The Ductility and Shape-Memory Properties of Ni–Mn–Ga–Cu Heusler Alloys

AGNIESZKA BRZOZA-KOS, EDUARD CESARI, and MACIEJ JAKUB SZCZERBA

The effect of Cu addition on crystal structure, compressive properties and shape-memory effect of $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ alloys was studied. With increasing Cu content, the type of crystal structure evolves following a sequence: $\text{L2}_1 \rightarrow 10\text{M} \rightarrow 2\text{M} \rightarrow 2\text{M} + \gamma$. Addition of Cu significantly improves room temperature ductility. In polycrystalline $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{17}\text{Cu}_8$ alloy, a full recoverable strain equal to 7 pct was achieved. High martensitic transformation temperature and large shape-memory effect makes this material potential candidate in high-temperature shape-memory applications.

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THE Ni–Mn–Ga Heusler alloys have been widely investigated in the last few decades as a potential material for actuator and sensor devices.^[1–4] This alloy exhibits shape-memory effect (SME) associated with the martensitic transformation, superelasticity, and magnetic field-induced strain (MFIS).^[5–10] In the off-stoichiometric Ni–Mn–Ga alloys, three types of crystal structures have been found, *i.e.*: five-layered (10M), seven-layered (14M), and a non-modulated martensite (2M).^[11,12] Many engineering applications require shape-memory alloys that operate at temperatures higher than 390 K. It is well known that in these alloys, martensitic transformation (MT) temperature is very sensitive to chemical modifications.^[13–16] Several papers revealed that a high MT temperature may be observed in the off-stoichiometric Ni_2MnGa alloys with enriched Ni or Mn content, showing their potentials as high-temperature shape-memory alloys (HTSMA).^[17,18] Also, the addition of a fourth element such as Cu or Fe to the ternary system can lead to a substantial increase of the MT temperature.^[19–21] The other drawback for practical applications of Ni–Mn–Ga alloys is their brittleness and low strength. Thus, improving the mechanical properties has become a priority in the development of these materials. Recent investigations have shown that the ductility of polycrystalline Ni–Mn–Ga alloys can be effectively improved through the formation of ductile γ

phase.^[22,23] In this paper, the influence of Cu additions instead of Ga on ductility and SME of quaternary $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ alloys were investigated.

Polycrystalline alloys of nominal composition $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1$ to 10 at pct) were prepared under argon protective atmosphere by arc melting method. The purity of nickel, manganese, gallium and copper was 99.95, 99.95, 99.99 and 99.999 pct, respectively. Each button-shaped ingot of about 8 g was re-melted four times to ensure good homogeneity. Also, an additional 5 wt pct of Mn was added to compensate for evaporation losses. Thereafter, the ingots were sealed into vacuum quartz ampules and annealed at 1173 K for 48 hours and then furnace cooled to ambient temperature. Due to the fixed content of Ni and Mn and increasing addition of Cu instead of Ga, the samples were hereafter referred to as Cu1, Cu2 and so on. The phase structure was identified at room temperature by X-ray diffraction (XRD) analysis using a Bruker D8-Discover with $\text{CoK}\alpha$ radiation. The microstructural observations were done by scanning electron microscopy (SEM) (Philips XL30). The volume fraction of γ phase and martensite were calculated from three SEM images taken in backscattered electron (BSE) mode at 1000 magnification and then processed using the ImageJ program. The mechanical properties and SME were measured at room temperature by uniaxial compression tests with a strain rate of 10^{-3}s^{-1} using an Instron 5566 machine. The rectangular samples of a height to width ratio of 3/2 for compression tests were cut out from bulk material using an electrical discharge machining. The lengths of the specimen were measured before loading (l_0), after unloading (l_1) and after heating to a temperature 100 K above the austenite finish temperature (A_f) for 15 min (l_2) using a micrometer with an accuracy of 0.001 mm. The permanent strain after unloading (ϵ_p) and the recovered strain due

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to the SME (ε_{SME}) were calculated as: $\varepsilon_p = \ln \frac{l_0}{l_f} \cdot 100pct$ and $\varepsilon_{SME} = \ln \frac{l_2}{l_1} \cdot 100pct$, respectively. The recoverable rates were calculated as: $R = \varepsilon_{SME} / \varepsilon_p$. Moreover, from stress–strain curves, the twinning stresses (σ_{tw}) were specified by measuring the stress level at half of the ε_p strain.

