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POSITRON STUDY OF DEFECTS IN TiNi ALLOYS

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A number of TiNi samples with different compositions and states were measured by positron annihilation technique. And microdefects and the influence of them on shape memory effect were analyzed, giving some valuable information for the study of technological processes of preparing TiNi functional shape memory devices.

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I. INTRODUCTION

Up to now, TiNi tops the list of all the shape memory materials. Due to its unimaginable properties, the alloy's manufacturing process and microstructure were studied extensively using physical metallurgy techniques (PMT), such as optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy, internal friction, resistivity and mechanical properties measurements, from which we have had a deeper understanding of the phases and transformations in TiNi shape memory alloy (SMA).

However, owing to the limitation of PMT themselves, the function of microdefects in TiNi alloy could not be effectively studied. As is well known, two of the most important factors dominating the properties of a metallic material are phases and defects, once its composition is determined. It should be noticed that the past publications by use of PMT have already found the contributions of defects to shape memory effect (SME) of TiNi alloy.[1−6] Positron annihilation technique (PAT) is characterized by testing microdefects in metals. But it is still in the process of accumulating experience and developing, only a few of related papers can be seen in the literature.

Focusing on technically practical processes with universality, this paper studies a number of TiNi samples with different compositions and states by means of PAT, giving some information regarding the influence of microdefects on macroscopic SME, which is difficult to obtain with traditional PMT.

II. EXPERIMENTAL

Positron source was a sandwiched ^{22}NaCl. The detector of positron annihilation Doppler broadening spectroscope was a highly pure Ge, with a full width at half maximum (FWHM) of less than 1.8 keV at 1.332 MeV γ-rays from ^{60}Co. The measured Doppler peaks were characterized by a conventional S-lineshape parameter defined as a count ratio of the central part to the wings or the total area of each peak. The relative error of the S-parameters was about $\pm 0.3\%$. Positron annihilation radiation 2γ one-dimensional angular correlation apparatus with long-slit geometry, in which the scanning range of the moving detector was between 0–15 mrad, had an optical FWHM of 0.46 mrad and its angular distribution curves were evaluated using an H-lineshape parameter defined as a count ratio of 0–3 mrad to 3.5–15 mrad. The greater the S and/or H, the more the defects contained in a sample. In addition, TEM, X-ray diffraction, and measurement of mechanical properties were also used.

III. RESULTS

A. About the point defects created during quenching

There exist point defects in a metal after quenching. One of the necessary processes, called pretreatment, by which SME could be produced, is the quenching or quickly-cooling of TiNi alloys. This implies that point defects play an important part.[7,8]

The alloys used were Ti-49.0 at% Ni, Ti-50.0 at% Ni, Ti-50.5 at% Ni, Ti-51.0 at% Ni, and Ti-51.5 at% Ni. Their samples were treated at 1050 ℃ for 0.5 h and quenched into water. Their S-parameters were then measured. Curve a in Fig.1 shows the S-parameter vs. Ni-content. It could be seen that the Ni-content is not a direct factor affecting S; other-

wise, the relation between S and content should be linear. Suppose that the point defects formed during quenching consist of vacancies only. And according to the relation between the melting point T_m of the alloy and the formation energy E_v of a vacancy and that between vacancy concentration C_v and E_v, vacancy concentrations produced during quenching are estimated for the as-quenched TiNi alloys with different compositions, as illustrated by curve b in Fig.1. It is apparent that the variation trends of C_v and S are basically identical, indicating that the point defects in the TiNi alloys introduced by quenching from 1050 ℃ are vacancies.

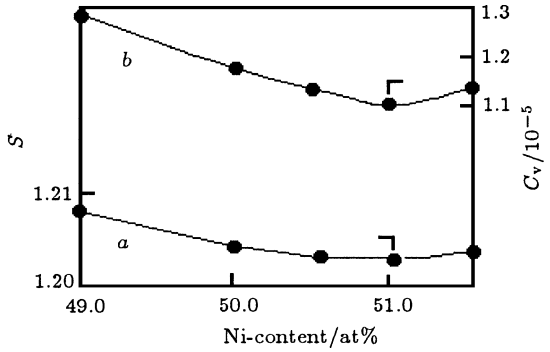


Fig.1. S-parameter (curve a) and vacancy concentration C_v (curve b) as a function of Ni-content for TiNi alloys after quenching from 1050 ℃.

