Quench-Hardening and Mechanical Properties of Ni-Rich NiTi Compounds*

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The relation between the nickel content and the hardening capability of Ni-rich NiTi compounds, and the effect of heat treatment on the mechanical properties of a NiTi compound containing 54.7 at% Ni have been investigated. NiTi compounds containing more than 52 at% Ni show a considerable increase in hardness by quenching, and the maximum hardness is obtained at about 54.5 at% Ni. According to the phase diagrams which are considered to be most reliable, the composition from which the hardening effect appears corresponds to the composition of the boundary between the NiTi phase and the NiTi + Ni₃Ti phase at lower temperatures and the composition at which the maximum hardness is obtained coincides with the composition of the same boundary at the quenching temperature. This fact seems to suggest that the hardening capability in Ni-rich NiTi compounds is related to the existence of excess point defects which are introduced by the deviation from the stoichiometric composition at the quenching temperature. The NiTi compound containing 54.7 at% Ni is hardened by quenching from temperatures above 600°C, and the hardness increases with increasing temperature. When the NiTi is quenched into water from 1100°C, the Vickers hardness of about 700 is obtained. The hardness of the quench-hardened NiTi decreases with annealing time. However, no hardening effect due to the precipitation of Ni₃Ti is observed. The tensile strength of the NiTi is 80 kg/mm² in the annealed state and 100 kg/mm² when annealed at a relatively high temperature after quenching. Although the Young's modulus of the NiTi in the annealed state is anomalously low as compared with the values of the constituent metals, quenching from 1000°C gives a nearly 20% increase of the value.

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I. Introduction

The compound NiTi exists over a wide range of composition from 48 to 55 at% Ni at high temperature^{(1)~(4)} and is considered to have a restricted homogeneity range even at low temperatures^{(1)(3)~(5)}. The equiatomic compound NiTi possesses unusual room temperature tensile properties quite unlike most of other compounds^{(5)~(7)}. The compound which exists in a CsCl type structure at elevated temperatures undergoes the martensitic transformation to a low-symmetry complex structure at around the ambient temperature^{(3)(5)(8)~(11)}. The change in various properties ascribed to the martensitic transformation has been the subject of a number of investigations⁽¹²⁾. The compounds containing excess nickel, on the other hand, show a considerable increase in hardness by quenching, while furnace cooling results in a substantially lower constant hardness. A hardness of Rockwell C-62 was obtained by quenching in 55 at% Ni compound⁽⁵⁾⁽¹³⁾. In addition to the hardening capability, NiTi compounds are extremely corrosion re-

sistant⁽⁵⁾⁽¹³⁾. This seems to indicate NiTi may be useful as a structural material. However, little has been known about their properties. The present paper describes the effect of the nickel content on the hardening capability of Ni-rich NiTi and the mechanical properties of the NiTi containing 54.7 at% Ni.

II. Experimental

Samples were prepared by non-consumable arc melting under gettered argon and subsequent electron beam melting. Sponge titanium (99.8% Ti) and electrolytic nickel (99.9% Ni) were used as starting materials. The bar-shaped ingots obtained weighed about 200 g and were 15 mm × 15 mm × 200 mm in dimension. All the ingots were annealed for 20 hr at 1000°C to ensure homogenization. The ingots were then canned in mild steel and forged on a conventional forging press. The forging temperatures ranged from 900 to 1000°C. The steel cans were then removed by machining.

The specimens for hardness and Young's modulus measurements were prepared from the forged plate by spark machining and grinding. Tensile test specimens of 20 mm in parallel length, 15 mm in gauge length and

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Table 1 Chemical analysis of Ni-rich NiTi compound.
(at %)

Ni	Ti	Impurities
54.7	45.1	0.2

2 mm in diameter were also machined from the plate. Chemical analyses of specimens used for this investigation are given in Table 1.

