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Structural and magnetocaloric effect studies of $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ Heusler alloys

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ABSTRACT

Cubic phases of bulk Mn-rich $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ Heusler alloys (with $x = 0$, 0.5, 1 and 2) were fabricated by arc melting and their temperature dependent magnetic properties studied. The addition of Ti enhanced the saturation magnetization. The coercive fields and the exchange bias fields increased at lower temperature. The coercive field attains a maximum value at a temperature T_{MC} below which the exchange bias field is higher. The bifurcation between the zero-field cooled and field cooled magnetization curves at low temperatures show evidence of transition from ferromagnetic (FM) to antiferromagnetic (AFM) interactions with large exchange bias fields as large as 496 Oe and 532 Oe for $x = 0.5$ and 1 alloys respectively at 10 K. The temperature dependence of coercivity appears to switch from noninteracting FM particles to interacting FM and AFM magnetic phases below, T_{MC}, and it is reported here for the first time. A first order magnetic transition occurs for $x \leq 1$ as deduced from the thermal hysteresis in the ZFC-FC measurements. We suspect coexistence of martensite and an austenite phases in all alloys, except for $x > 1$ which shows a second order magnetic transition. The austenitic Curie temperature T_C^A decreased from 282 K to 258 K. The martensitic transition temperature also decreases for $x \leq 1$. Peak magnetic entropy changes of 29 J kg^{-1} K^{-1}, 21 J kg^{-1} K^{-1} and 32 J kg^{-1} K^{-1} at 5 T were estimated from the magnetic isotherms for $x = 0$, 0.5 and 1 with corresponding refrigerant capacities of 217 J kg^{-1}, 134 J kg^{-1} and 77 J kg^{-1} respectively.

1. Introduction

The physics and potential applications of Ni – Mn – *M* (where *M* = Ga, In, Sn, and Sb) Heusler shape memory alloys have given rise to research interest in investigating these materials which are interesting because they are rare-earth-element-free and are economical to produce. In addition to fundamental studies, the alloys show potential applications as actuators, solid state refrigerants and magnetoresistance materials [1–12]. They also exhibit exchange bias effect due to the antiferromagnetically coupled excess Mn atoms in the *M* sites and surrounding Mn atoms on regular Mn sites [3,11,13–15]. Depending on the synthesis conditions and compositions, these alloys can crystallize in the austenite (high temperature), martensite (low temperature) phases or in mixed phase. This has an overall effect on the magnetic properties [5,6,14,16–18]. The magnetocaloric effect (MCE) and other interesting properties usually occur at the magneto-structural phase transitions. However, the large refrigerant capacity, negligible thermal and magnetic hysteresis associated with second order magnetic transitions also make the alloys interesting to study. The phase transitions are observed at certain critical temperatures known as the martensitic transition temperature T_M and at the austenitic Curie temperature, T_C^A. First-order magnetic transitions usually occur at T_M while second-order transitions are associated with T_C^A [1]. The magnetic entropy change, ΔS_M and the refrigerant capacity (RC) at T_M and T_C^A are critical parameters for consideration in materials to be used for solid-state refrigeration.

Off stoichiometric Ni – Mn – Sn alloys have also shown magnetocaloric effect [1,14,19]. The Mn-rich alloys exhibit remarkable properties due to localized Mn moments. Their magnetic properties are largely dependent on the Mn-Mn distance which result in a negligible 3*d*-band electron overlap between neighboring Mn atoms [9]. The magnetic properties can be modified by the synthesis method, changes in the elemental compositions or substitutions at the Ni and Mn sites by other elements [3,8,9,11,12,18]. Melt-spun samples show improved magnetocaloric effect (MCE) and require drastically reduced homogenizing annealing time of

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the samples as reported by Zhang et al. [19] who investigated the magnetic refrigeration properties in Mn-rich $Ni_{43}Mn_{46}Sn_{11}$ ribbons annealed from 0 to 180 min. They obtained a magnetic entropy change and refrigeration capacity from 18.4 J kg^{-1} K^{-1} to 43.2 J kg^{-1} K^{-1} and from 107 J kg^{-1} to 221 J kg^{-1} respectively. The addition of Co increased T_C^A of Ni-rich $Ni_{48.5-x}Co_xMn_{36}Sn_{14.5}$ alloys from 317 K to 341 K while the martensitic transition temperature decreased [20]. There are similar increasing effects in Fe substituted $Ni_{40.5-x}Fe_xMn_{50}Sn_{9.5}$ and $Mn_{50-x}Fe_xNi_{39.5}Sn_{10.5}$ alloys [6]. However, this appears to be almost temperature independent for Cr substituted $Mn_{37-x}Cr_xNi_{50}Sb_{13}$ alloys [21]. The sensitivity of the characteristic temperatures observed for Fe substituted $Ni_{50-x}Fe_xMn_{39}Sn_{11}$ alloys also show that the magnetic properties of these alloys can be tuned either by elemental composition or substitution [12]. Chen et al. [22] have studied the effect of Ti substitution of Mn on the martensitic transformation of $Mn_{48-x}Ti_xNi_{42}Sn_{10}$ alloys. The martensitic transition and the austenitic Curie transition temperature were reported to decrease. The magnetization was found to decrease with increase in Ti content and the thermal hysteresis collapsed for $x = 4$. Comparable results for $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ have been reported by Dong et al. [23]. The current work extends these studies in order to better understand the effects of structural properties on the observed magnetic transitions from second order to first order. With this objective in mind, we investigated the structural stability, magnetocaloric and exchange bias effects of Ti substituted $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ Heusler alloys.

