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Influence of the cooling/heating rate on the martensitic transformation and functional properties of the quenched $Ni_{51}Ti_{49}$ shape memory alloy

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The influence of the cooling/heating rate on the martensitic transformation temperatures and the strain variation in the quenched $Ni_{51}Ti_{49}$ alloy was studied. It was found that a decrease in the cooling/heating rate increased the temperatures of the forward transformation. It was assumed that this was due to the fact that the $Ni_{51}Ti_{49}$ alloy was able to undergo the forward transformation on cooling, as well as during isothermal holding, which increased the transformation temperatures on slow cooling. The influence of the cooling/heating rate on the transformation temperatures depended on whether the stress affected the cooling and heating or not. It was shown that if the forward transformation occurred under a constant stress, then the influence of the cooling/heating rate on its temperatures became weak. However, the temperatures of the reverse transformation under load depended on the cooling/heating rate and this dependence was more significant for the start temperature of the reverse transformation A_s than for the finish temperature. It was found that the cooling/heating rate did not affect the shape memory effect, however, this influenced the irreversible strain depending on the stress acting on cooling and heating. It was assumed that this might be caused by different mechanisms of the oriented martensite appearance.

Keywords: martensitic transformation, cooling/heating rate, functional properties, NiTi.

1. Introduction

NiTi-based shape memory alloys demonstrate the unique ability to recover a large inelastic strain on heating or unloading and create a high recovery stress on heating, which makes them very attractive for many applications, such as sensors and actuators [1–2]. To produce a strain or stress variation, shape memory alloy elements are subjected to cooling and heating within the temperature range of the martensitic transformation, but the temperature variation rate is not usually controlled. This is due to the fact that the functional behaviour of the shape memory alloy is controlled by the thermoelastic martensitic transformations that are the first-order phase transition with athermal kinetics [3]. This means that the variation in the volume fraction of the new phase depends only on temperature and external parameters, such as stress or hydrostatic pressure, and does not occur during isothermal holding. Thus, a variation in the temperature rate cannot influence the martensitic transformation temperatures and the functional properties of NiTi-based alloys, and this parameter should not be controlled. In experiments, the control of the cooling/heating rate is carried out to provide a uniform temperature variation in the bulk samples and it has no relation to the influence of the temperature rate on the functional properties.

However, in the last decade, it was found that the martensitic transformations in some NiTi-based alloys, such as Ni-rich binary NiTi and ternary or quaternary NiTi-based alloys, might occur under isothermal conditions [4–11]. In this case, the cooling/heating rate should affect the martensitic transformation temperatures and functional properties of the alloys. This was confirmed in [12], where the influence of the cooling rate on the forward B2→R martensitic transformation was studied for the $Ti_{50}Ni_{47}Fe_3$ alloy and it was found that a decrease in the cooling rate increased the start transformation temperature. The same phenomenon was observed in [13], where it was shown that a decrease in the cooling/heating rate from 25 to 5°C/min increased the temperatures of the forward transformations in a binary Ni-rich NiTi alloy. Moreover, the influence of the cooling/heating rate (dT/dt) on the strain variation on cooling and heating under stress was first investigated and it was shown that a twice decrease in the dT/dt parameter from 7.4 to 3.8°C/min changed the slope of linear dependence of the M_s (start temperature of the forward martensitic transformation) on the stress.

It was assumed that the cooling/heating rate influenced the dislocation movement that affected the martensitic transformation temperatures. However, this assumption was not confirmed by the experimental data. First of all, the movement of the dislocation should induce the observation of the irrecoverable strain on cooling and heating under the stress, however, the results in [13] showed that a complete strain recovery was observed. In addition, no dependencies of the irreversible strain on the stress or on the cooling/heating rate were presented in [13]. Thus, it may be concluded that the influence of the cooling/heating rate on the martensitic transformation in the non-stoichiometric NiTi alloy was found, and it might be assumed that this was caused by the isothermal martensitic transformation. At the same time, it is not clear how the cooling/heating rate influences the strain variation and whether the influence of the cooling/heating rate on the transformation temperatures and strain is the same. These items are very important for applications of the NiTi alloy. That is why the aim of the present work is to study the martensitic transformation and strain variation in the $Ni_{51}Ti_{49}$ alloy on cooling and heating under various stresses with different cooling/heating rates.