In order to normalize, all specimens were annealed for 1 hr at 1000°C prior to further heat treatment. All of the heat treatments were performed in a vacuum of less than 5×10^{-5} mmHg to prevent oxidation. For water quenching, the specimens were sealed in quartz ampoules under a pressure of 10^{-5} mmHg and heated at the desired temperature. The ampoules were then broken mechanically immediately after quenching.

Micro-hardness at elevated and ambient temperatures, the tensile strength and Young's modulus of the NiTi containing 54.7 at% Ni were measured. The micro-hardness measurement at elevated temperatures was performed by a conventional high-temperature micro-hardness tester with a load of 300 g. In this measurement, the specimens were held for 30 min at each temperature and the loading time was fixed at 1 min. Tensile tests were carried out on an Instron type tensile tester at a strain rate of 5×10^{-4} sec⁻¹. Dynamic-modulus measurements were made at a low kilocycle frequency with a commercially available apparatus. Metallographic observations were also conducted on the same specimens used for hardness measurement.

III. Results and Discussion

1. Hardenability and its mechanism

Hardness measurements were made on the NiTi containing 49 to 57 at% Ni† after water quenching or furnace cooling. The results obtained are given in Fig. 1. The hardness obtained by Buehler and Wiley⁽⁵⁾

Fig. 1 Hardness as a function of nickel content for furnace cooled and the water-quenched NiTi compounds.

† These compositions were calculated from the weights of starting materials assuming the arc melting is performed without any weight loss.

is also given in this figure. Though the specimens containing less than 51 at% Ni show no quench hardening, the specimens containing 52 to 57 at% Ni exhibit a considerable increase in hardness with quenching, and the maximum hardness occurs at about 54.5 at% Ni. This is consistent with the observation of Buehler and Wiley that the hardening effect appears at 51 at% Ni and an extended hardness peak occurs from 53 to 57 at% Ni.

The studies on the homogeneity range and the low-temperature stability of the NiTi phase have been done by many investigators⁽¹⁾⁻⁽⁴⁾⁽¹⁴⁾. Some of these results are shown in Fig. 2. It seems certain that the homogeneity range of the NiTi phase extends to the Ni-rich side, in contrast to the restricted homogeneity range on the Ni-deficient side, and the homogeneity range near room temperature is very narrow.

As mentioned above, NiTi containing 52 to 57 at% Ni is hardened by quenching. The composition at which the hardening effect appears corresponds to the composition of the phase boundary between NiTi and NiTi + Ni₃Ti in the phase diagrams presented by Purdy and Parr⁽³⁾ and by Hirano and Ouchi⁽⁴⁾. On the other hand, the composition at which the maximum hardness is obtained is within the NiTi + Ni₃Ti phase region, according to the observations of Margolin et al.⁽¹⁾ and Purdy and Parr⁽³⁾ that the maximum solubility of nickel in NiTi at 1000°C is about 53.5 at%. According to the phase diagram

Fig. 2 Titanium-nickel phase diagram in the vicinity of the NiTi phase.

(14) P. Duwez and J. L. Taylor: Trans. AIME, **188** (1950), 1173.

Photo. 1 Microstructures of the NiTi compound containing 54.7 at % Ni ($\times 250$).

- (a) Annealed at 1000°C for 5 hr and furnace cooled
 (b) Annealed at 1000°C for 5 hr and water quenched
 Etchant: 5 parts HF, 15 parts HNO₃, 80 parts H₂O

given by Poole and Hume-Rothery⁽²⁾, however, the composition of the boundary between NiTi and NiTi + Ni₃Ti at 1000°C is about 54.5 at% Ni and is the same as the composition at which the maximum hardness is obtained.