The X-ray diffraction technique was used to determine the type of crystal structure at room temperature. The type of crystal structure evolution and the corresponding lattice parameters are collected in Table I. In the first sample (Cu1), the major peaks were indexed as those of L2₁ cubic structure (parent austenite phase) with the lattice parameters of $a = 5.8282 \text{ \AA}$. When Cu content increases to 2 at pct, some new peaks from the second phase were detected. Due to their weak intensity, only the lattice parameters of the parent austenite phase could be calculated as $a = 5.8346 \text{ \AA}$. In the subsequent sample (Cu2.75), a pure 10 M martensite structure appeared. Upon further alloying, another transformation was detected, to the so-called non-modulated martensite phase, which has been observed in samples from Cu4 to Cu8. It is well known that the chemical modifications introduce changes in the tetragonality of the martensite unit cell. In this case, the lattice parameter “a” decreases from 5.4857 to 5.3840 $\text{\AA}$, and “c” increases from 6.5327 to 6.7241 $\text{\AA}$ for Cu4 and Cu8, respectively (Figure 1), keeping the volume constant. Samples with the highest amount of Cu addition exhibit additional diffraction peaks apart from the peaks coming from the martensite phase only. The new phase was confirmed to be the γ phase with a face-centered cubic structure.^[18]

To assess the influence of substitution of Ga by Cu on mechanical properties and SME, compression tests were carried out at room temperature. The representative stress–strain curves are presented in Figure 2(a). The compression curve of Ni₅₀Mn₂₅Ga₂₄Cu₁ showed the superelastic character with forward and reverse martensitic transformation.^[24] The stress required for the parent austenite phase to undergo stress-induced martensitic transformation was calculated as about 250 MPa. The stress–strain curve of Ni₅₀Mn₂₅Ga₂₃Cu₂ shows some

fluctuations. Due to the mixed character of the microstructure of this sample, the first plateau could be associated with the martensite deformation, whereas the second would represent the austenite to martensite transformation. In this particular case, the stress of 60MPa measured at half permanent strain (ε_p) corresponds to the parent austenite $\rightarrow$ martensite ($A \rightarrow M$) transformation.

The stress–strain curves of samples from Cu2.75 to Cu10 consist of three stages associated with the elastic deformation of the multivariants, reorientation of martensitic variants and/or detwinning, and the elastic and plastic deformation of fully reoriented martensites. Figure 2(b) shows the twinning stress values that increase when the amount of Cu also increases. Moreover, the substitution of Ga by Cu brings significant improvement of room temperature ductility of Ni–Mn–Ga–Cu alloys, which is important in case of potential applications (Figure 3(a)). Furthermore, in alloys that exhibited one type of crystal structure at room temperature, namely the 2M martensite (*i.e.* from Cu4 to Cu8), a linear behavior in ductility improvement upon an increase of Cu concentration was observed. The occurrence of the second phase in samples with the highest amount of Cu instead of Ga brings a significant increase in ε_p strain. To obtain the shape-memory behavior, after compression tests samples were heated, and then their recovery strain, a mean value of recovery strain and recovery ratios were measured and plotted in Figure 3(b).

The maximum recoverable strain between the parent austenite phase and martensite is determined by the magnitude of the shear required to go from one structure to the other. Moreover, the theoretical values of achievable reversible strain are lower for modulated martensitic structures than for non-modulated crystal structure. This is the reason why we observe lower values of the SME of samples with a small amount of Cu addition (up to Cu2.75), where the modulated structure predominates. The recoverable strain was increasing together with the increase of Cu content for samples where the single 2M martensite phase was observed at room temperature. Moreover, the tetragonality of the martensite unit cell (see the c/a ratio in Table 1) also increases upon alloying. When the c/a ratio of the martensite unit cell deviates further away from 1, the transformation strain increases. A high c/a ratio signifies a greater distortion from the cubic parent austenite phase, and thus a higher SME with increasing Cu addition may be observe in Ni–Mn–Ga–Cu alloys. Furthermore, the Ni₅₀Mn₂₅Ga₁₇Cu₈ alloy after heating exhibits a full recoverable strain. Furthermore, the SME value of 7 pct observed in this polycrystalline alloy is greater than values previously reported in the ternary Ni–Mn–Ga system, even for single crystals.^[18,25]

