Fabrication of composition-controlled TiNi shape memory wire using combustion synthesis process and the influence of Ni content on phase transformation behavior

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Received 28 January 2003; revised 27 February 2003; accepted 27 February 2003

Abstract

TiNi intermetallic compounds were manufactured on an industrial scale using a combustion synthesis process that exploits the heat of formation between Ti and Ni. In this paper we investigate the influence of Ni content on the phase transformation temperature. The TiNi shape memory intermetallic compounds manufactured are homogeneous, show no gravity segregation, and have low oxygen content. Hot and cold plastic working can be carried out without difficulty. The martensitic (Ms) transformation temperatures of specimens that were solution-treated and heat-treated for aging fall rapidly with increased Ni content. However, the transformation temperature bottoms out at 51.4 at.% Ni and begins to rise again at 51.7 at.% Ni. The reason why the Ms temperature, etc., of the specimens heat-treated for aging rise more than for solution-treated specimens is that the Ti3Ni4 precipitates, causing the Ni content of the matrix to fall. The pattern of change in transformation temperature as a function of Ni content in the present experiment agrees with other researchers’ data in spite of the combustion synthesis process fundamentally different from the conventional melting process.

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Keywords: TiNi; Combustion synthesis; Intermetallic compound; Shape memory material; Phase transformation temperature; Ni content

1. Introduction

It has been more than 30 years since TiNi shape memory material was invented [1], and in that time many more materials have been discovered that demonstrate this effect, recognized as the important material. However, active research has led to the conclusion that only TiNi intermetallic compounds have potential for practical application as shape memory material. TiNi intermetallic compounds have up to now generally been manufactured using a conventional high frequency induction vacuum melting process. However, the challenge facing this process is to prevent gravity segregation of the chemical composition caused by the large difference in specific gravity between Ti and Ni. The most important property of a shape memory material is its austenite–martensite transformation temperature. Homogeneity of the material is extremely important in the TiNi shape memory material produced in conventional processes, since a change of 0.1% in the proportion of Ni causes a 10 K change in the transformation temperature [2–4]. For convenience in application, shape memory material is often manufactured as a coil of thin wire. To take an example, when a 100 kg ingot is made into a wire 0.1 mm in diameter, this wire is 2000 km long. It would be problematic if such a long wire showed different transformation temperatures along its length. Slight segregation, which does not present a problem in materials like normal steels, becomes a major problem in shape memory material.

To solve the heterogeneity problem facing shape memory material, the author has been researching combustion synthesis methods for synthesizing homogeneous intermetallic compounds, using the heat of formation of the starting powder of Ti and Ni [5–7]. Using a 100 kg batch combustion synthetic apparatus would enable TiNi shape memory intermetallic compound to be manufactured on a production scale of 30 Mg per year. The TiNi shape memory intermetallic compound ingots are processed into thin wires and/or plates by
extensive plastic working such as hot forging and rolling, cold rolling and wire drawing. The author has manufactured on an industrial scale many TiNi intermetallic compound wires with compositions in the vicinity of the stoichiometric ratio (Ti:Ni = 1:1) using this combustion synthesis process. This report mainly describes the results of experiments on the influence of Ni content on the transformation temperature designed to throw light on the material’s transformation behavior. The transformation temperatures are influenced by the type of manufacturing process. The data collected enables the range of its applications to be expanded when this material is industrially manufactured using the combustion synthesis process.

2. Experimental

2.1. Starting materials

The starting powders adopted in the industrial combustion synthesis process for TiNi production used in the present research are as follows: Ti, made by Sumitomo Titanium Corporation; grain size: 150 μm or less. Ni, made by INCO; grain size: 8–15 μm.

The chemical compositions of impurities are shown in Table 1.