B. About the selecting of alloying compositions

TiNi alloys showing SME exist in a narrow range of composition. Even so, their SME varies strongly with the content. The information from the past publications as well as our technical practice revealed that the TiNi alloys containing near 51 at% Ni could easily display good SME and have been widely used in engineering. This paper will give an explanation by angular correlation measurement. Alloys of Ti-50.0 at% Ni, Ti-50.5 at% Ni, Ti-51.0 at% Ni, and Ti-51.5 at% Ni were treated under the same processes and then their H-lineshape parameter (a), work output (b), and shape recoverability (c) were measured, as shown in Fig.2. Making a comparison between the three curves, it could be found that when Ni-content increases, H goes down, work output and recoverability go up. When Ni further increases, H rises, work output and recoverability reduce. The smallest H and the best SME appear just at a composition of Ti-51.0 at% Ni. This fact indicates that macroscopic SME of the TiNi alloys has close relations to microdefects.

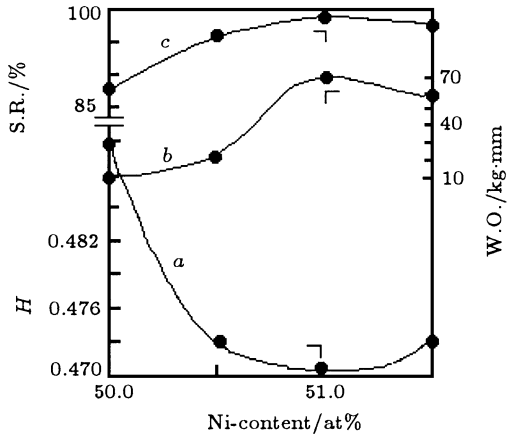


Fig.2. (a) H-parameter, (b) work output (W. O.), and (c) shape recoverability (S.R.) as a function of Ni-content.

The researchers for SMA have known that one of the reasons for the TiNi alloys containing near 51 at% Ni to be often selected in practical applications is that the alloys have a transformation at about room temperature, which is convenient for fabricating SME devices. The present positron experiment may reveal another reason: there exist the fewest defects in the alloys of near 51 at% Ni compared with other alloys treated by the same process.

C. About the origin of SME

How to interpret the reversible SME of TiNi alloys has always been a very interesting subject.

A number of U-shaped specimens of Ti-51.0 at% Ni possessing reversible SME were prepared. The preparation procedure was as follows: The strips with dimensions of 100 mm×12 mm×0.45 mm were solution-treated and followed by constrainedly-aging conducted at different distances AB and temperatures, as shown in Fig.3.

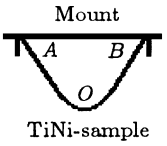


Fig.3. Schematic of a Ti-51.0 at% Ni sample to be constrainedly-aged.

After the specimens had been taken off the mounts, their S-parameters at O zone were measured. The Doppler measurements having been completed, the reversible SME between 0 ℃ and 100 ℃ of the specimens was examined. When heated and cooled, the two end portions of the specimens would turn upwards and downwards in sequence. The schematic of the shapes at 100 ℃ and 0 ℃ is shown in Fig.4 for one of the specimens. Reversible SME could be characterized roughly by angle $\angle AOA'$ (or $\angle BOB'$). The

larger the $\angle AOA'$, the better the reversible SME of a specimen.

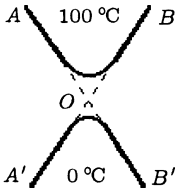


Fig.4. Schematic of the shapes at 100 ℃ and 0 ℃ for one of the constrainedly-aged specimens.

