Effect of Preannealings on the Temperature Spectra of Internal Friction and Shear Modulus of Ti–51Ni

By Kunihiko Iwasaki* and Ryukiti R. Hasiguti**

Internal friction, shear modulus and released shear strain of Ti–51Ni are measured with an inverted torsion pendulum in the temperature range between 90 and 350 K both in heating and in cooling runs. The effects of preannealing temperature \( T_a \) on their temperature spectra are systematically investigated. Only premartensitic transformation is observed for \( 573 \text{ K} \leq T_a \leq 773 \text{ K} \), both premartensitic and martensitic ones for \( 873 \text{ K} \leq T_a \leq 1073 \text{ K} \), and only martensitic one for \( T_a \geq 1173 \text{ K} \). Precipitation and retained high temperature phase are supposed to play an important role in these transformation variations. A peak observed at 200 K for \( T_a \leq 773 \text{ K} \) is shown to be of a relaxation-type and to have nothing to do with the transformations.

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I. Introduction

Internal friction and elastic modulus of TiNi have been investigated by many authors. Hasiguti and Iwasaki(1), for example, measured them in a wide temperature range about 20 years ago. At that time, however, only a speculative interpretation was possible, because even the crystal structure of the alloy had not been known exactly. During the past 20 years there has been much progress in understanding the fundamental properties of the alloy. Nevertheless the complicated behavior of internal friction and elastic modulus around, especially below, the martensitic or premartensitic transformation temperature has not been clarified yet. Recently, for example, a two-step transformation has been detected as two internal friction peaks and/or two elastic modulus minima in certain specimen conditions(2)–(7). The behavior, however, differs from author to author, depending on the alloying composition including the third element and on heat treatments. The situation seems to be in confusion now, and no clear general explanation has been attained yet.

In order to solve this confusion, more systematic experiments are highly desired. This work is undertaken along this line, and as a first step the effects of preannealing temperature on the temperature spectra of internal friction, shear modulus and released shear strain are systematically investigated.

II. Experimental Procedures

The specimen and the measuring apparatus are the same as before(1)(8). Successive isochronal annealing experiments are carried out with an identical specimen in the following sequences.

1. Specimen annealing at temperature \( T_a \) for 7.2 ks in vacuum and furnace-cooling down to room temperature with an electric fan. It takes about 180 s to cool from 1273 K down to 573 K and much more for the subsequent cooling down to room temperature, which corresponds to "fast cooling" in a previous paper(8).

2. Specimen setting in the measuring apparatus and additional annealing in situ at
453 K for 1.8 ks to remove setting strain.
(3) Cooling down to 90 K and the measurement of internal friction, shear modulus (period of vibration) and released shear strain (zero-point movement of the pendulum) first in heating and then in cooling runs between 90 K and 350 K, where the temperature is changed continuously (not step-wise) at a rate of about 0.017 K/s. The continuous heating or cooling in which the temperature changing direction is never reversed except at the terminal points, 90 K and 350 K, is indispensable to obtain reproducible data.

(4) Specimen demounting from the measuring apparatus. These processes are repeated with different values of $T_a$ which is increased step-wise from 573 to 1273 K by 100 K. As the effective length of the specimen changes after each specimen setting, it is meaningless to compare absolute values of the period of vibration. The periods are, therefore, normalized with respect to the first value of each heating run.

III. Experimental Results

The temperature spectra of internal friction ($Q^{-1}$), normalized period of vibration ($t$) and zero-point (ZP) movement of the pendulum are shown in Fig. 1 for $T_a=673$ K. The ZP movement is expressed by the maximum surface shear strain of the specimen, of which the magnitude is indicated with a bar of $1 \times 10^{-5}$ in the figure. The value of $Q^{-1}$ changes abruptly by a factor of about 100 and $t$ exhibits a sharp minimum at about 310 K in the heating run and at about 290 K in the cooling run. These temperatures are designated as $T_1$ in this paper. There appear a series of sharp peaks (called "serration" here) in the temperature range between $T_1$ and about 250 K. In the serration temperature range a large difference between the heating and the cooling runs (called "temperature hysteresis") is observed and the ZP moves largely. A clear and well-shaped peak appears at 200 K (called "200 K peak"). This peak shows little temperature hysteresis, and no peculiar ZP movement is associated with it, which should be compared to the case of the serration.