2.2. Manufacturing of samples

The actual production process shown in Fig. 1 was used to manufacture the samples. Single-phase TiNi is obtained in the range of a few percentage near the stoichiometric composition from the phase diagram shown in Fig. 2 [8]. The 100 kg starting powders were precisely weighed and fully mixed using a Henschel mixer to obtain 10 kinds of Ni content TiNi samples near 50 at.% Ni stoichiometric composition. Combustion synthesis was carried out after the mixed starting powders were loaded into the industrial combustion synthesis reactor shown in Fig. 3. This apparatus has an annual production capacity of 30 Mg at 100 kg/batch. The combustion synthesis conditions were furnace temperature 623 K, vacuum of 1 × 10⁻³ Pa and keeping time 10.8 ks. The top surface of the mixed powder of Ti and Ni was first ignited using a tungsten coil as shown in Fig. 4. As a result of ignition TiNi was synthesized generating heat of formation (ΔH = −67.8 kJ/mol [9]) that propagated to adjacent parts of the mixed powder. The resulting chain reaction caused the whole of the mixed powder to react and synthesize TiNi. In this process there was no macroscopic melting, since the whole reaction occurred macroscopically in the solid state. Therefore, there was no macroscopic mass transfer in the gravitational direction. Because the relative density of combustion-synthesized TiNi ingots was about 60%, the ingots were vacuum-sealed in stainless steel capsules, and the ingots of true density were manufactured by hot isostatic pressing at a pressure of 100 MPa and a temperature of 1200 K for a keeping time of 10.8 ks. After the capsules were removed by machining, extensive plastic working such as hot forging, hot rolling, cold wire-drawing, cold rolling and about 20% final cold rolling were carried out. A flat wire 2.18 mm in width and 0.92 mm in thickness was manufactured. The cross-sectional microstructure is shown in Fig. 5. The sectional area, measured from the sectional photograph, was 1.88 mm². Fig. 5 shows a sample of 49.9 at.% Ni before heat-treating: it exhibits a homogeneous microstructure. The flat wires were heat-treated and made into samples for measurement of transformation temperature.

To allow comparison with other researchers’ data, the most standard solution heat treatment with water quenching was done at a temperature of 1193 K and keeping time of 2.4 ks. However, as described in Section 3, the transformation temperature fell to a very low value in the vicinity of 51 at.% Ni in the solution-treated samples, making the measurement of the transformation temperature impossible. Therefore, heat treatment for aging using water quenching, which raised the transformation temperature, was carried out at 783 K for 1.5 ks. This brought the transformation temperature to within the measurable range for all the Ni compositions examined in the present study.

2.3. Measurement of transformation temperature

The transformation temperatures of the TiNi shape memory intermetallic compound were measured using differential scanning calorimetry (DSC). The apparatus used was a DSC-8230D calorimeter (Rigaku, Tokyo, Japan). Heating and cooling were controlled by regulating an electric furnace and using liquid nitrogen. The measurement

| Table 1 | Chemical composition of impurities in starting powders (mass%) |
|---------|---------------------------------------------------------------|
|         | O  | N  | C  | Fe | Cr | Si | Mg | Mn | H  | Cl |
| Ti powder | 0.060 | 0.02 | 0.01 | 0.035 | 0.01 | 0.007 | 0.001 | 0.002 | 0.006 | <0.001 |
| Ni powder | 0.06 | 0.1 | 0.01 |    |    |    |    |    |    |    |
Conditions were as follows: the standard material was alumina powder, the weight of the measured sample was 30–40 mg and heating and cooling speeds were 0.17 K/s (10 K/min).

### 3. Results

#### 3.1. Chemical analysis of sample

Gravity segregation is apt to occur in the ingot of TiNi shape memory intermetallic compounds if manufactured using the conventional melting process. The difference in performance in different locations of the final sample manufactured by the combustion synthesis process and made into a flat wire by means of cold rolling was examined. The DSC measurements were carried out on the final three flat wires manufactured from both ends and
the center of the first ingot. As a result, the TiNi shape memory intermetallic compound, manufactured by the present combustion synthesis process, showed no gravity segregation. Moreover, chemical analysis revealed impurities to be extremely few, and the amount of oxygen was about 600–700 ppm. In the present experiment, the flat wire sample manufactured from the vicinity of the center of the ingot was used. The amount of Ni revealed by chemical analysis of 10 kinds of samples used in the present experiment is shown in Table 2 with at.% and mass%. The chemical analysis method for determining Ni content was the gravimetric method after separation by dimethylglyoxime precipitation. Table 2 shows the added Ni as at.%.

Judging from the comparison between added and resident Ni content, the control of Ni content was successful. Thereafter, the data of the transformation temperature is categorized in at.%.

