

Dynamic Mechanical Analysis of TiNbAl Biomedical Shape Memory Alloys

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In order to evaluate physical properties of shape memory alloys (SMAs), a method called dynamic mechanical analysis (DMA) is applied in terms of phase transformation behavior and mechanical properties. DMA can reveal stress, strain, storage modulus, loss modulus and internal friction simultaneously in addition to their dependence on temperature and frequency. In this work, such elastic and anelastic behavior was investigated for a TiNbAl SMA which exhibits superelasticity at room temperature. It was found that strain change due to martensitic transformation (transformation strain) was evaluated to be around 1.1%, Young's modulus was ranged from 28GPa to 60GPa and that internal friction was 0.05-0.15. Besides, strong temperature dependences of Young's modulus and internal friction were confirmed and the dependences were similar to those of Ti-Ni SMAs. It is concluded that DMA is a powerful method to clarify elastic and anelastic properties of SMAs as well as phase transformation behavior.

keywords: martensitic transformation, shape memory alloys, dynamic mechanical analysis, Young's modulus, internal friction

1. INTRODUCTION

This paper describes a method called dynamic mechanical analysis (DMA) in order to investigate phase transformation behavior of shape memory alloys (SMAs), and some results obtained by DMA are shown. Firstly the characteristics of two typical methods are described; differential scanning calorimetry (DSC) and constant stress tests during thermal cycles (strain-temperature relationship under constant stresses). Then, the principle of DMA is explained. DMA is often used for polymers in order to evaluate viscosity and damping properties. However, recently we have been applied DMA for the evaluation of transformation behavior and damping properties of SMAs [1-3], and revealed that DMA is quite a powerful method to clarify the transformation behavior as well as elastic and anelastic properties of SMAs. It is noted that SMAs are high efficient damping materials due to large internal friction around transformation temperatures when applied strain is large enough for reorientation of martensite variants or stress induced martensitic transformation [1, 4]. Finally, DMA is applied for a new Ti-base biomedical SMA. The Ti-base SMAs are composed of nontoxic elements and expected to replace Ti-Ni in the biomedical field [5-8].

2. EVALUATION METHODS

2.1 DSC

DSC is the most conventional method to evaluate the transformation temperature. The principle of DSC is to detect the temperature difference between a sample and a reference material, and the difference is caused by

the enthalpy change due to the phase transformation of the sample, for example. Figure 1 (a) shows a schematic illustration of DSC measurements for a diffusion transformation and for a diffusionless transformation of SMA. The martensitic transformation of SMA starts at M_s and finishes at M_f . The accuracy of transformation temperature in DSC determination depends on heat flow per second (J/s); therefore, DSC is beneficial and determines transformation temperature precisely when the phase transformation occurs quickly with a large heat transfer. From the viewpoint of transformation heat, the diffusionless martensitic transformation in nature exhibits a small heat flow in comparison with diffusion transformation. Moreover, the heat transfer of martensitic transformation is smaller in thermoelastic type as compared with non-thermoelastic type. The non-thermoelastic martensite is generally seen in iron, steel, titanium and many materials equipping with large lattice distortion during transformation. On the other hand, the thermoelastic martensite is generally seen in SMAs. Therefore, the transformation heat of SMAs is small, and thus DSC is in nature not suitable to determine phase transformation temperature of SMAs.

2.2 Constant stress test

Constant stress test during thermal cycles (usually called as strain-temperature or S-T curve) is effective to clarify the transformation behavior of SMAs. The principle of constant stress test under thermal cycles is shown in Figure 1 (b). The constant stress test provides a strain change as a function of temperature including thermal expansion. When a sample is cooled down

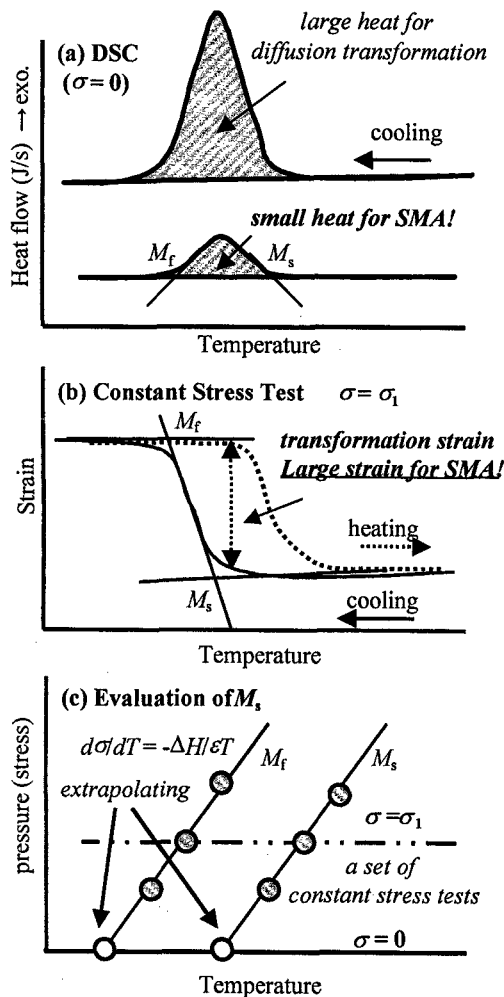


Figure 1 Schematic illustrations of (a) DSC, (b) constant stress test (S-T curve) and (c) evaluation of M_s from a set of constant stress tests.

