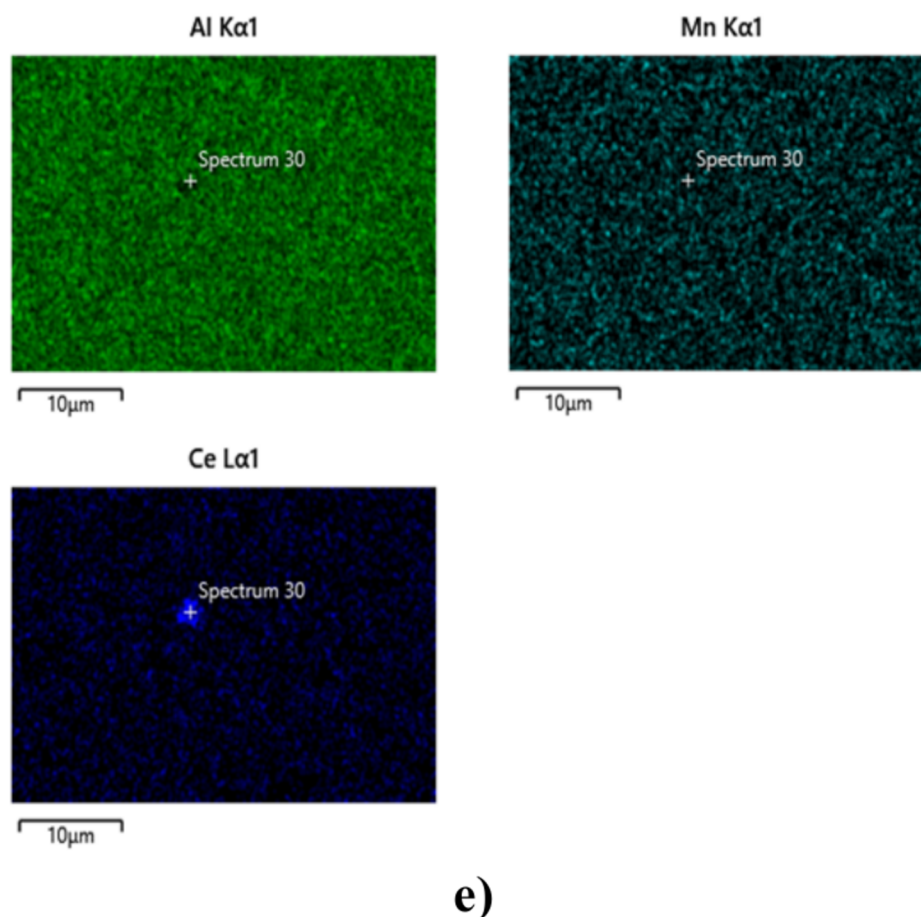


Fig. 5. continued

interaction between Ce and the Cu-Al-Mn matrix primarily enhances the paramagnetic response of the material, which could have implications for the alloy's potential applications in environments where both shape memory and magnetic properties are critical.

CONCLUSION

This study has investigated the effects of cerium addition on the transformation temperatures, martensitic properties, and microstructure of Cu-Al-Mn SMAs. The results show that adding CE increases the transformation temperatures, with the most significant rise in the Ce-3 alloy, where the start of martensitic transformation (A_s) reached 194.88 °C. This is attributed to the formation of new Ce-containing phases like $CeCu_5$ and $Mn_{1.15}Cu_{3.85}Ce$, which stabilize the parent phase and introduce internal stresses, raising the energy required for phase transitions. The presence and distribution of Ce in the microstructure were examined using SEM-EDS and XRD analyses. The results indicated

that Ce forms secondary phases such as $CeCu_5$ and $Mn_{1.15}Cu_{3.85}Ce$, which were identified in the XRD patterns and observed as fine precipitates in the SEM images. In microstructural analysis, Ce causes localized lattice distortions, initially increasing the crystallite size and lattice strain. However, excessive Ce concentrations (Ce-4) lead to over-stabilization of the secondary phases. The optimal Ce concentration (0.6 wt.% in Ce-2) enhances the stability and improves the shape memory properties without compromising phase transition behavior. The magnetic characterization results show that Ce shifts the material towards paramagnetic behavior by introducing localized magnetic moments that interact with the alloy matrix. The absence of significant coercive fields and remanent magnetization suggests that Ce mainly enhances paramagnetism.

