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Suppressing heating rate-dependent martensitic stabilization in ductile Cu-Al-Mn shape memory alloys by Ni addition: An experimental and first-principles study

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ABSTRACT

The present paper aims to suppress the heating rate-dependent martensitic stabilization of ductile Cu-Al-Mn shape memory alloys through restricting the mobility and thus the behavior of vacancies. A combined study based on first-principles calculation and experimental results were presented to unveil the effect of Ni addition into ternary Cu-Al-Mn alloys on the bonding force between atoms. The results showed that additional nearest neighbor bond between Ni and Al atoms in quaternary Cu-Al-Mn-Ni alloys can be produced. The addition of Ni (≤ 2 at.%) into ternary Cu-Al-Mn alloys can not only efficiently increase the shape memory effect, but also suppress the occurrence of heating rate-dependent martensitic stabilization. The addition of 2 at.% Ni improved the shape memory effect of ternary Cu-Al-Mn alloys from 85% to 92% when heated at 20 k/min. The shape memory effect of ternary Cu-Al-Mn alloys dropped to 10% as the heating rate decreased to 1 K/min, but it remain at 92% even when the heating rate was sufficiently lowered to 0.01 K/min after the addition of 2 at.% Ni.

1. Introduction

Shape memory alloys (SMAs) are a unique class of functional materials with the potential of providing high power output as actuators and sensors [1]. Currently, because of the extraordinary shape memory property, dimensional stability and biocompatibility, Ni-Ti alloys are the most widely utilized SMAs [2–4]. Nevertheless, expensive alloying ingredients and low cold-workability restrict their widespread use. Compared with Ni-Ti SMAs, Cu-based SMAs are relatively inexpensive and Cu-Al-Mn SMAs with Al content below 18 at.% are the most commercial ones due to their good shape memory effect (SME) and excellent ductility [5–7]. In recent years, many attempts to put ductile Cu-Al-Mn SMAs into practical use have been made, such as the guidewire for medical use [8,9]. Unfortunately, the existence of heating rate-dependent martensitic stabilization restricted the application of ductile Cu-Al-Mn alloys [10,11]. As revealed by the work of Yang et al. [11], as the heating rate decreased form 20 K/min to 1 K/min, the SME of 15 min up-quenched Cu-17.0Al-10.5Mn (at.%, here and after) alloy sharply dropped form 84% to 10% because of the occurrence of martensitic stabilization.

Martensitic stabilization occurs usually after ageing in the martensitic state, resulting in the variation of transformation temperatures or/and the deterioration of SME [12]. Over the last decades, numerous studies have been conducted to reveal its origin. Currently, a common sense has been reached that the occurrence of martensitic stabilization is closely related to the behaviors of vacancies, such as kinetic stabilization (pinning of moving interfaces by vacancies) [13,14], static stabilization (a change in long-range or short-range order brought about by the redistribution of vacancies) [15,16] and symmetry-conforming short-range order (atomic rearrangement within the same sublattice of martensite through the movement of vacancies) [17,18]. Therefore, lowering vacancy concentration through up/step-quenching treatment was proposed to suppress the occurrence of martensitic stabilization [19–21]. Nevertheless, the work of Yang et al. [11] revealed that the duration of up/step-quenching treatment needed to suppress martensitic stabilization depended on the recovery heating rate. For instance,

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as the recovery heating rate decreased from 20 K/min to 1 K/min, the up-quenching time need to be increased form 15 min to 180 min to suppress martensitic stabilization in Cu-17.0Al-10.5Mn alloy. In terms of cost and the strengthening effect of vacancies on matrix, it is not advisable to increase the up/step-quenching time infinitely to avoid the occurrence of heating rate-dependent martensitic stabilization. Therefore, instead of lowering the vacancy concentration, restricting the vacancy behavior was considered in this paper to suppress the occurrence of heating rate-dependent martensitic stabilization in ductile Cu-Al-Mn alloys.

The migration of vacancies accomplishes through the movement of atoms. The mobility of atoms depends on the bonding force between atoms. Two important factors in determining the bonding force between atoms are the distance and the chemical interaction between atoms. For the ductile Cu-Al-Mn alloys, Al and Mn atoms were next nearest neighbored in a $L2_1$ structure [22]. Nakata et al. clarified that the nearest neighbor bond between Ni and Al atoms can be produced in the $L2_1$ structure [23]. Moreover, the work of Tan et al. revealed that the interaction parameter between Ni and Al atoms (−90.3 kJ/mol) was higher than that between Mn and Al atoms (−76.8 kJ/mol) [24]. Therefore, we attempt to enhance the bonding force between atoms and thus restrict the behavior of vacancies through the addition of Ni into ternary Cu-Al-Mn alloys. In the present paper, the effect of Ni addition on bonding force between atoms was theoretically analyzed based on the calculation results from first-principles. The corresponding experimental results of the Ni addition were also presented to confirm the theoretical analysis.