Figure 5 shows the change of angle $\angle AOA'$ with S-parameter, in which point D (■) stands for the S-parameter of the specimens whose zones O have been

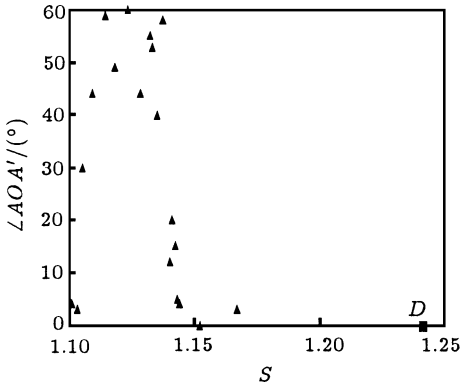


Fig.5. $\angle AOA'$ of reversible SME as a function of S-parameter.

bent many times after constrainedly-aging (Zone O of the specimens surely contained a large sum of defects). It can be seen from the distribution of symbols ▲ that every specimen whose S-parameter is too large or too small will have a smaller angle $\angle AOA'$, that is, any of the specimens that possess a moderate S-parameter will bring about a remarkable reversible SME. Some investigations have mentioned the influence of structural defects on the origin of two-way and/or all-round SME in near-equiatomic TiNi alloys of Ni-rich compositions: the preferential growth of martensitic variants should rely upon the control of structural defects bound with them, and there would not be SME of TiNi alloys without the structural defects. The present study by positrons indicates that the origin of SME of Ti-51 at% Ni alloy is related to the structural defects indeed. This is well consistent with the past publications; However, not all the specimens containing structural defects can show a good SME. For instance, the specimens having larger S-parameters and those whose zone O has been bent many times only show a little oreven no SME; Obviously, in order to obtain a good SME of an alloy, the existence and an appropriate density of structural defects in it are equally important. Without structural defects, martensitic variants could not be controlled in such a way as to grow preferentially. On the contrary, with too many structural defects, preferential growth of martensitic variants would be restrained.

D. About the hysteresis temperature

The technology for preparing TiNi devices has been advanced to such a point that fabrication of devices showing one-way, two-way, and all-round SME is an immediate possibility. However, it is most troublesome to prepare a useful device that has a desired and defined hysteresis temperature to meet the needs of a particular engineering. How to control hysteresis temperature is essentially a problem of altering the direct and reverse transformation temperatures of martensitic, premartensitic, and austenitic phases. It has been known from the previous studies that the possible affecting factors are many and varied. The first is the composition of alloys.[1,9−12] The next is the thermomechanical process used, such as preparation method, treatment temperature and duration, the value and direction of applied stress.[1,2,13−18] Moreover, there are a lot of microstructural factors, e.g., grain size[19], lattice parameter of the phase[19,20], relative amounts of preferred and stabilized martensites[1,3,4,6,19,21], transformation sequence[13,15,17,21,22], precipitates[1,3,4,13,17,22], defects[1−6], internal stress field[1,3,4,14,17,21], anisotropy[18] and surface state. But, no matter how the above factors are modified, it could not be sure that the hysteresis temperature obtained is the desired one. In fact, this comes from the fact that the details of thermoelastic martensitic transformation and the factors affecting them have not fully been clarified.

Alloy of Ti-51.0 at% Ni was solution-treated at 700 ℃ and was cut into rectangles with a size of 60 mm×8 mm×0.4 mm. The rectangles were made into U-shaped devices through different treatments.

The distance L (Fig.3) between the two terminals AB of the U-shaped devices were then measured during heating and cooling, forming a distance L-temperature T loop. A typical L- T loop of the U-shaped device treated at 450 ℃ is shown in Fig.6. The maximum of the temperature differences on each L- T loop was selected to be its hysteresis temperature ΔT used in this study.