As $T_a$ is increased, the serration becomes lower and wider, where the high temperature edge is always kept at $T_1$, and the 200 K peak becomes also lower, disappearing after annealing at 873 K, as shown in Fig. 2 (see also Fig. 6(A)). The ZP movement in the serration range also becomes smaller. The $Q^{-1}$ step at $T_1$, however, becomes steeper here than that shown in Fig. 1. It is also to be noted that an additional peculiar ZP movement is observed at about 240 K here for $T_a=873$ K.

After annealing at 973 K a second minimum in $t$ begins to appear at $T_2$ (240 K) in addition to the first one at $T_1$ and the ZP movement

![Fig. 1 Temperature spectra of internal friction ($Q^{-1}$), normalized period of vibration ($t$) and zero-point (ZP) movement after preannealing at 673 K for 7.2 ks ($T_a=673$ K).](image1)

![Fig. 2 Temperature spectra of internal friction ($Q^{-1}$), normalized period of vibration ($t$) and zero-point (ZP) movement for $T_a=873$ K.](image2)
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around \( T_2 \) becomes more distinct, as shown in Fig. 3. As \( T_a \) is increased further up to 1073 K, the second minimum becomes much clearer (see Fig. 5 below).

If \( T_a \) reaches 1173 K, the first minimum at \( T_1 \) disappears and only the second one is observed at \( T_2 \), as shown in Fig. 4. The ZP movement around \( T_1 \) becomes very small and the steep step of \( Q^{-1} \) at \( T_1 \) changes into a sluggish or gradual one. It is to be noted that the second minimum is not so sharp as the first one and appears at about the same temperature \( T_2 \) in the heating and cooling runs. Though there seems to be a \( Q^{-1} \) peak at about \( T_2 \), its identification is difficult because of a large scattering of the \( Q^{-1} \) data in the serration range.

The change in the temperature spectra of \( t \) with respect to \( T_a \) is schematically summarized in Fig. 5. Only the first minimum appears at \( T_1 \) for \( T_a \) between 573 K and 873 K, and there is a temperature hysteresis of about 20 K between the heating (shown with solid lines) and the cooling (dotted lines) runs. If \( T_a \) reaches 973 K, the second minimum begins to appear at \( T_2 \), becoming much clearer for \( T_a = 1073 \) K. If \( T_a \) is increased further up to 1173 K or 1273 K, the minimum at \( T_1 \) disappears, leaving only the second one at \( T_2 \).

The \( T_a \) dependence of the 200 K peak height, the maximum \( Q^{-1} \) in the serration (\( Q^{-1}_{\text{max}} \)) and the \( Q^{-1} \) value taken at 123 K (\( Q^{-1}_{123} \)) are shown in Figs. 6(A), (B) and (C), respectively. The 200 K peak disappears completely after annealing at 873 K. As \( T_a \) is increased, \( Q^{-1}_{\text{max}} \) decreases, while \( Q^{-1}_{123} \) increases, which means the lowering and widening of the serration. This is also clear from the fact that the temperature range where the \( Q^{-1} \) values show a distinct temperature hysteresis becomes wider as \( T_a \) is increased (compare Figs. 1–4).

![Fig. 3 Temperature spectra of internal friction (\( Q^{-1} \)), normalized period of vibration (\( t \)) and zero-point (ZP) movement for \( T_a = 973 \) K.](image1)

![Fig. 4 Temperature spectra of internal friction (\( Q^{-1} \)), normalized period of vibration (\( t \)) and zero-point (ZP) movement for \( T_a = 1173 \) K.](image2)

![Fig. 5 Summary of \( T_a \) dependence of shear modulus (period of vibration).](image3)
The well-shaped 200 K peak is not associated with any peculiar ZP movement and the temperature hysteresis is also negligibly small. In these points this peak is quite different from the sharp peaks in the serration which are considered to be related to premartensite and/or martensite as will be described later. The 200 K peak showed a measuring frequency dependence from which the activation energy of 0.38 eV, the frequency factor of $6 \times 10^9$ Hz and the width ratio of 1.9 were obtained. From these experimental results the 200 K peak is supposed to be of a thermally activated relaxation-type. The values of the activation energy and the frequency factor indicate that the peak may be related to dislocations, which must have been introduced during the specimen-wire manufacturing processes at high temperature. The annealing behavior of the peak shows that the effects of the manufacturing are removed only after annealing above 873 K. The peak $P_0$ observed by Sugimoto et al. seems to correspond to this peak, though they attribute it to twin boundaries. The slightly duller step of $Q^{-1}$ at $T_1$ for $T_a=673$ K compared to that for $T_a=873$ K may also be due to the dislocations, because the step is known to become sluggish by deformation.