### 3.2. Transformation temperature measurement result of solution-treated samples

Fig. 6 shows an example of original DSC data of the transformation temperature measurement of the 10 kinds of Ni content samples heat-treated at 1193 K for 2.4 ks, the most standard solution heat treatment. The martensitic start temperature (Ms), the martensitic finish temperature (Mf), the austenitic start temperature (As) and the austenitic finish temperature (Af) are shown in Fig. 6 for the example of the sample of 49.9 at.% Ni, which is close to stoichiometric composition. The austenite phase of this maternal has a B2 structure (CsCl type, bcc) and the martensite phase is monoclinic.

Table 2

| Added Ni at.% | 49   | 49.5 | 49.75 | 50  | 50  | 50.5 | 50.75 | 51  | 51.5 | 51.75 |
|---------------|------|------|-------|-----|-----|------|-------|-----|------|-------|
| Found Ni at.% | 48.9 | 49.4 | 49.7  | 49.9| 50.1| 50.5 | 50.7  | 51.1| 51.4 | 51.7  |
| Found Ni mass%| 54.0 | 54.5 | 54.8  | 55.0| 55.2| 55.6 | 55.8  | 56.2| 56.4 | 56.7  |

Atomic weight: Ti = 47.88, Ni = 58.69.

Data on four kinds of transformation temperatures measured in this way compared with Ni content are shown in Fig. 7, where it can be observed that the transformation temperatures fall rapidly with increasing Ni content. The transformation temperatures fell too far and measuring them clearly became impossible in the vicinity of 51 at.% Ni. However, at 51.7 at.% Ni, the transformation temperatures rose, and measuring them again became possible.

### 3.3. Transformation temperature measurement result of samples heat-treated for aging

In the present experiment, when it appeared that that transformation temperatures of the solution-treated samples would descend so far to make them impossible to measure, heat-treatment for aging at 783 K for 1.5 ks was carried out to raise the transformation temperatures and allow comparison within the range of the entire amount of Ni content. Fig. 8 shows an example of the original DSC data for the transformation temperature measurement. Fig. 8 shows the measurement of the sample with 49.9 at.% Ni, close to the stoichiometric composition, the same as the sample shown in Fig. 6. In this case, it differed from the case of the solution heat treatment, and another phase transformation appeared. This was R-phase transformation [10,11] shown in Fig. 8. The R-phase transformation start temperature (Ms) and the R-phase transformation finish temperature (Mf) are also shown in Fig. 8. The R-phase has a rhombohedral crystal structure. The other labels are the same, as explained in Section 3.2.

Fig. 9 shows the change in six kinds of transformation temperatures compared with Ni content measured this way. In Fig. 9, although the transformation temperatures fell rapidly with increased Ni content, as did the solution-treated samples, they bottomed out at 51.4 at.% Ni, then rose again at 51.7 at.% Ni. The R-phase transformations were observed at more than 49.7 at.% Ni, but were not observed in the low Ni content region.

### 4. Discussion

#### 4.1. Change in transformation temperature

The transformation temperature change of the TiNi shape memory intermetallic compound is influenced in
complex fashion by the elemental ratio of Ti and Ni content, the manufacturing methods and conditions, the plastic working conditions, and the shape memory heat-treatment, etc. The most important factor is the elemental ratio of Ti and Ni content. This significantly influences the transformation temperatures of this material. In short, the austenite–martensite transformation temperature falls rapidly with increased Ni content. On the other hand, when the Ni-rich samples were heat-treated for aging, Ti$_3$Ni$_4$ was precipitated [12]. The transformation temperature rises again because the Ni content in the matrix decreases to a greater extent when Ti$_3$Ni$_4$ is precipitated. This is one reason why the Ms temperature, etc., rises when the samples are heat-treated for aging, as shown in Fig. 9.

In the present study, Ni content in the matrix was observed to decrease because Ti$_3$Ni$_4$ precipitated in the region of more than 50.5 at.% Ni. Therefore, the transformation temperatures rose, bringing them within measurable range. Moreover, there was no rapid change in the R-phase transformation temperature as a function of Ni content, unlike the change in Ms and the Mf temperatures shown in Fig. 9. Therefore, if an R-phase transformation is detected, a phase transformation process occurs, with the R-phase at the midway point of the martensitic transformation, that is, austenite → R-phase → martensite, with a decrease in temperature. However, when the martensitic transformation temperature rises, it becomes unnecessary to have an R-phase.