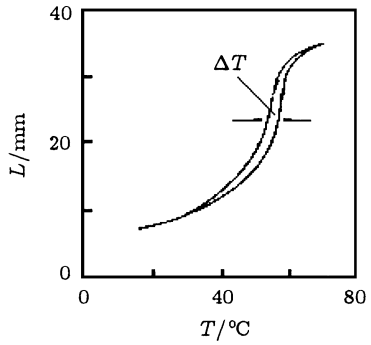


Fig.6. The loop of distance L-temperature T for the TiNi U-shaped device treated at 450 ℃.

After the loop measurements, the S-parameters were determined at parts A (or B) and O (Fig.3) of the U-shaped device, respectively. Figure 7 gives the variation of S-parameters with hysteresis temperature ΔT for parts A and O.

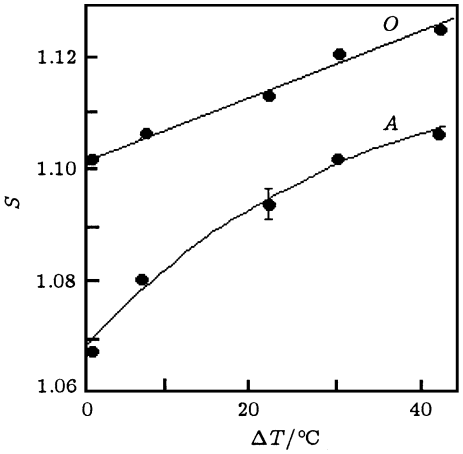


Fig.7. The S-parameter as a function of hysteresis temperature ΔT for parts A and O of the TiNi U-shaped device.

Figure 7 displays that each S-parameter on curve O is larger than its corresponding one on curve A. That is to say, the defects capable of trapping positrons inside part O are more than inside part A of the same device. Clearly, this is due to the fact that part A is subjected only to a general aging, and part O is bent before the treatment and undergoes a constrainedly-aging. The bending mainly results in stress-induced martensite, it also creates defects, which become irreversible through aging. Figure 7 shows ΔT is connected with S-parameter, exhibiting that microdefects play an important role for adjusting the barrier potential of transformations, the degree of overheating and overcooling (or direct and reverse transformation temperatures). If one wants to obtain an SME device with a small ΔT, then simultaneous-decrease of defects in parts A and O may be required. On the contrary, if a device with a large ΔT is needed, then simultaneous-increase of defects in the two parts should be adopted.

E. About the stability of SME

It has been found that the reversibility of a two-way SMA fabricated by constrainedly-aging attenuates in initial use and tends to stabilize after thermally-cycling for several times. There is not any effective method for analyzing and examining this phenomenon, so far as we know.

Constrainedly-aged Ti-51.0 at% Ni two-way devices were cycled between boiling water (100 ℃) and liquid nitrogen (−196 ℃). Every thermal-cycle consisted of the following steps: placing the devices into boiling water for about 30 s and taking them out → holding for a little while → putting them into liquid nitrogen for 30 s. and taking them out. After the devices were thermally balanced with room temperature, S-parameters were measured. During the cycle, the radius of curvature of the devices and S-parameter were getting bigger with increasing number of cyclings. And after some 30 times, the radius was tending towards stabilization and S-parameter approached saturation. Figure 8 gives the curve of S-parameters vs number of cyclings, demonstrating that the reversibility and S-parameter are mutually dependent. The evaluation of the macroscopic performance and measured data of positrons are in agreement with each other. Positrons here become a probe for measuring the stability of SMA.

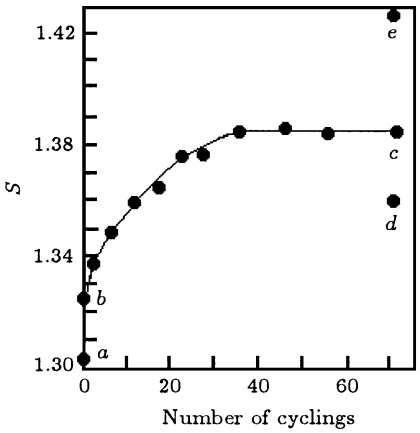


Fig.8. S-parameter as a function of number of cyclings for Ti-51.0 at% Ni two-way SME.

