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Order–disorder transition of vacancies from the full- to the half-Heusler structure in $Ni_{2-x}MnSb$ alloys

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ABSTRACT

The thermal transformations and crystal structures in the ordered bcc phases appearing in $Ni_{2-x}MnSb$ alloys have been investigated. Thermo-analyses on NiMnSb($x = 1$) show three λ-shaped peaks suggesting a magnetic and chemical ordering transitions at approximately 450, 865 and 965 °C. With decreasing x, the first and second peak temperatures gradually decrease, while the third one increases. By Z-contrast imaging technique, it was confirmed that the second peak corresponds to the order-disorder transition of vacancies from the $L2_1$ to the $C1_b$ structure.

1. Introduction

In the Ni–Mn–Sb system, there are two kinds of similarly ordered bcc phases, the half-Heusler (HH) NiMnSb phase with the $C1_b$ (space group: F-43m) structure and the full-Heusler (FH) Ni_2MnSb phase with the $L2_1$ (space group: Fm-3m) structure. The HH-NiMnSb alloy is well known as a candidate for half-metallic ferromagnetism that can be applied in spintronic devices [1]. Off-stoichiometric FH-Ni_2MnSb alloys are reported [2] to have ferromagnetic shape memory properties associated with a martensitic transformation accompanying a large change of magnetization. Fig. 1(a) and (b) show a schematic illustration of the ordered bcc structures consisting of four equivalent FCC sublattices: A, B, C and D. In the FH-Ni_2MnSb structure, the Ni atoms occupy both the A and C sites, and the Mn and Sb atoms the B and D sites, respectively, as shown in Fig. 1(c). In contrast, in the HH-NiMnSb structure the C site that was one of the Ni sites in the FH structure becomes occupied by vacancies, as shown in Fig. 1(d).

Using mainly X-ray and neutron diffraction (XRD and ND) techniques the crystal structure and magnetic properties of alloys with intermediate compositions, i.e., $Ni_{2-x}MnSb$ (x = 0–1.0), have been systematically investigated by Webster and Mankikar [3]. According to their experimental results, the HH structure is basically stable over the whole composition range with the vacancies having a strong tendency to occupy the C site, even for compositions close to Ni_2MnSb ($x = 0$). On the other hand, it was also reported that even in the stoichiometric NiMnSb alloy, the degree of atomic order depends on the heat-treatment and that a large number of vacancies occupy not only the C site, but also the A site [4]. This observation suggests that the $Ni_{2-x}MnSb$ alloys may exhibit an order-disorder transition from the $L2_1$ to the $C1_b$ structure due to ordering of vacancies, which at elevated temperatures are randomly dispersed between the A and C sites. It was also reported by Webster and Mankikar [3] that the spontaneous magnetization of $Ni_{2-x}MnSb$ alloys annealed at 700 °C increased with increasing x below $x = 0.4$, while decreasing for $x > 0.5$. Since the magnetic properties in ordered alloys are usually affected by the degree of atomic order [5], this tendency also suggests the existence of a phase transition between the $C1_b$ and another ordered phase that belongs to a different space group, such as the $L2_1$.

In this paper the thermal transformation and crystal structures of the ordered bcc phases in $Ni_{2-x}MnSb$ alloys were investigated by thermal analysis and the observation of atomic columns using high

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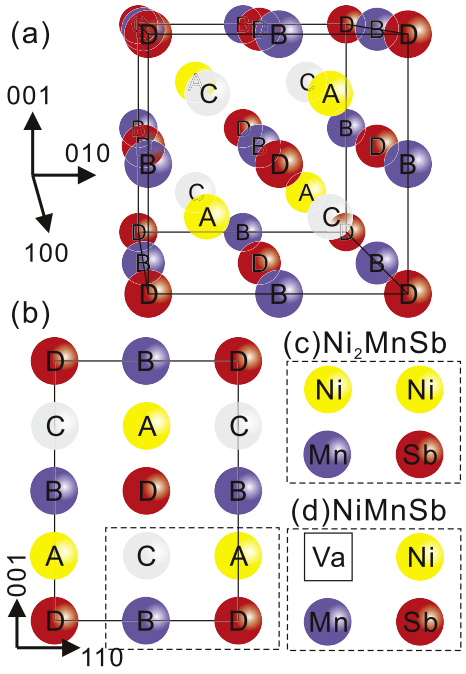

Fig. 1. A schematic drawing of the bcc-based crystal structure. (a) and (b): the atomic site configurations of the 4 fcc sublattices that describe the Heusler structure. (c) and (d): represent the atomic configurations in <110> projection for the full-Heusler Ni_2MnSb and the half-Heusler NiMnSb structures, respectively.

angle annular dark field-scanning transmission electron microscopy (HAADF-STEM).