Fig. 6. Phase transformation temperatures measured using differential scanning calorimetry. The sample, containing Ni at 49.9 at.%, was solution-treated at 1193 K for 2.4 ks after 20% cold rolling.

Fig. 7. Change in transformation temperature of TiNi wire solution-treated at 1193 K for 2.4 ks after 20% cold rolling as a function of Ni content.
transformation at the midway point in the martensitic transformation [10]. Direct transformation of austenite → martensite takes place. Therefore, no R-phase transformation was observed below 49.7 at.% Ni, as shown in Fig. 9.

4.2. Comparison with other research data

The transformation temperature of the TiNi shape memory intermetallic compound manufactured by the combustion synthesis process descended rapidly with an increased Ni content, and it rose to a greater extent as a function of Ni content than did 51.4 at.% Ni in the present research. This tendency is compared with other data [2–4] of the TiNi shape memory material manufactured using the conventional melting process. Fig. 10 shows a comparison of Ms temperature with other research data, since other research data mostly concerns the Ms temperature. The tendency for the transformation temperature to decrease rapidly with increased Ni content in the present experiment is generally supported by other researchers’ data. Therefore, although the manufacturing process of the present material is fundamentally different from the conventional process, the relationship between the Ni content and the transformation temperature can be controlled under similar conditions when applied to TiNi shape memory intermetallic compounds manufactured by the combustion synthesis process described in the present research.

Fig. 8. Phase transformation temperatures measured using differential scanning calorimetry. The sample, containing Ni at 49.9 at.%, was heat-treated for aging at 783 K for 1.5 ks after 20% cold rolling.

Fig. 9. Change in transformation temperature of TiNi wire heat-treated for aging at 783 K for 1.5 ks after 20% cold rolling as a function of Ni content.
5. Conclusions

TiNi intermetallic compound was manufactured industrially using a combustion synthesis process that employed the heat of formation of the reaction to trigger a chain reaction between the elemental starting powders of Ti and Ni. The 10 kinds of sample were made in the vicinity of stoichiometric composition (Ti:Ni = 1:1). In the present research, the influence of the Ni content on the phase transformation temperatures was the chief focus of interest. The samples were heat-treated using the most standard treatment at 1193 K for 2.4 ks, and aged at 783 K for 1.5 ks to raise the transformation temperature. The results obtained are as follows:

1. The heat of formation, $\Delta H$, of TiNi is $-67.8$ kJ/mol. The present study provides clear evidence that the use of the combustion synthesis method, using the above-described starting materials and under the present conditions, is ideal for industrial production. The TiNi shape memory intermetallic compound produced by the present combustion synthesis process showed no gravity segregation, had a low oxygen content, and was extremely homogeneous. Industrial production of thin flat wire is enabled since the hot and cold plastic workings were carried out without encountering any problems.

2. The martensitic transformation temperature of the solution-treated material falls rapidly with increased Ni content. The transformation temperature fell outside the measurable range in the vicinity of 51 at.% Ni. However, resumption of measurement of the transformation temperature was possible, since it rose again at 51.7 at.% Ni.

3. Another R-phase transformation appeared in material heat-treated for aging. This phenomenon was seen at greater than 49.7 at.% Ni but was not observed at low Ni content. The martensitic transformation temperature fell rapidly with increasing in Ni content as well as the solution-treated material. However, the transformation temperature bottomed out at 51.4 at.% Ni, then reversed and rose at 51.7 at.% Ni. When heat-treatment for aging was carried out, the Ms temperature, etc., was increased more than in the case of the solution-treated material, making measurement possible. This is because heat treatment causes Ti$_3$Ni$_4$ to precipitate, causing the Ni in the matrix to decrease further, with the result that the transformation temperature rises.

4. The tendency of the transformation temperature to decrease rapidly with increased Ni content observed in this study agrees with other researchers’ data. For TiNi shape memory intermetallic compounds manufactured by the combustion synthesis process, the relationship between the Ni content and the transformation temperature can be controlled in a similar fashion to the conventional procedure, even though the manufacturing process of the present material is fundamentally different from the conventional process.

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