Martensitic Transformation in NiCoMnSn Metamagnetic Shape Memory Alloy Powders

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RAPID PUBLICATION

Martensitic Transformation in NiCoMnSn Metamagnetic Shape Memory Alloy Powders

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Martensitic and magnetic properties of NiCoMnSn metamagnetic shape memory alloy powders obtained by a gas atomization method were investigated. The as-atomized powders showed a dendritic structure which changed to a single-phase one by annealing at 1173 K for 2 h. Although the martensitic transformation behavior was almost the same as that in bulk samples, the transformation thermal interval, namely, $M_s - M_f$, of the as-annealed powders decreased with increasing annealing time. In the powders annealed at 1173 K for 144 h, a reversible metamagnetic phase transition was confirmed by the application of a magnetic field of 7 T. [doi:10.2320/matertrans.MRP2008126]

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1. Introduction

Recently, our group has found an unusual type of ferromagnetic shape memory alloys (FSMAs) in the Ni-Mn-X (X = In, Sn and Sb) based Heusler alloy systems, which show a drastic change of magnetization accompanied by martensitic transformation from the ferromagnetic parent phase to the very weak magnetic martensite phase.[1–3)] The martensitic transformation temperatures of these alloys are drastically decreased by an applied magnetic field, and magnetic field-induced transformation (MFIT), which is a kind of metamagnetic phase transition, has been confirmed in the martensite state near the martensitic transformation starting temperature M_s. Moreover, the shape memory effect induced by a magnetic field, i.e., the metamagnetic shape memory effect, has been found in $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ and $Ni_{43}Co_7Mn_{39}Sn_{11}$ at room temperature.[2–5)] Since they show some other interesting properties, such as giant magnetoresistance (GMR)[6,7)] and the inverse magnetocaloric effect (MCE),[8,9)] these alloys have received much attention as high performance multiferroic materials. It has been reported that the metamagnetic shape memory effect due to magnetic field-induced reverse transformation is obtained in not only single-crystalline, but also polycrystalline specimens.[3)] The polycrystalline specimens obtained by conventional melting, however, are difficult to use for the application of actuators because of their considerable brittleness. Moreover, the thermal hysteresis and interval in the martensitic transformation are too large. Powder metallurgy is one of the methods to reduce the brittleness.

In the present study, the fundamental properties of the powder specimens were investigated by microstructural observation, differential scanning calorimetric (DSC) examination and magnetic measurement.

2. Experimental Procedures

A $Ni_{43}Co_7Mn_{39}Sn_{11}$ (at%) alloy was melted by high frequency induction. Powders with a particle diameter of about 10 to 250 μm were obtained using conventional nitrogen gas atomization under an argon atmosphere whose pressure was about 1.5 to 5 MPa. After classification of these powders into four groups according to size, those with a diameter between 25 and 63 μm, which constituted the major group in the powder size distribution, were selected for the present study. The obtained powders were sealed in a quartz capsule filled with argon gas. The specimens were annealed at 1173 K for 2 to 144 h, followed by quenching in ice water. The microstructures of the specimens were examined by optical microscopy (OM). The magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer in a magnetic field range up to 7 T at heating and cooling rates of 2 K min^{-1}.

3. Results and Discussion

Figures 1(a) and 1(b) show the thermomagnetization (TM) curves for the as-atomized powders and for the powders annealed at 1173 K for 2 h, 24 h and 96 h which were obtained in a magnetic field of $H = 0.05$ and 4 T, respectively. The martensitic transformation temperatures, namely, the transformation starting and finishing temperatures (M_s and M_f) and the reverse transformation starting and finishing temperatures (A_s and A_f) were defined as the intersection of the tangent line with the largest slope of the curve and the base line in the curves in the field of 0.05 T, as demonstrated in Fig. 1(a). Whereas the martensitic transformation of the as-atomized powders is not clear, the as-annealed specimens show a drastic change in magnetization due to martensitic transformation similar to that reported in the bulk alloy.[3)] The data obtained by these examinations are listed in Table 1 and plotted in Fig. 2, where the transformation interval T_i and the thermal hysteresis T_h for the annealed powders are defined by $M_s - M_f$ and $A_f - M_s$, respectively. It is seen that while the M_s, A_s and A_f temperatures are almost constant, M_f increases with annealing time. This behavior means that the transformation interval drastically decreases as represented in Fig. 2(b). The transformation behavior in the magnetic