under a constant stress and a martensitic transformation starts at M_s , a strain change occurs due to crystallographic anisotropy of martensite and finishes at M_f . Then, M_s and M_f are determined by using S-T curve. However, the M_s and M_f obtained using S-T curve are not equal to those obtained by DSC under zero pressure (usually 1 atm). If M_s and M_f under zero pressure are required to be evaluated, a set of constant stress tests under various constant stresses must be carried out and the transformation temperatures can be obtained by extrapolation using the Clausius-Clapeyron relationship: $d\sigma/dT = -\Delta H/\epsilon T$ where σ is stress, T is temperature, ΔH is heat of transformation and ϵ is transformation strain. The evaluation of M_s and M_f using the Clausius-Clapeyron relationship is shown in Figure 1 (c). Although the strain-temperature relationship is useful, total testing time of constant stress tests requiring several thermal cycles is much longer than that of DSC requiring one or a few thermal cycles. Besides, damages and plastic deformation introduced during thermal cycles should be considered in many cases.

2.3 DMA

DMA is a method that measures the relationship between strain and stress simultaneously as a function of time and frequency. A schematic illustration of DMA measurement in tensile mode is shown in Figure 2. A sample is prestrained by a static force, and a wavy dynamic force with a constant frequency is applied. Then, the strain output is measured. Therefore, DMA can reveal elastic and anelastic properties such as storage modulus, loss modulus, Young's modulus E , thermal expansion, transformation strain and internal friction IF (or called Q^{-1}). Besides, temperature dependence of these factors can be evaluated. It should be emphasized that SMAs in nature possess large shape recoverable strain over a few percent instead of small phase transformation heat. Therefore, DMA measuring strain change is effective for SMAs in comparison with DSC measuring heat change.

DMA can estimate phase transformation behavior when one or some of measured factors change by phase transformation. In SMAs, E and Q^{-1} usually change around transformation temperatures. The change of E is caused by "lattice softening" and the change of Q^{-1} is caused by reorientation of martensite variants and/or stress-induced martensitic transformation (SIMT). It should be noted that DMA is carried out with a large vibration amplitude around 0.1-1% in strain on the contrary to general Q^{-1} measurements with small strain amplitude ($<10^{-5}$ in strain). The reorientation of martensite variants and/or SIMT dominantly occur at large strain region. Therefore, DMA is suitable to evaluate Q^{-1} of SMAs. The recent DMA work for Ti-Ni base alloys were reported elsewhere [1-3].

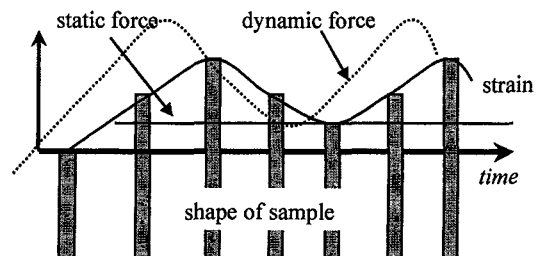


Figure 2 Schematic figure showing strain change as a function of time under a static force and a dynamic force with a frequency.

3. EXPERIMENTAL PROCEDURE

A Ti-Nb-Al SMA (abbreviated as TiNbAl) was chosen in this study. The details of alloy composition and fabrication method were described in Ref. [9]. The alloy was prepared by Ar arc melting method, homogenized at 1273K, cold-rolled to be 95% in thickness reduction and then solution-treated at 1273K. The alloy exhibits superelasticity at room temperature [9]. DMA was carried out under tensile mode at temperature ranging from 128K to 470K using NETZSCH DMA242C. The specimen size was 10mm in length, 0.87mm in width and 0.24mm in thickness. The heating/cooling rate and the frequency were selected to be 5K/min and 2Hz under the single-frequency mode. The static force was 8N (≈ 39 MPa in stress) and maximum dynamic force was 6.7N (≈ 33 MPa in stress). Thus, the applied stress was ranged from 6MPa to 72MPa in this case.