In summary, the addition of Ce to Cu-Al-Mn SMAs offers a promising route for improving their high-temperature performance, phase stability, and mechanical properties. The findings of this study provide valuable insights into the role of cerium in tailoring the behavior of high-temperature SMAs,

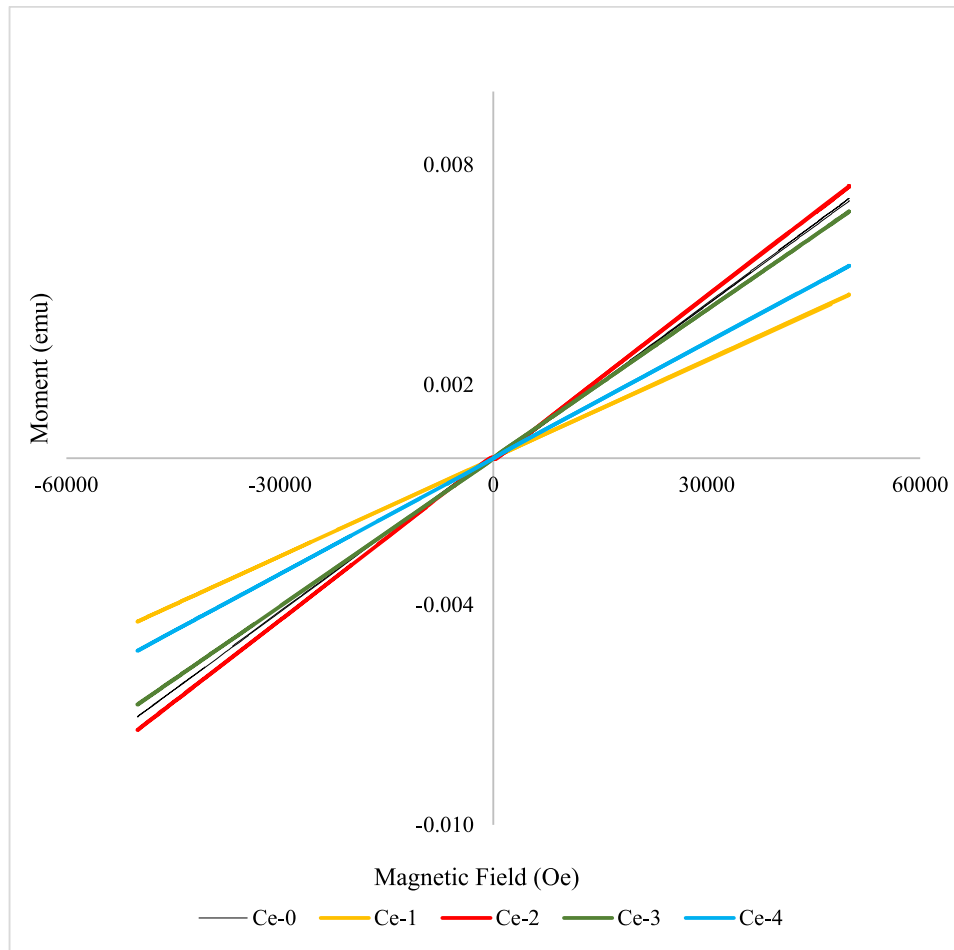


Fig. 6. M-H curves of CuAlMn $\pm$ Ce HTSMAs.

potentially guiding the development of advanced materials for industrial applications where thermal and mechanical stability are crucial.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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