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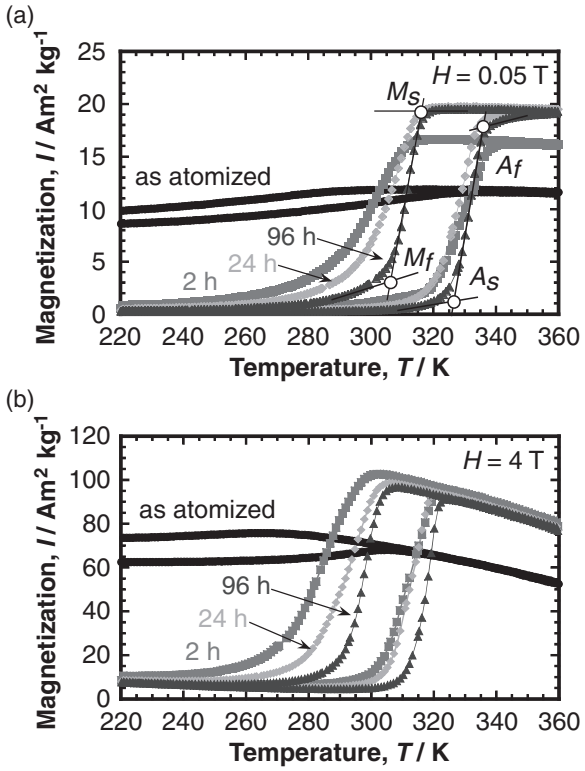

Fig. 1 Thermomagnetization (TM) curves at magnetic field strength of H = (a) 0.05 and (b) 4 T in the as-atomized powders and the powders annealed at 1173 K.

Table 1 Martensitic transformation temperatures, transformation interval and thermal hysteresis of the powders and the polycrystalline bulk alloy annealed at 1173 K.

Heat treatment time, t/h	M_s/K	M_f/K	A_s/K	A_f/K	T_i/K	T_h/K
2	311	278	317	339	33	28
24	315	290	319	335	25	20
96	317	301	326	338	16	21
144	314	303	326	337	11	22
24 (bulk)	330	290	311	345	40	15

field of 4 T is basically the same as that of 0.05 T, except for the shift of 10 to 20 K in the transformation temperatures in the lower temperature direction due to the stabilization of the parent phase by the high magnetic field as shown in Fig. 1(b). Data for a polycrystalline bulk alloy obtained by magnetic measurement in the magnetic field of 0.05 T are also listed in Table 1. It is seen that while T_h of the bulk alloy is slightly smaller, T_i is much larger than those of the powders.

In order to understand the changes in the martensitic and magnetic properties due to the annealing time, the microstructures of these powders were examined by optical microscopy. Figures 3(a), 3(b) and 3(c) show the microstructures of the as-atomized powders, and the powders annealed for 2 h and 24 h, respectively. Since the as-atomized powders show a dendritic structure as shown in Fig. 3(a), a solidification segregation would exist in these powders, which corresponds to the indistinct transformation behavior in the thermomagnetization curves shown in Fig. 1. This