4. RESULTS AND DISCUSSION

4.1 Strain-temperature curve

Figure 3 shows a strain-temperature relationship obtained by DMA where the strain employed was the averaged strain in each cycle of 2Hz. It should be noted that this strain-temperature curve is similar to that obtained by a constant stress test but that the strain-temperature in Fig. 3 was not measured under a constant stress. However, this S-T curve is believed to be similar to the S-T curve under a constant stress of 39MPa (static stress). It is clear that large shape change starts at 212K on cooling which corresponds to M_s and that the shape change does not finish in the temperature range. M_f of this alloy is judged to be lower than 128K. On the other hand for the heating process, the shape recovery starts at 187K and finishes at 274K. These temperatures correspond to A_s and A_f . The transformation temperatures obtained are listed in Table 1. The transformation temperature hysteresis between M_s and A_s is 25K. The difference between A_s and A_f is 62K. If the temperature difference between M_s and M_f is equal to that between A_s and A_f , M_f is thought to be 125K. It should be emphasized that transformation temperature of Ti-base SMAs is difficult to be measured by DSC, in many cases no data obtained by DSC in our experience. Thus, DMA is said to be a powerful method to evaluate transformation temperature of SMAs even if transformation temperature is not detected by DSC.

The transformation strain between M_s and A_s was 1.1%. This value is comparable to that of Ti-Ni thin film under the constant applied stress of 100MPa [10]. Then, the shape memory properties of TiNbAl seem to be comparable to those of Ti-Ni thin film.

4.2 Young's modulus

Figure 4 shows Young's modulus E of TiNbAl as a function of temperature. Young's modulus at 400K is around 60GPa, and gradually decreases with decreasing temperature on cooling. The lowest value is 29GPa at 194K. This temperature corresponds M_s . The decrease of Young's modulus at temperature above M_s must be caused by lattice softening similar to Ti-Ni [1]. With further decreasing temperature, E value slightly increases and becomes 40GPa at 130K. On heating, Young's modulus decreases, reaches the minimum value of 28GPa at 234K, then increases with increasing temperature. It is clear that the Young's modulus strongly depends on temperature and thermal process. Besides, Young's modulus becomes the minimum values near M_s on cooling and A_s on heating. In order to substitute for hard tissue in biomedical applications, Young's modulus of biomaterials is preferably closer to that of hard tissue: 18GPa for bone [11]. Since the lowest Young's modulus of TiNbAl is close to that of bone, this material is promised to be a structural biomaterial substituting for hard tissue.

4.3 Internal friction

Internal friction Q'' of TiNbAl is shown in Figure 5 as a function of temperature and in Figure 6 as a function of reciprocal temperature. With decreasing temperature on cooling, Q'' is almost constant value of 0.05 above 230K, rapidly increases between 230K and 200K and then gradually decreases. On heating, the

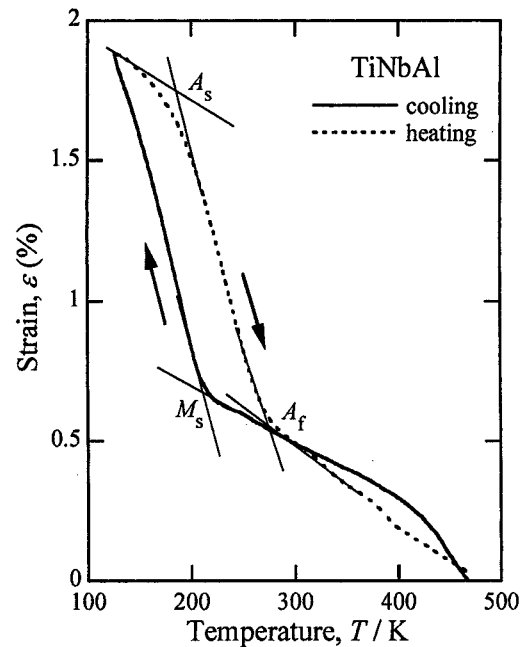


Figure 3 Strain-temperature relationship of TiNbAl estimated using DMA.

Table 1 Martensitic transformation temperatures of TiNbAl obtained by DMA.

Temp. T / K	M_s	M_f	A_s	A_f
	212	-	187	274

M_s : martensitic transformation start temperature
 M_f : martensitic transformation finish temperature
 A_s : austenite transformation start temperature
 A_f : austenite transformation finish temperature