2. Experimental details

Polycrystalline ingots of $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ alloys at $x = 0$, 0.5, 1 and 2 were prepared on an Edmund Bühler MAM1 arc-melting instrument. The stoichiometric amounts of pelletized Mn, Ni, Ti, and Sn powders with purity >99% were used. About 1% extra mass of Mn was added to compensate for the possible evaporation of Mn atoms during synthesis. The preparation of the samples was carried out in a chamber of high purity argon atmosphere. The chamber was flushed with argon gas at least 4 times to minimize oxidation of the samples. The samples were re-melted for 4 times and after each instance of melting, the sample was flipped-over in readiness for subsequent arc melting which was performed on a water-cooled copper plate. We sealed the samples in quartz tubes under vacuum atmosphere and annealed them at 900 °C for 24 h. Finally, the samples cooled naturally to room temperature. The phase and structural information were obtained by using a PANalytical X-ray diffractometer equipped with a Co-Kα radiation source. High resolution surface electron microscopy (HRSEM) was used to investigate the morphology of the samples. The temperature dependent magnetizations were measured using a vibrating sample magnetometer (VSM) mounted on a Cryogenic Limited mini cryogen free measurement system in the temperature range of 2–320 K.

3. Results and discussions

3.1. Crystal structure

Fig. 1 shows the room temperature XRD patterns for the as-melted $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ alloys for, $x = 0$, 0.5, 1 and 2. The characteristic crystalline peaks which correspond to the high-symmetry austenite phase for all the samples, suggest that the low-symmetry martensitic phase is below room temperature [22]. The strong intensity of the (220) peak is an indication of well-developed preferred orientation and the textured polycrystalline nature of the samples [17]. The samples show single phase of the

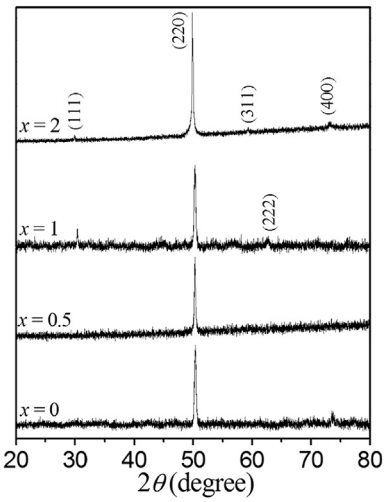

Fig. 1. Room temperature X-ray diffraction patterns for, $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ alloys.

$L2_1$ cubic structure of the Fm3m space group [19,24]. The (220) peak for $x = 2$ crystallized with a slight shift in the peak to a lower 2θ angle. The calculated lattice parameters a based on the (220) highest intensity peaks are found to be 5.958 (6) Å, 5.963 (9) Å, 5.967 (5) Å and 6.004 (11) Å for $x = 0$, 0.5, 1 and 2 respectively. Fig. 2, shows that the lattice parameter obeys Vegard's rule [25] except for $x = 2$ where we find a slight shift of the peak to lower 2θ angle.

The increase in a is due to the replacement of smaller size Ni atoms (radius 0.78 Å) by Ti (radius 0.86 Å) [26,27]. This negative chemical pressure effect from the Ti atoms might be the cause of the lower value in 2θ for the (220) peak of the sample at $x = 2$ [28]. The HRSEM images in Fig. 3 confirm the well-textured polycrystalline nature of the samples. The addition of Ti reveals a more regular pattern of layers across the samples.

3.2. Characterization of the phase transitions

Fig. 4 shows the zero-field cooled (ZFC) and field cooled (FC) measurements in the temperature range of 2–320 K under an applied magnetic field of 100 Oe. The ZFC magnetization measurements were performed by first cooling the sample from 320 to 2 K in zero-magnetic field and then a magnetic field of 100 Oe was applied to the sample at 2 K. The magnetizations were recorded during the warming up of the sample to 320 K. FC measurements were performed while cooling the sample from 320 to 2 K

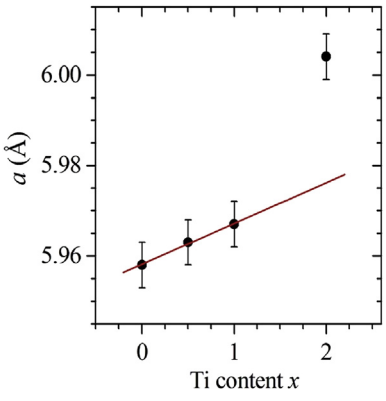

Fig. 2. Lattice parameter dependence of Ti content x for, $Ni_{43-x}Ti_xMn_{46}Sn_{11}$ alloys.