This can be also confirmed by Photo. 1. When the NiTi containing 54.7 at% Ni is annealed at 1000°C and then furnace cooled, Ni₃Ti precipitates in the matrix[†]. On the contrary, when the specimen is quenched from the same temperature, the second phase observed is scarce. The fine particles observed in the quenched specimens are believed to be a titanium-nickel oxide of the form Ti₃Ni₂O₇, as has been observed by Rozner et al.⁽¹⁵⁾ and Scholl et al.⁽⁷⁾ in the stoichiometric NiTi and by Wasilewski et al.⁽¹¹⁾ in NiTi and Ni-rich NiTi.

In the following, the mechanisms of quench hardening observed in Ni-rich NiTi will be discussed. Several quench hardening mechanisms acting on the intermetallic compounds^{(16)~(19)} are considered:

(1) Defect hardening

(1-a) hardening by structure defects which are introduced by the deviation from the stoichiometric composition at the quenching temperature, effective only when the homogeneity range becomes narrower with decreasing temperature, and

(1-b) hardening by quenched-in vacancies thermally equilibrated at the quenching temperature.

(2) Order and domain hardening

(2-a) when the change in the crystal structure occurs on ordering, and

(2-b) when an intermediate degree of order or a suitable domain size is obtained by quenching without change in the crystal structure.

(3) Hardening by phase transformation

Now, let us consider the mechanism (1). In Ni-rich NiTi either vacancies or substitutional atoms in

titanium sublattices^{††} are formed to achieve the required composition. If we assume that the maximum nickel content in NiTi phase at 1000°C is 55 at% and the structure defect is of the vacancy type, 9×10^{-2} of vacancy concentration can be introduced. If substitutional atoms are formed as the structure defect, the concentration of the defects attains 5×10^{-2} . It is considered that the greater part of the defects are in the super-saturated state at room temperature by quenching. In NiAl and CoAl which have the same crystal structure as NiTi and a wide homogeneity range, a drastic increase in hardness was observed with increasing amount of defects⁽²⁰⁾. The Ni-rich NiTi may also be hardened by the same mechanism.

The contribution of thermal vacancy to the hardening (1-b) seems to be unlikely as a single mechanism, because the stoichiometric NiTi is not hardened by quenching as illustrated in Fig. 1.

In the next step, we will evaluate the possibility of order hardening. It has been believed that the crystal structure of the NiTi phase between the martensitic transformation temperature and the melting point is of the CsCl type^{(1)~(3)(5)(7)(8)(11)(14)(19)(21)~(25)}. Recently, Wang et al.⁽⁹⁾ reported that the stoichiometric NiTi undergoes an order-disorder transformation at about 700°C, and the crystal structure of NiTi between the martensitic transformation temperature and 700°C forms a rather complex ordered lattice

†† If an atomic size is only the factor to control the type of defect structure, substitutional atoms would be preferable. But no evidence has been obtained.

† Precipitation of Ni₃Ti was confirmed by the measurements using an electron probe micro-analyser.

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instead of the CsCl type and a body-centered cubic lattice above 700°C. The presence of the order-disorder transformation was confirmed by Zijderfeld et al.⁽¹⁰⁾ On the contrary, Hirano and Ouchi⁽⁴⁾ denied the existence of the order-disorder transformation in the stoichiometric NiTi, because no anomaly was observed around 700°C in the specific heat measurement. Wasilewski et al.⁽¹¹⁾ also did not support Wang's study in view of the rather high formation energy of NiTi. Thus, the existence of the order-disorder transformation in the NiTi phase is still not clear. If it does not exist, the hardening of Ni-rich NiTi is of course due to the other mechanisms. But if it exists, order hardening, domain hardening and hardening by crystal structure change must be considered.

Lastly, we will discuss whether the mechanism (3) is involved or not. Though the martensitic transformation in the NiTi phase occurs at about 100°C at the stoichiometric composition, the transformation temperature decreases steeply with increasing nickel content⁽⁹⁾⁽²⁶⁾. Wasilewski et al.⁽¹¹⁾ reported that at 52 at% Ni the transformation starts at about -50°C on cooling, but it does not go to completion even at -180°C. On the other hand, Takeuchi et al.⁽²⁷⁾ observed that the *M_s* temperature decreases to about -50°C at 51.2 at% Ni then increases with increasing nickel content up to about 10°C at 52 at% Ni. If the *M_s* temperature of NiTi containing 54 to 55 at% Ni is down below room temperature, no hardening effect is concerned with the martensitic transformation. Even if the *M_s* temperature is around room temperature, the contribution may be small.