The common explanations of SME attenuation during initial cycles are that the internal stress stored in the process of fabricating two-way device is unstable and would be stabilized after cycling for several times and/or the diffused precipitates formed during aging make the matrix distorted. From the measured

X-ray diffraction patterns of the specimens, we know that the amount of martensites after cycling for 70 times is larger than that before cycling. However, the martensite, which forms by twinning, does not trap positrons. In another experiment of ours, we find that only a small change of S-parameters occurs even if all the parent phase in the alloy turns to martensitic phase. Therefore, it may be suggested that the main factor affecting S-parameters and/or stability of the devices is the microdefects introduced by cycling.

In order to get further information on the behavior of the introduced microdefects, the specimens cycled for 70 times were aged in boiling water for 0.5 h and cooled down slowly to room temperature. Their S-parameters decreased from 1.385 to 1.361, indicating that the microdefects created by thermally-cycling include mobile (vacancies) and immobile (dislocations) defects. Indeed, a few of dislocations were observed in the same specimen by means of TEM.

In Fig.8, points a (1.301), b (1.324), c (1.385), d (1.361), and e (1.429) represent the S-parameters of the alloy solution-treated, constrainedly-aged, thermally-cycled for 70 times, aged in boiling water for 0.5 h after cycling, and cold-rolled, respectively. It is quite evident that constrainedly-aging creates a part of microdefects in the sample, and cycling makes microdefects increase further. However, the density of the microdefects is much lower than those formed by cold-rolling. Hence, the alloy still exhibits a spontaneous and reversible shape change. Perhaps, it is the small density of defects that affects the stability of the two-way SME during the initial stage of thermally-cycling.

IV. DISCUSSION

The TiNi alloy showing SME is a material containing various defects, or non-homogeneity, such as, grain boundary, stacking fault, twin, dislocation, precipitate, microstructural anisotropy, and substitutional nickel atom in the Ni-rich TiNi alloy. In the light of the results given from ⅢA to ⅢE, it may be considered that the memory performances are related only to the fraction of the defects capable of trapping positrons. The grain sizes of the above specimens range between 0.01 and 0.1 mm, much larger than the diffusion length of positrons and therefore have no influence on the annihilation of positrons. Stacking faults and twins do not capture positrons under the first approximation.[23,24] Figure 9 shows TEM-microstructure taken from the U-shaped device constrainedly-aged at 500 ℃, showing that there exist lenticular precipitates $Ti_{44}Ni_{56}$ pervading matrix. $Ti_{44}Ni_{56}$ precipitates' sizes are a few ten nm wide and a few hundred nm long, just within the distance of positrons diffusion. As a consequence, the interfaces (or misfit dislocations) between $Ti_{44}Ni_{56}$ and the matrix are the centers of trapping positrons. It may be suggested that one kind of the structural defects contained in a good SME Ti-51.0 at% Ni is the interfaces between $Ti_{44}Ni_{56}$ and the matrix. This would not seem enough because the straight samples (not bent) which are subjected to treatment at moderate temperatures also contain $Ti_{44}Ni_{56}$ precipitates. But, with these samples only the one-way SME can be generated. So the existence of $Ti_{44}Ni_{56}$ precipitates is the necessary condition for generating SME, but not sufficient. A good SME specimen must contain other kinds of structural defects. It is likely that they are the structural defects or phases induced by bending, probably including stress-induced martensites, staking faults, twins, dislocations, internal stress field, distortion of lattice, microstructural anisotropy, etc., some of which become irreversible. It seems that these irreversible stress-induced structural defects together with $Ti_{44}Ni_{56}$ make it possible to generate a good SME. According to the positron lifetime experiments the authors have done, it is impossible to differentiate these structural defects by fitting the lifetime spectra at present.



Fig.9. Microstructure by TEM for the U-shaped device constrainedly-aged at 500 ℃.