2. Material and methods

The $Ni_{2-x}MnSb$ alloys listed in Table 1 were prepared by induction melting in an Ar atmosphere. Each ingot was cut into small pieces and encapsulated into quartz tubes under a reduced atmosphere of high purity Ar. They were then solution treated at 900 °C for 3 days and subsequently quenched into water, breaking the quartz tube during cooling. In order to control the atomic configuration some specimens were further heat-treated at lower temperatures followed by quenching. The microstructure of every specimen was investigated using optical microscopy that confirmed a single phased structure. The composition of several specimens was determined using an electron probe micro analyzer (EPMA), the results of which are shown in Table 1. The difference between the nominal and analyzed compositions was less than 1 at.% for each element. The structural and magnetic transition temperatures of all alloys were determined by differential scanning calorimetry (DSC) under an Ar atmosphere. The heating/cooling rate of the DSC measurements was 10 °C/min. The atomic arrangements were observed using a *Z*-contrast imaging method by Cs-corrected STEM (JEOL-ARM200F) operated at 200 kV. The fine powder specimens used for the TEM observations were obtained by crashing bulk specimen in a mortar. The experimental results were compared to simulated images calculated using xHREM software [6,7].

Table 1
The compositions determined by EPMA and the magnetic and chemical ordering temperatures determined by DSC for $Ni_{2-x}MnSb$ alloys annealed at 900 °C for 3 days. The composition of alloys with $x = 0.875$ and 0.375 were not analyzed. The critical temperatures for the three reactions indicated by double and single arrows and solid circles in DSC heating curves of Fig. 2(a) are notated as T_c, $T_t^{L21/C1b}$ and $T_t^{X/L21}$, respectively.

Nominal composition	Analyzed composition (at.%)			Transformation temperature (°C)		
x	Ni	Mn	Sb	T_c	$T_t^{\{L2_1/C1_b\}}$	$T_t^{\{X/L2_1\}}$
1.0	33.0	33.8	33.2	453	867	965
0.875	–	–	–	397	863	985
0.75	38.2	30.9	30.9	319	832	–
0.625	40.6	30.0	29.4	250	780	–
0.5	42.5	28.8	28.7	–	713	–
0.375	–	–	–	–	571	–
0.25	46.6	26.7	26.7	–	–	–
0.125	48.1	25.9	26.0	–	–	–
0	49.3	25.4	25.2	–	–	–

3. Results and discussion

Fig. 2(a) shows the DSC cooling and heating curves for $Ni_{2-x}MnSb$ alloys quenched after solution-treatment at 900 °C. For the NiMnSb alloy with $x = 1$, three peaks were detected at approximately 450, 865 and 965 °C in both the cooling and heating curves. It is important to note that the thermal hysteresis of all three reactions is very small, a characteristic feature of second order phase transitions, such as magnetic or atomic ordering reactions. Actually, the peak detected at the lowest temperature is due to a magnetic transition from a ferromagnetic to a paramagnetic state in agreement with the Curie temperature reported by Webster and Mankikar [3]. On the other hand, to the best of our knowledge, no transformation in $Ni_{2-x}MnSb$ alloys has been reported in the high temperature region. Fig. 2(b) shows the composition dependence of the three transformation temperatures determined from the DSC heating curves. The critical temperatures defined as the peak temperature in the λ anomaly observed in the DSC curves are listed in Table 1 and indicated by single or double arrows and solid circles in Fig. 2(a). With decreasing x, the magnetic transition temperature, T_C, monotonically decreases, which is consistent with the variation reported by Webster and Mankikar [3]. Similarly, the transition temperature of the unknown reaction appearing at 867 °C decreases with decreasing x, whereas its intensity gradually diminishes disappearing completely for samples with $x \leq 0.25$. The transition temperature of the unknown reaction detected at approximately 965 °C increases with decreasing x and disappears for the samples with $x \leq 0.75$, owing to the melting temperature being exceeded.

In order to clarify the origin of the thermal reactions in $Ni_{2-x}MnSb$ alloys that appear at the high temperatures, a HAADF-STEM examination was carried out at room temperature. The HAADF-STEM images taken from Ni_2MnSb and NiMnSb alloys exhibiting typical $L2_1$ and $C1_b$ structures are shown in Fig. 3(a) and (b), respectively. In order to identify the four atomic sites occupied by Ni, Mn, Sb or vacancy, as shown in Fig. 1, the $[1\text{-}10]_{bcc}$ axis was chosen as the incident beam direction. All the atomic columns were successfully observed as white dots. Here, the intensity of the atomic column in the HAADF-STEM image is almost proportional to the square of the average atomic number Z, in each atomic column. That is, the order of the brightness for the atomic column in the present case is Sb > Ni > Mn as labeled in Fig. 3. It is very important to note that in the HH-NiMnSb alloy, the vacant *C* sites clearly show a dark contrast, while the atomic contrast at the *C* sites in the FH-Ni_2MnSb alloy is almost equivalent to that at the Ni *A* sites. Furthermore, each atomic contrast pattern observed in these experiments is in almost perfect agreement with that predicted by the simulations as shown in the insets of Fig. 3(a) and (b). Thus, the existence of the vacant site can be satisfactorily confirmed using the HAADF-STEM technique.

Then, NiMnSb specimens quenched from the high temperature phase regions were observed by the HAADF-STEM to characterize