These findings suggest that when a single mechanism is involved, the quench hardening in Ni-rich NiTi is due to the existence of the structure defects which are introduced by deviation from the stoichiometric composition at the quenching temperature.

2. Changes in mechanical properties by heat treatment

Figure 3 shows a relation between quenching temperature and the hardness of the NiTi containing 54.7 at% Ni. The NiTi is hardened by quenching from temperatures above 600°C and the hardness increases with increasing quenching temperature. When the NiTi is quenched from 1000°C the hardness reaches about 650 DPN, and quenching from 1100°C gives a hardness of the order of 700 DPN. When the NiTi is heated above 1100°C incipient melting occurs.

The fact that the NiTi is hardened by quenching from temperatures above 600°C seems to suggest the existence of order-disorder transformation, because the critical quenching temperature lies near the order-disorder transformation temperature of about 700°C which was proposed by Wang et al.⁽⁹⁾ Generally

Fig. 3 Relation between quenching temperature and the hardness of the NiTi compound containing 54.7 at% Ni.

speaking, the compounds which undergo order-disorder transformation show the maximum strength at some intermediate degree of order, and show, therefore, the maximum hardness or the maximum stress to rupture when the compounds are quenched from just below the transformation temperature⁽²⁸⁾. In this investigation, the hardness of the NiTi containing 54.7 at% Ni tends to increase with increasing temperature up to 1100°C. Therefore, it is difficult to explain the quench-hardening by the order-disorder transformation.

On the other hand, the equilibrium concentration of thermal vacancies in metallic crystals is given by the following equation:

$$X_v = \exp(-U_f/kT)$$

where U_f is formation energy of vacancy. From this equation we understand that the number of vacancies increases with increasing temperature. From the solubility curve of nickel in the NiTi phase given in Fig. 2, the number of point defects which are introduced by deviation from the stoichiometric composition also increases with increasing temperature up to 1100°C. The relation given in Fig. 3, therefore, seems to suggest rather defect hardening. The fact that the hardening occurs from temperatures around 600°C can be interpreted in terms of structure defects in a super-saturated state, because the homogeneity range of NiTi, especially the solubility of nickel in the NiTi phase, increases with increasing temperature above 500°C, but the range is restricted and parallel to the temperature axis below 500°C⁽³⁾⁽⁴⁾ as seen from Fig. 2.

The change in hardness of the NiTi containing 54.7 at% Ni with annealing temperature after quenching from 1000°C is shown in Fig. 4. A series of specimens were cooled in a furnace and the other series of specimens moved to a cold part of the furnace after the annealing heat was turned off. Up to 400°C, the specimens maintain the initial hardness. When the temperature exceeds 400°C, the hardness decreases steeply with increasing temperature. The change in hardness, however, depends upon cooling rate above 650°C. In the furnace cooling, the hardness decreases

(26) J. E. Hanlon, S. R. Butler and R. J. Wasilewski: *Trans. Met. Soc. AIME*, **239** (1967), 1323.

(27) S. Takeuchi, T. Honma, K. Suzuki and I. Yamazaki: *Abstracts of the 1966 Autumn Meeting of the Japan Institute of Metals*, p. 195.

(28) For example, M. J. Marcinkowski and D. S. Miller: *Phil. Mag.*, **6** (1961), 871; A. Lawley, E. A. Vidoz and R. W. Cahn: *Acta Met.*, **9** (1961), 287.