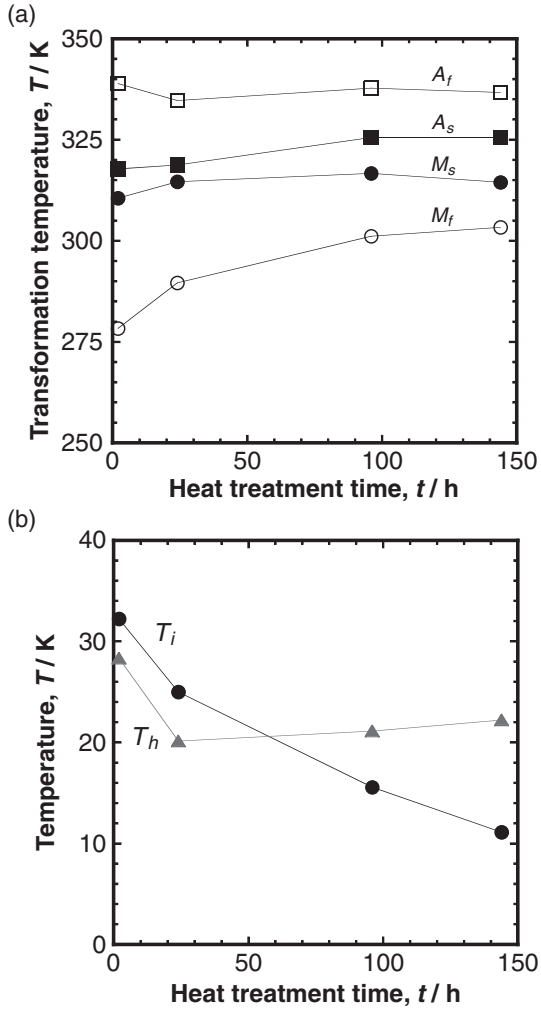

Fig. 2 Annealing time dependence on (a) the martensitic transformation temperatures and (b) the transformation interval T_i and the thermal hysteresis T_h determined from Fig. 1(a).

dendritic structure immediately disappears as the result of annealing for 2 h as shown in Fig. 3(b). The microstructure of the powders annealed for a longer time hardly changes, although a sintering reaction has already proceeded, as shown in Fig. 3(c). While grain boundaries were observed in most powder particles in the 2 h specimen, there were the single-crystalline powders with no grain boundary in a certain amount of the powders annealed for 24 h. Figure 3(d) shows the fraction of single-crystalline particles f_{SC} in all the observed particles. The number of single-crystalline particles was evaluated by the microstructural observation. The f_{SC} drastically increases to about 40% in the early stage until 24 h and then gradually increases to about 50%. It is known that the transformation interval results from an elastic energy stored in the microstructure during martensitic transformation, and the transformation interval for a polycrystalline specimen is generally larger than that for a single-crystal.[10] Actually, in the present alloy, the T_i for the polycrystalline bulk specimens is larger than those for the powder specimens as shown in Table 1. Consequently, it can be concluded that the decrease of the transformation interval as shown in Fig. 2(b) is brought about by the increase of the fraction of the single-crystalline particles.

