The Influence of Chemical Composition on Shape Memory Effect of TiNi Bulk Alloy Produced by Mechanical Alloying

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Three kinds of elemental powders consisted of Ti and Ni, with different chemical compositions, $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$, were mechanically alloyed for 30h by a planetary ball mill, compacted, sintered at 973K and annealed at several temperatures, 673K, 773K and 873K, and the martensitic transformation behaviors for those bulk samples were investigated. All three samples turned into amorphous state after mechanical alloying for 30h. After compacting, sintering and annealing, however, TiNi (B2) phase with a small amount of Ti_2Ni phase formed in the $\text{Ti}_{50}\text{Ni}_{50}$ sample, while TiNi (B2), Ti_2Ni and TiNi_3 phases formed in $\text{Ti}_{45}\text{Ni}_{55}$, and TiNi (monoclinic), Ti_2Ni and Ti_3Ni_4 phases in $\text{Ti}_{55}\text{Ni}_{45}$. The fraction of Ti in all the samples was reduced by approximately 1at% after a series of fabrication processes, suggesting that mechanical alloying (MA) process contributed to the phenomenon. Martensitic transformation behavior was observed in all the samples after a series of fabrication processes. Several precipitated phases influenced the martensitic transformation behavior, temperature and enthalpy for the transformation, suggesting that the precipitated phases have possibility to control martensitic transformation temperature. The martensitic transformation behavior was also dependent on annealing temperature.

Key words: TiNi shape memory alloy, chemical compositions, martensitic transformation, mechanical alloying, current sintering

1. INTRODUCTION

TiNi alloy is widely used for several industrial fields because of their good mechanical properties, corrosion resistance and fascinating behavior called as shape memory effect due to the thermo-elastic martensitic transformation. In terms of using TiNi shape memory alloy in several industrial fields, fabrication processes of the alloy are imperative to be investigated. Powder metallurgy has been attracted much attention, when compared to the conventional way, because of simplicity, cheapness and being able to apply complex shape as near-net-shape product. Mechanical alloying (MA) has some advantages to produce intermetallic compounds like TiNi [1]. It helps to change the local chemical compositions in the alloys and to form a near-net-shape product, after sintering the powders. In this study, powders with three kinds of chemical composition width consisted of Ti and Ni, $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ were mechanically alloyed by a planetary ball mill, sintered and annealed, and the martensitic transformation behavior for those bulk samples were investigated.

2. EXPERIMENTAL PROCEDURE

Commercially pure Ti (99.9%) and Ni (99.9%) powders were used in this study. Three kinds of different chemical compositions, $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ were mechanically alloyed by a planetary ball mill with stainless steel balls in an argon atmosphere in order to minimize the oxygen contamination during MA. The ball-to-powder weight ratio was approximately 8:1. The maximum milling time was 30h. The alloying period of 30min was alternated with an equal rest time in order to

avoid increasing temperature. The powder after MA was compacted and sintered at 973K for 10min under vacuum condition (2Pa) at a pressure of 20MPa. The sintered bulk sample was then annealed in a furnace at several temperatures (673K, 773K and 873K) for 1h under a high vacuum condition (10^{-3}Pa). The phases of the samples were determined by X-ray diffraction (XRD) measurement using Cu-K α radiation at 20kV and 40mA. The martensitic transformation behavior of the samples was observed by differential scanning calorimetry (DSC). The chemical compositions of the samples were determined by energy-dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns for $\text{Ti}_{50}\text{Ni}_{50}$ powder after several alloying times, indicating that elemental powders, Ti and Ni, remain at the early stage of mechanical alloying, however, the elemental powders turned into amorphous state after MA for 30h. XRD patterns for other powder samples, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$, also showed the similar patterns after MA for 30h. Thus, all three kinds of powder samples, $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$, turned into amorphous state after MA for 30h. Fig.2, 3 and 4 shows XRD patterns for $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ samples, respectively, after sintering at 973K and annealing at 773K. After sintering and annealing, TiNi (B2) phase with a small amount of Ti_2Ni phase formed in the $\text{Ti}_{50}\text{Ni}_{50}$ sample, while TiNi (B2), Ti_2Ni and TiNi_3 phase formed in the $\text{Ti}_{45}\text{Ni}_{55}$ sample, and TiNi (monoclinic), Ti_2Ni and Ti_3Ni_4 phases in the $\text{Ti}_{55}\text{Ni}_{45}$ sample.

Fig.1 XRD patterns for $\text{Ti}_{50}\text{Ni}_{50}$ powders after several alloying time.

Fig.4 XRD pattern for $\text{Ti}_{55}\text{Ni}_{45}$ sample after sintering at 973K and annealing at 773K.

Fig. 2 XRD pattern for $\text{Ti}_{50}\text{Ni}_{50}$ sample after sintering at 973K and annealing at 773K.

Fig.3 XRD pattern for $\text{Ti}_{45}\text{Ni}_{55}$ sample after sintering 973K and annealing at 773K.

Chemical compositions of each sample measured by EDX after a series of fabrication processes were shown in Table. I. It is indicated that fraction of Ti was reduced by approximately 1at% after a series of fabrication processes. MA process contributed to the phenomenon because the powders heavily adhered to the vial inner wall as well as the surface of the stainless ball after MA. It leads to change the chemical compositions and produce precipitated phases.