V. SUMMARY

Summing up the above experimental results by PAT associated with some PMT for a number of the samples with different compositions and states, the obtained information in regard to the microdefects and their function in TiNi alloys may be summarized as follows:

1. The point defects in the TiNi alloys introduced by quenching from 1050 ℃ are monovacancies.

2. Microdefects play an important role in generating and controlling SME. But, not all the specimens containing structural defects (or structural imperfection) can exhibit good SME; The structural defects have to be appropriate in density. Without or with too many structural defects, a good SME could not be obtained.

3. The structural defects contained in the alloy showing a good SME may be suggested to consist of two kinds-one is the interfaces between $Ti_{44}Ni_{56}$ and the matrix, the other is the so-called stress-induced structural defects which transform to what is referred to as irreversible through aging.

4. Instability of the two-way SMA during the initial stage of thermally-cycling is due to the increase of a small amount of defects.

REFERENCES

[1] M. Nishida, T. Honma, *Scripta Met.*, **18**(1984), 1293.
[2] M. Nishida, T. Honma, *Scripta Met.*, **18**(1984), 1299.
[3] M. Nishida, C. Wayman, T. Honma, *Scripta Met.*, **18**(1984), 1389.
[4] T. Honma, Shape Memory Alloy '86-Proc. Int. Sym. on Shape Memory Alloys (China, 1986), p.83.
[5] B. G. Mellor, J. M. Guilemany, J. R. Miguel, J. Fernandez, A. Amengual, F. C. Lovey, V. Torra, *Scripta Met.*, **24**(1990), 241.
[6] K. K. Jee, M. C. Shin, Y. G. Kim, *Scripta Met.*, **24**(1990), 921.
[7] D. P. Dautovich, G. R. Purdy, *Can. Met. Quart.*, **4**(2)(1965), 129.
[8] R. J. Wasilewski, S. R. Butler, J. E. Hanlon, D. Worden, *Met. Trans.*, **2**(1971), 229.
[9] T. Honma, H. Takei, *J. Japan Inst. Met.*, **39**(1975), 175.
[10] S. Miyazaki, Y. Ohmi, K. Otsuka, Y. Suzuki, Proc. Int. Conf. on Martensitic Transformations (ICOMAT-1982), p.C4-255.
[11] T. Saburi, T. Tatsumi, S. Nenno, Proc. Int. Conf. on Martensitic Transformations (ICOMAT-1982), p.C4-261.
[12] C. M. Hwang, M. Meichlc, M. B. Salamon, C. M. Wayman, *Phil. Mag.*, **A47**(1983), 9 and 31.
[13] M. Nishida, C. M. Wayman, T. Honma, *Scripta Met.*, **19**(1985), 983.
[14] S. K. Wu, H. C. Lin, T. S. Chou, *Scripta Met.*, **23**(1989), 2043.
[15] H. C. Lin, S. K. Wu, *Scripta Met. Mater.*, **25**(1991), 1295.
[16] S. K. Wu, H. C. Lin, *Scripta Met. Mater.*, **25**(1991), 1529.
[17] D. Favier, Y. N. Liu, P. G. McCormick, *Scripta Met. Mater.*, **28**(1993), 669.
[18] P. Y. Manach, D. Favier, *Scripta Met. Mater.*, **28**(1993), 1417.
[19] T. Saburi, M. Yoshida, S. Nenno, *Scripta Met.*, **18**(1984), 363.
[20] K. Otsuka, T. Sawamura, K. Shimizu, *Phys. Stat. Sol.*, (**a**)**5**(1971), 457.
[21] Y. N. Liu, P. G. McCormick, *Scripta Met.*, **22**(1988), 1327.
[22] C. Y. Xie, L. C. Zhao, T. C. Lei, *Scripta Met. Mater.*, **24**(1990), 1753.
[23] G. Dlubek, O. Brummer, Ashraful Alem, *Phys. Stat. Sol.*, (**a**)**52**(1979), 217.
[24] T. D. Troev, K. Hinode, S. Tanigawa, M. Doyama, *Appl. Phys.*, **13**(1977), 105.