The $Q^{-1}$ forms a steep step at $T_1$, while it shows peak-like behavior at $T_2$, though the latter is not so clear. The corresponding two minima in $t$ are also quite different in shape and temperature hysteresis. The temperatures of the two minima do not change but only their depths change with $T_a$. All these results indicate that quite different phenomena take place at $T_1$ and $T_2$. The martensitic transformation is known to proceed in two steps in certain conditions, that is, parent phase first transforms into premartensite (R-phase) and then into martensite in the cooling run. In the TiNi system, however, the premartensitic transformation is not a precursor of the martensitic one but they are in a competitive relation. In this sense these two transformations are different or independent, though they are crystallographically interrelated.

It seems to be reasonable then to attribute the two minima in $t$ observed at $T_1$ and $T_2$ to the premartensitic and the martensitic transformations, respectively. The high value of $Q^{-1}$ in the serration is considered to arise from the motion of interfaces between different variants of premartensite and/or martensite. The peak-like behavior seems to be possible to occur, if the interfacial area becomes maximum at a certain temperature. The peaking mechanism, however, is not so simple, because the value of $Q^{-1}$ depends on many factors such as cooling rate and vibrational frequency. The vibration during the measurements is also expected to promote stress-induced transformation, which may be one of the reasons for the irregular nature of the serration. The peculiar ZP movements around $T_1$ and $T_2$ are the results of strain accommodation among different variants.

The appearance of the martensitic transformation at $T_2$ is already detected for $T_a=873$ K as a peculiar ZP movement (Fig. 2), though the corresponding minimum in $t$ does not appear before $T_a$ is increased up to 973 K (Fig. 3). As $T_a$ is increased above 873 K, the martensitic transformation becomes clearer, while the premartensitic one weaker. These phenomena are observed only when the specimen is rapidly cooled down. This indicates that some kind of diffusion-involved and cooling-rate-dependent...
phase change may exist at about 870 K, as will be described below.

In the previous paper(1) a $Q^{-1}$ peak and a local maximum in $t$ were observed at about 870 K and 790 K, respectively, and they were considered to correspond to the order-disorder transition(10). According to a recent neutron diffraction study by Matsumoto et al.(11), however, the order-disorder transition temperature is estimated to be about 1370 K. Then the order-disorder transition is excluded from consideration here. The phase change at about 870 K is now considered to be related to some kinds of precipitation processes(12). They are reported to proceed very slowly especially on the Ni rich side, and a metastable high temperature phase is easily retained if a specimen is cooled down rapidly from high temperature(13).

The appearance of the second minimum and the disappearance of the first one are then considered to be related to this metastable state, in which the retained high temperature phase and/or the precipitation may play an important role. These effects seem to increase with the increase in $T_a$ above 873 K. The details of the precipitation processes and their effects on the transformations, however, have not been known yet. The precipitation itself, for example Ti$_2$Ni$_3$, is known to undergo both types of transformations(14), and internal stress produced by the precipitation is expected to yield some structural changes in the matrix(15). Besides these examples many other factors are possible to modify the transformation characteristics.

Among many possible factors only the preannealing temperature was chosen here as a first step. The present results demonstrate the importance of the preannealing treatments, and the following two points are especially to be emphasized.

1) The 200 K peak has nothing to do with the transformation. It is removed by annealing above 873 K.
2) Some kind of diffusion-involved phase change is expected to exist at about 870 K. This must be taken into account, when the specimen is cooled down from temperatures above 870 K.

This kind of work where some of the important factors such as preannealing temperature are systematically controlled is necessary. Though only the preannealing temperature was considered in this paper, other factors such as a small amount of impurity are also important to solve the existing controversies and to reach the final conclusions.

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