Table. I Chemical compositions of each sample after a series of fabrication processes.

composition before MA	Precise compositions
$\text{Ti}_{45}\text{Ni}_{55}$	$\text{Ti}_{44.1}\text{Ni}_{55.9}$
$\text{Ti}_{50}\text{Ni}_{50}$	$\text{Ti}_{48.7}\text{Ni}_{51.3}$
$\text{Ti}_{55}\text{Ni}_{45}$	$\text{Ti}_{54.2}\text{Ni}_{45.8}$

Fig.5 DSC curves for equiatomic $\text{Ti}_{50}\text{Ni}_{50}$ sample.

Fig.6 DSC curves for equiatomic $\text{Ti}_{50}\text{Ni}_{50}$ sample before annealing (after sintering).

DSC curves for the $\text{Ti}_{50}\text{Ni}_{50}$ sample after a series of fabrication processes are shown in Fig.5. It is indicated that clear peaks, martensitic transformation (exothermic) and reverse transformation (endothermic), were observed in the $\text{Ti}_{50}\text{Ni}_{50}$ sample. A transformation temperature width between M_s and M_f or A_s and A_f was approximately 20K, where M_s is the martensitic transformation start temperature, M_f the martensitic transformation finish temperature, A_s the reverse transformation start temperature, and A_f the reverse transformation finish temperature. Fig.6 shows DSC curves for equiatomic $\text{Ti}_{50}\text{Ni}_{50}$ sample before annealing (after sintering), which indicates that no martensitic transformation behavior was observed before annealing (after sintering), although the martensitic transformation behavior was observed in the sample after annealing. This suggests that the annealing process is important to produce phase homogenization in the sample.

Fig.7 DSC curves for $\text{Ti}_{45}\text{Ni}_{55}$ sample.

DSC curves for $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ samples after a series of fabrication processes are shown in Fig.7 and 8 respectively, showing clear peaks for both $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ samples. A transformation temperature width of $\text{Ti}_{45}\text{Ni}_{55}$ sample was less than 10K, which is smaller than that of $\text{Ti}_{50}\text{Ni}_{50}$ sample, showing better temperature response. On the other hand, two-stage transformation was confirmed in $\text{Ti}_{55}\text{Ni}_{45}$ sample, whereas no such behavior was observed in other samples ($\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{50}\text{Ni}_{50}$). In the case of $\text{Ti}_{55}\text{Ni}_{45}$ sample, Ti_3Ni_4 phase formed after sintering and annealing, but, this phase was not formed in $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{50}\text{Ni}_{50}$ samples as mentioned earlier, which suggests that the Ti_3Ni_4 phase may contribute to the two-stage transformation.

Fig.9 shows DSC curves for chemical compositions, $\text{Ti}_{45}\text{Ni}_{55}$, $\text{Ti}_{50}\text{Ni}_{50}$ and $\text{Ti}_{55}\text{Ni}_{45}$ sample after a series of fabrication processes, respectively. It is indicated that several precipitated phases in TiNi influenced martensitic transformation behavior, transformation temperature and enthalpy, which means several precipitated phases have possibility to control martensitic transformation temperature of TiNi shape memory alloy. In terms of martensitic transformation enthalpy, $\text{Ti}_{50}\text{Ni}_{50}$ sample had relatively low enthalpy compared to the others. Several precipitated phases interrupt the transformation. Thus, the transformation enthalpy of $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ sample was larger than that of $\text{Ti}_{50}\text{Ni}_{50}$ sample.

Fig.8 DSC curves for $\text{Ti}_{55}\text{Ni}_{45}$ sample.

Fig.9 DSC curves for chemical composition, $\text{Ti}_{45}\text{Ni}_{55}$, $\text{Ti}_{50}\text{Ni}_{50}$ and $\text{Ti}_{55}\text{Ni}_{45}$ respectively.

DSC curves for $\text{Ti}_{50}\text{Ni}_{50}$ sample after sintering at 773K and at different annealing temperatures, 673K, 773K and 873K are shown in Fig.10. Martensitic transformation temperature and enthalpy are linearly depended on annealing temperature. The martensitic transformation temperature was lowered with increasing annealing temperature, while the martensitic transformation enthalpy was decreased.

Fig.10 DSC curves for $\text{Ti}_{50}\text{Ni}_{50}$ sample annealed at different temperatures, 673K, 773K and 873K.

4. CONCLUSIONS

Three kinds of powders consisted of Ti and Ni, with different chemical compositions, $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{45}\text{Ni}_{55}$ and $\text{Ti}_{55}\text{Ni}_{45}$ were mechanically alloyed by a planetary ball mill, compacted, sintered and annealed, and the martensitic transformation behavior for those bulk samples was investigated. The results are summarized as follows:

1. The martensitic transformation behavior was observed in the samples after a series of fabrication processes for all compacted samples.
2. Several precipitated phases influenced martensitic transformation behaviors like transformation temperature and the enthalpy.
3. The martensitic transformation temperature was changed after annealing of several temperatures.

REFERENCES

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