Fig. 4 Effect of annealing temperature and subsequent cooling on the hardness of the water-quenched NiTi compound containing 54.7 at % Ni.

with increasing annealing temperature. On the other hand, in the relatively rapid cooling, the hardness rather increases with increasing annealing temperature. This fact seems to suggest that the point defects which are introduced by deviation from the stoichiometric composition at the quenching temperature contribute to the hardening even at a relatively slow quenching rate such as air cooling. It becomes clear that Ni-rich NiTi is hardened not only by water quenching but also by air cooling. Since the hardening is considered to be controlled by the diffusion process because the martensitic transformation does not affect the quench-hardening as mentioned in the preceding section, the hardening is thought to be induced when the process in which the activation energy is relatively high is prevented or proceeds incompletely by quenching.

The change in hardness of the NiTi containing 54.7 at % Ni with annealing at 400, 500 and 600°C for 20 hr after water-quenching is shown in Fig. 5. At the beginning of annealing the hardness decreases rapidly and then decreases gradually with time at all temperature. The higher the annealing temperature, the faster becomes the softening speed.

It is found from Fig. 2 and Photo. 1 that the precipitation of Ni_3Ti is prevented by quenching even at the composition of 54.7 at % Ni and the single phase can be brought to room temperature. On the other hand, when the NiTi is slowly cooled from the temperature at which a wide homogeneity range exists or annealed at elevated temperatures after quenching Ni_3Ti

Fig. 5 Effect of annealing time on the hardness of the water-quenched NiTi compound containing 54.7 at % Ni.

precipitates in the NiTi matrix. If we assume that the change in hardness, shown in Fig. 5, by annealing reflects the precipitation process, the softening at the early stage of annealing is considered to be related to the annihilation of thermal vacancies and some point defects which can move easily and the subsequent softening may be interpreted in terms of the diffusion of nickel atoms and the growth of Ni_3Ti . No evidence for the hardening by the precipitation of Ni_3Ti was observed within 20 hr of annealing.

The hot-hardness curve for the NiTi containing 54.7 at % Ni which was quenched from 1000°C is shown in Fig. 6. Hot-hardness for the stoichiometric NiTi similarly quenched is shown in the same figure. In Ni-rich NiTi the hardness remains constant up to about 400°C and above this temperature the hardness decreases rapidly with increase in temperature. The stoichiometric NiTi shows a low initial hardness and a secondary hardening peak at about 350°C. Buehler and Wiley⁽⁵⁾, in similar work, also observed the significant secondary hardening peak at about 460°C and considered that the hardening is attributable to an atomic ordering phenomenon. If the NiTi phase undergoes order-disorder transformation at an intermediate temperature the hardening at about 350°C may be explained by the transformation. However, since the existence of the transformation is still uncertain it should be considered that some other mechanisms contribute to the hardening. No secondary hardening peak was observed in the NiTi containing 54.7 at % Ni.

Fig. 6 Hot hardness curves for the water-quenched NiTi compounds.

Tensile properties of the NiTi containing 54.7 at % Ni in various heat treatments are shown in Table 2. Tensile strength of about 80 kg/mm² was obtained for furnace cooled specimens after annealing at 1000°C. On the contrary, quenched and subsequently annealed specimens exhibit a tensile strength of 100 kg/mm² with undetectable elongation. No reliable tensile strength data were obtained for the specimens which were as-quenched or annealed at a relatively low temperature because these specimens did not undergo normal fracture.

Table 2 Tensile properties of the NiTi compound containing 54.7 at % Ni.