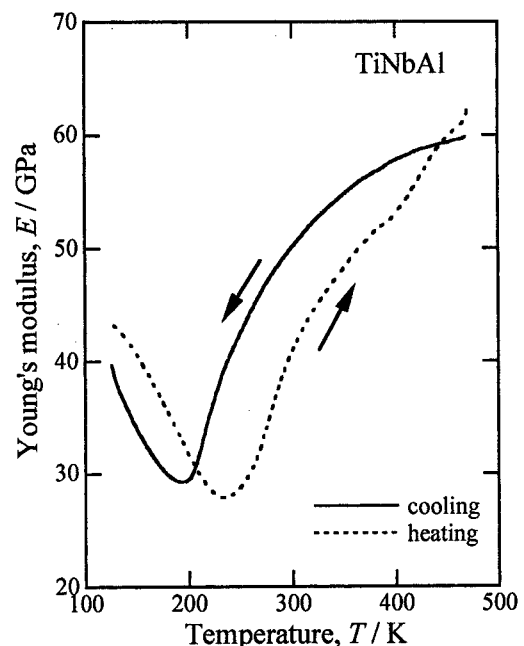


Figure 4 Young's modulus of TiNbAl as a function of temperature.

temperature dependence of Q^{-1} is almost similar to that seen on cooling. The highest Q^{-1} obtained is 0.15 at 230K on heating. The Q^{-1} values are quite high around 0.1-0.15 at temperatures below 200K (close to M_s) on cooling and 230K (close to A_s) on heating. Then, it can be said that TiNbAl exhibits high damping properties when the alloy is martensite phase or martensite/austenite two phases. Besides, the Q^{-1} value is higher than that of Ti-Ni (Q^{-1} : 0.05-0.1 below A_f) [1]. The high damping of TiNbAl may be due to the large transformation hysteresis in comparison with Ti-Ni. The details of high damping

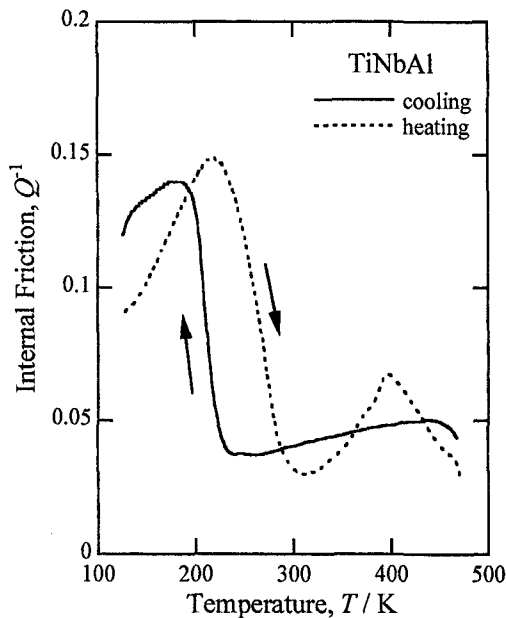


Figure 5 Internal friction of TiNbAl as a function of temperature.

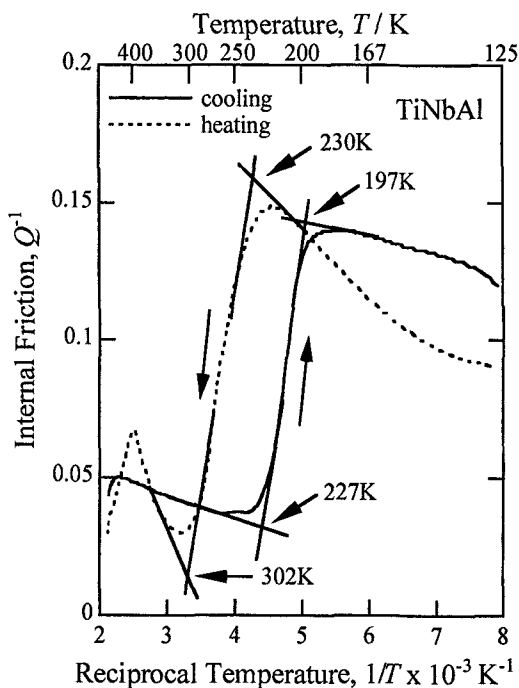


Figure 6 Internal friction of TiNbAl as a function of reciprocal temperature.

should be further investigated.

5. CONCLUSIONS

- (1) Strain-temperature relationship of superelastic TiNbAl was obtained by DMA. Transformation temperatures of TiNbAl are evaluated to be 187K for M_s , 212K for A_s and 274K for A_f , and transformation strain is 1.1% under static stress of 39MPa and dynamic stress of 33MPa.
- (2) Young's modulus of TiNbAl is ranged from 28GPa to 60GPa depending on temperature, and becomes the lowest value around 28-29GPa near M_s and A_s .
- (3) TiNbAl exhibits high damping and the internal friction Q^{-1} exceeds 0.1 at temperature below 197K on cooling and below 230K on heating. These temperatures are close to M_s and A_s . Besides, internal friction strongly depends on thermal process (*i.e.* heating or cooling) and temperature.
- (4) TiNbAl is concluded to possess good shape memory properties, low Young's modulus and large damping properties.
- (5) DMA is quite useful for the evaluation of martensite-related elastic and anelastic properties of shape memory alloys.

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