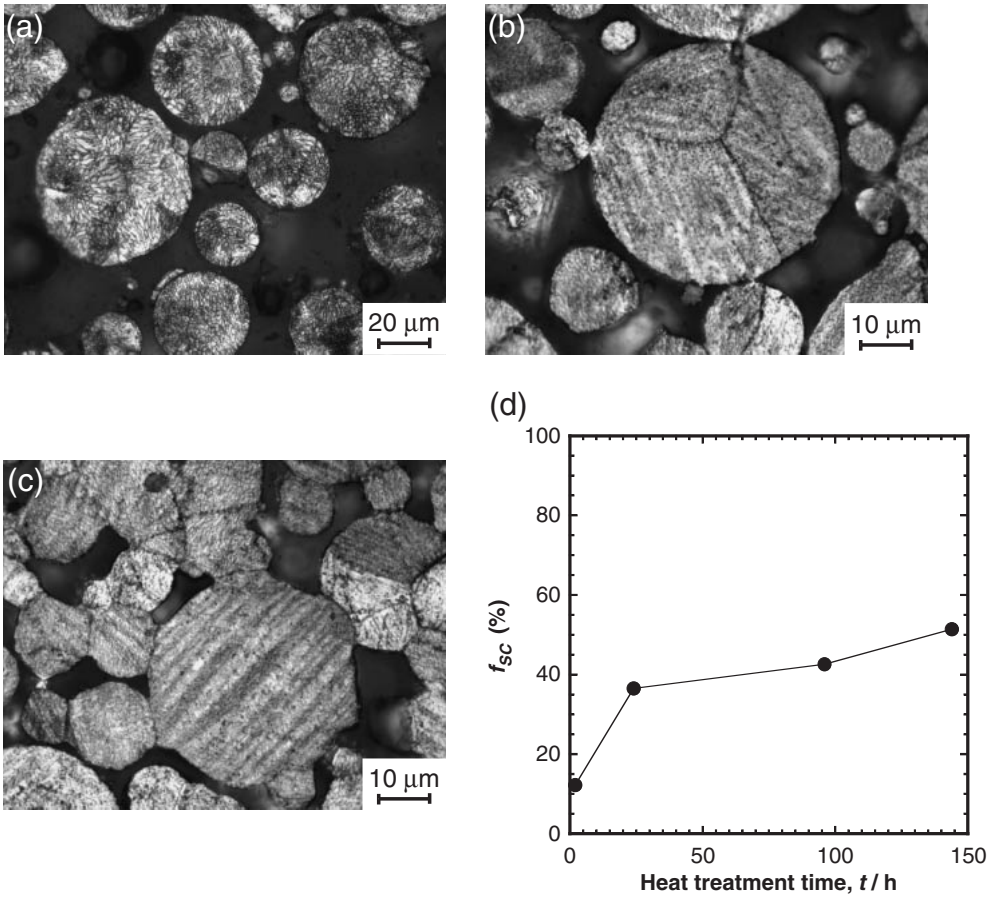

Fig. 3 Optical micrographs taken from (a) the as-atomized powders and the powders annealed at 1173 K for (b) 2 h and (c) 24 h. (d) shows the annealing time dependence on the fraction of single-crystalline particles f_{SC}.

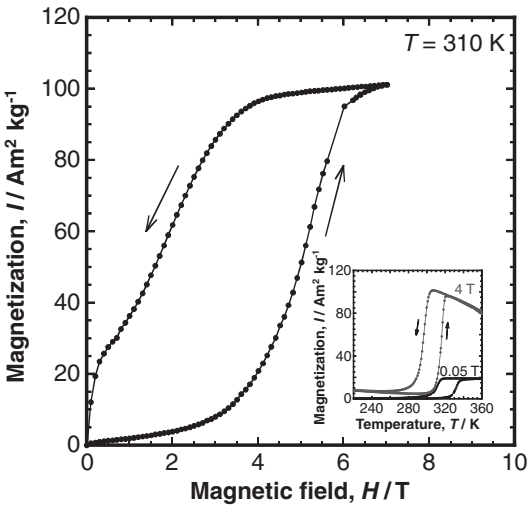

Fig. 4 Magnetization curve of powders annealed at 1173 K for 144 h measured at 310 K, the thermomagnetizaton curves for this specimen being exhibited in the inset.

Figure 4 shows the magnetization curve of the powders annealed at 1173 K for 144 h measured at 310 K, the thermomagnetizaton curves for this specimen being exhibited in the inset. Since the martensitic transformation temperatures decrease about 15 K due to application of the magnetic field of 4 T, reversible metamagnetic phase transformation is expected to result by application of a magnetic field of 7 T. As expected, the magnetization curve shows reverse and forward martensitic transformations by application and release of the magnetic field, respectively. Thus, a reversible metamagnetic phase transition was confirmed in the as-annealed powder specimen.

4. Summary

In summary, the martensitic transformation behavior and magnetic properties of $Ni_{43}Co_7Mn_{39}Sn_{11}$ powders obtained by a conventional gas atomization method were investigated. The microstructure of as-atomized powders showed a dendritic structure, and their martensitic transformations were incomplete. Annealing at 1173 K resulted in martensitic transformation, the transformation interval decreasing with increasing annealing time as a result of microstructural change in the particles. The metamagnetic phase transition was confirmed in the powders annealed at 1173 K for 144 h.

Acknowledgments

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