Condition	Tensile strength (kg/mm ²)	Elongation (%)
1000°C × 2 hr, furnace cooled	79	4
1000°C × 2 hr, water quenched and annealed at 600°C for 1 hr	97	1
1000°C × 2 hr, water quenched and annealed at 800°C for 1 hr	99	1

The effect of quenching and subsequent annealing on the Young's modulus of the NiTi containing 54.7 at % Ni is shown in Fig. 7. Young's modulus of the specimens which were furnace cooled from 1000°C is 7700 kg/mm², but water quenching from the same temperature gives 9000 to 9500 kg/mm². The Young's modulus does not change by annealing up to 600°C, but in the range from 600 to 800°C it decreases steeply as the annealing temperature increases. Above 800°C the Young's modulus increases again with increasing temperature and 9000 kg/mm² is obtained at 1000°C. All specimens for the Young's modulus measurement were cooled in the cold part of a furnace after annealing. The Young's modulus of about 8000 kg/mm² for Ni-rich NiTi is extremely low in comparison with 21000 kg/mm² for Ni and 10500 kg/mm² for Ti. It is worth noting that when the same heat treatment is applied the behaviour of the Young's modulus with temperature is similar to that of hardness.

Fig. 7 Effect of annealing on the Young's modulus of the NiTi compound containing 54.7 at % Ni.

The Young's moduli of 7900 to 8300 kg/mm² (room temperature) and 7900 kg/mm² (75°C) to 8800 kg/mm² (150°C) for the stoichiometric NiTi were obtained by Buehler and Wiley⁽⁵⁾ and by Wasilewski⁽²⁹⁾, respectively. Buehler and Wiley confirmed by the vibration damping method that their specimens still have a CsCl type structure. In this investigation, the specimens for Young's modulus measurements are rather high in nickel content (54.7 at % Ni), but the values in the annealing state agree well with their values.

Wasilewski⁽²⁹⁾ has reported that the stoichiometric NiTi has the minimum of Young's modulus at the martensitic transformation temperature. The Young's

modulus increases on both sides of this temperature, and at 500°C an increase of about 50% in the modulus was obtained. If we assume that the NiTi containing 54.7 at % Ni has the same elastic modulus anomaly and a high temperature phase which has relatively high Young's modulus is obtained by quenching at room temperature, it is easy to explain the fact that the modulus increases about 20% by quenching. The fact that the modulus increases with increasing temperature above 800°C also may be explained by assuming that a high temperature phase with a relatively high Young's modulus can be obtained even by air cooling at room temperature. But there is no evidence to support that both the mechanism for increasing Young's modulus by quenching and the quench-hardening mechanism for Ni-rich NiTi are controlled by the same factor. It will be clarified by further investigations in the near future.

IV. Conclusions

The relation between the nickel content and the hardening capability of Ni-rich NiTi and the effect of heat treatment on the mechanical properties of the NiTi containing 54.7 at % Ni have been investigated. The results are summarized as follows:

(1) Hardening effect appears at about 52 at % Ni which corresponds to the composition of the boundary between the NiTi phase and NiTi + Ni₃Ti phase at lower temperatures. The maximum hardness is obtained between 54 and 55 at % Ni. This coincides with the composition of the above mentioned boundary at the quenching temperature. When the nickel content is in excess of 55 at % Ni, the hardness decreases with increasing nickel content.

(2) The NiTi containing 54.7 at % Ni is hardened by quenching from temperatures above 600°C, and the hardness increases with increasing quenching temperature. When the NiTi is quenched from 1100°C into water, the Vickers hardness of about 700 is obtained. Ni-rich NiTi is hardened even by air cooling.

(3) The highest hardness of the NiTi containing 54.7 at % Ni is obtained in the as-quenched state. The hardness of quench-hardened NiTi decreases with annealing time. No hardening effect due to the precipitation of Ni₃Ti was observed.

(4) The tensile strength of the NiTi containing 54.7 at % Ni is 80 kg/mm² in the annealing state with detectable elongation and attains 100 kg/mm² when annealed at a relatively high temperature after quenching.

(5) Although the Young's modulus of 7700 kg/mm² for the NiTi containing 54.7 at % Ni in the annealing state is anomalously low compared with the values of the constituent metals, quenching from 1000°C gives a nearly 20% increase, amounting to 9000 to 9500 kg/mm².

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