2. Calculation

Fig. 1 schematically represented the unit cell of $L2_1$ structure with three typical sites labeled as A, B and C [22]. For the ternary Cu-Al-Mn alloys, Al and Mn atoms preferentially occupied B and C sites, respectively, producing the next nearest bond between them [23]. Particularly, taking the non-stoichiometric Cu-17.0Al-10.5Mn alloy as an example, it can be seen that Cu and Al atoms provided a fertile environment for the Mn atoms. The work of Sutou et al. indicated that the element Ni was completely soluble in the ductile Cu-17Al-10Mn-xNi ($x \leq 2$ at.%) alloys, possessing single $L2_1$ structure without the formation of brittle precipitates [25]. Consequently, it can be expected that there were two potential sites for Ni in Cu-17.0Al-10.5Mn-xNi ($x \leq 2$ at.%): i) Substitution of Cu, Al or Mn atoms in original $L2_1$ structure; ii) Matching the excess Cu and Al atoms to form new $L2_1$ structure.

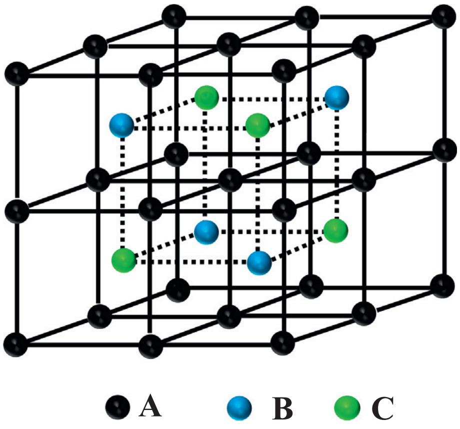

Fig. 1. Unit cell of $L2_1$ structure with three typical kinds of atomic sites (A, B and C sites).

As well known, the dopant tended to occupy an energetically favorable site. Here, we theoretically investigated the occupation of Ni atoms in $L2_1$ structure based on the density functional theory (DFT), which was performed using the Vienna Ab initio Simulation Package (VASP) [26,27]. The Projector Augmented Wave (PAW) potential was used for electron-ion interaction and the Perdew-Wang (PW91) form of generalized gradient approximation (GGA) was employed to describe exchange-correlation approximation [28]. To obtain the accurate total energy of the system, the wavefunctions were expanded in a plane-wave basis with cutoff-energy up to 600 eV [29] and the irreducible Brillouin zone was sampled with a regular Monkhorst-Pack grid of $13 \times 13 \times 13$ k-points till energy convergence < 1 meV/atom [30]. All atoms and lattice constants were allowed to be fully relaxed approaching the ground-state of system using the conjugate gradient algorithm until the magnitude of Hellmann-Feynman force on each atom converged to < 0.03 eV/Å and energy converged to < 10^{-5} eV/Å [31]. The relatively energetic stabilities of different stoichiometries were evaluated by their formation enthalpies relative to the products of dissociation into constituent elements (i.e. solidified phases of Cu, Al or Ni(Mn)) [32]:

$$\Delta E = (E_{Cu_xAl_yNi_z} - xE_{Cu} - yE_{Al} - zE_{Ni})/(x + y + z) \quad (1)$$

where x, y, z donated the number of atoms in the composite, and E_A (A = Cu, Al, or Ni) was the enthalpy of bulk counterpart. A negative ΔE indicated stability or metastability of a structure. The relative stabilities were as follows:

1. Cu(Ni)-Al-Mn: −0.21 eV/atom (*Ni substitutes Cu*)
2. Cu-Al(Ni)-Mn: −0.13 eV/atom (*Ni substitutes Al*)
3. Cu-Al-Mn(Ni): −0.17 eV/atom (*Ni substitutes Mn*)
4. Cu-Al-Ni: −0.39 eV/atom (*Ni matched excess Cu and Al*)

Based on the calculated results, it was found that Ni atoms were energetically favorable to match excess Cu and Al atoms to form ternary Cu-Al-Ni compound in the quaternary Cu-17.0Al-10.5Mn-xNi ($x \leq 2$ at.%). Thus, Ni atoms preferentially occupied both B and C sites in the $L2_1$ structure, enclosing by four nearest neighbored Al atoms in the A site [23]. Therefore, the additional nearest neighbor bond between Ni and Al atoms was produced. Consequently, it can be expected that the bonding force between atoms was remarkably improved and thus the behavior of vacancies was restricted through the addition of Ni into ternary Cu-Al-Mn alloys.

3. Material and Methods

Alloys with different Ni contents were prepared in vacuum induction furnace using high pure Cu (purity > 99.9%), Al (purity > 99.9%), Mn (purity > 99.9%) and Ni (purity > 99.9%). After homogenization at 1093 K for 23 h, the ingot was forged into flats at 1073 K. The chemical compositions of the homogenized alloys measured by wet-chemical analysis were listed in Table 1. All samples cut from the flat were solution treated at 1123 K for 15 min and then directly quenched into water at room temperature (RT), which was about 293 K. Immediately, all the as-quenched samples were held at 373 K for 15 min, i.e. up-quenching treatment. The martensitic transformation temperatures of 15 min up-quenched samples were investigated by the differential scanning calorimetry using Netzsch 200PC calorimeter at a heating/cooling rate of 20 K/min. The transformation temperatures

Table 1
Chemical compositions of the homogenized alloys. ± indicates the standard deviation over 3 measurements.

Alloys	Composition (at.%)			
	Al	Mn	Ni	Cu
0Ni	17.0 ± 0.4	10.5 ± 0.3	/	Bal.
1Ni	17.3 ± 0.3	10.7 ± 0.5	0.7 ± 0.4	Bal.
2Ni	17.2 ± 0.4	10.4 ± 0.3	2.1 ± 0.5	Bal.