Many engineering applications need shape-memory alloys to function at higher temperatures (*i.e.*, higher than 473 K), as a response to the demand from the different highly technological areas, such as automotive or aerospace industries. Currently, several alloy systems have been investigated, such as FeMnSi-, CuAlNi-, NiMn-, NiAl-, Ti(Pt, Pd, Au,-) and NiTi-based^[26,27] but until now a number of problems (*e.g.*, martensite

Table I. Type of Crystal Structure and Lattice Parameters of Ni₅₀Mn₂₅Ga_{25-x}Cu_x (x = 1 to 10 at pct) Alloys at Room Temperature

Alloy	Crystal Structure	Lattice Parameters		a/c c/a
		a [$\text{\AA}$]	c [$\text{\AA}$]	
Cu1	L2 ₁	5.8282	—	—
Cu2	L2 ₁	5.8346	—	—
	10M	—	—	—
Cu2.75	10M	5.9305	5.5957	1.0598
Cu4	2M	5.4857	6.5327	1.1909
Cu5	2M	5.4476	6.6201	1.2152
Cu6	2M	5.4182	6.6739	1.2317
Cu7	2M	5.3971	6.7057	1.2425
Cu8	2M	5.3840	6.7241	1.2489
Cu9	2M	5.3814	6.7565	1.2555
Cu10	2M	5.3736	6.7287	1.2522

Fig. 1—Evolution of lattice parameters of $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1$ to 10 at pct) alloys.

Fig. 2—(a) Compressive true stress–true strain curve of $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1, 2, 2.75, 4, 9$ at pct) tested at room temperature. (b) Evolution of stress required for the parent austenite phase to undergo a stress-induced martensitic transformation for Cu1 and Cu2 and the twinning stress for the rest of the samples, *i.e.*, from Cu2.75 to Cu10.

stabilization, thermal and thermomechanical instability) have remained unresolved in these alloys. In our previous work,^[19] we have reported that the increasing amount of Cu instead of Ga also increases the MT temperature up to 720 K for the Cu8 sample (Figure 4), making this alloy a promising candidate for industrial application as HTSMA. Unfortunately, further alloying promotes the formation of the so-called γ phase that leads to a reduction of recoverable strain. In addition, a slight decrease of martensitic start transformation

temperature by -15 K in dual-phase samples was observed. This effect may be a consequence of additional internal stresses generated by the lattice incompatibility between the two phases.

The negative effect of the γ phase on shape recovery of Cu10 alloy is more remarkable than in the case of Cu9 alloy. The volume fractions of γ phase were measured to be about 12 and 24 pct for Cu9 and Cu10, respectively. The γ phase contribution caused improvement of the materials ductility. However, it also drastically decreases

Fig. 3—(a) Permanent strain after unloading of $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1$ to 10 at pct) alloys. (b) Recovered strains of $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1$ to 10 at pct) alloys upon heating to 100 K above austenite finish temperature (A_f).

Fig. 4—Compositional dependence of martensitic start transformation temperature in $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{25-x}\text{Cu}_x$ ($x = 1$ to 10 at pct) alloys.

the SME itself. The recoverable rates showed similar behavior as recoverable strain during the substitution of Ga by Cu. The rather unexpected low value of R for $\text{Ni}_{50}\text{Mn}_{25}\text{Ga}_{22.25}\text{Cu}_{2.75}$ may be caused by discontinuities of surface that have been observed after compression test. The modulated structures (10M, 14M) of Ni-Mn-Ga alloys are more brittle than the non-modulated ones, which could be the reason for the low value of SME and R in this particular case.

Based on the experimental results, the following conclusion can be drawn:

- The substitution of Ga by Cu introduces changes in the type of crystal structure and the tetragonality of the unit cell, which increases with increasing Cu addition.
- The room temperature ductility of Ni-Mn-Ga-Cu alloys can be greatly improved through the addition of Cu and formation of γ phase. However, the introduction of the latter phase significantly decreases the SME.

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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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