2. Materials and Methods

Wire samples from the $Ni_{51}Ti_{49}$ alloy (produced by the "Matek-SMA Ltd." Moscow, Russia) with a diameter of 1.5 mm and a length of 100 mm were water quenched from 850°C (15 min) and subjected to 100 thermal cycles within the temperature range of the martensitic transformation (from −196 to 100°C) to stabilise the phase transition temperatures. The X-ray study that was carried out using a Bruker D8 DISCOVER diffractometer ($Cu_{K\alpha}$) at the X-ray Diffraction Centre, Saint Petersburg State University, showed that after such a heat treatment, the sample was in the NiTi phase without any precipitates and 100 thermal cycles did not affect the phase state (Fig. 1).

To study the influence of the cooling/heating rate on the martensitic transformation, the sample with a mass of 15 mg was cut from the wire and subjected to cooling and heating with different rates of 10, 5 or 1°C/min in a differential scanning calorimeter ("Mettler Toledo 822^e" apparatus). To study the influence of the cooling/heating rate on the strain variation, the $Ni_{51}Ti_{49}$ alloy samples with a length of 100 mm were put to special grips of the Shimadzu 50kN-AG testing machine. The samples were loaded by a constant stress σ that belonged to the range of 50 ÷ 250 MPa at a temperature of 100°C where the alloy was in the austenite state and subjected to cooling and heating into the temperature range from 100 to −70°C with a rate of 10, 5 or 1°C/min under a constant stress.

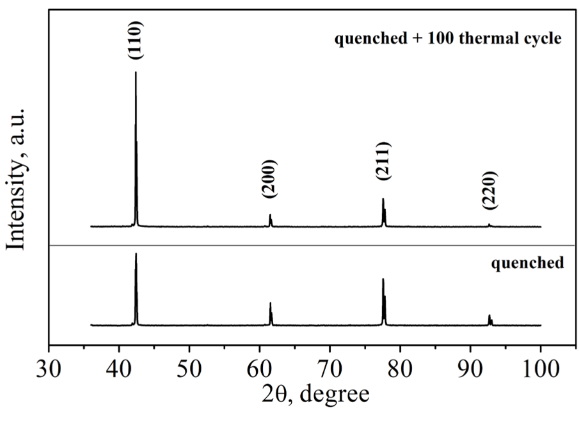


Fig. 1. X-ray patterns obtained from the $Ni_{51}Ti_{49}$ alloy after quenching and 100 thermal cycles.

3. Results and Discussion

Fig. 2 shows the calorimetric curves obtained on cooling and heating of the quenched $Ni_{51}Ti_{49}$ alloy in the temperature range of the martensitic transformation at different cooling/heating rates (dT/dt). It was found that a decrease in the dT/dt value from 10 to 1°C/min shifted the peak of the heat release on cooling to the higher temperature and narrowed the temperature range of the heat absorption peak on heating, that was in good agreement with the data published in [12–13]. The temperatures of the martensitic transformation were determined using the ASTM F-2004 standard as the intersection of the tangent lines.

Fig. 3 shows the strain vs temperature curve that was found on cooling and heating of the quenched $Ni_{51}Ti_{49}$ alloy under a constant stress of 100 MPa with a cooling/heating rate of 5°C/min. It is seen that on cooling under stress, the strain increases and it partially recovers on subsequent heating (the shape memory effect). As the strain recovery is not complete, hence the plastic strain is measured after heating. The same ε(T) curves were obtained on cooling and heating with different rates and under different stresses. The temperatures of the martensitic transformation under stress (M_s^σ, M_f^σ, A_s^σ and A_f^σ) and the value of the shape memory effect (ε^{SM}) and irrecoverable strain (ε_{irr}) were determined using the ε(T) curves, as shown in Fig. 3.

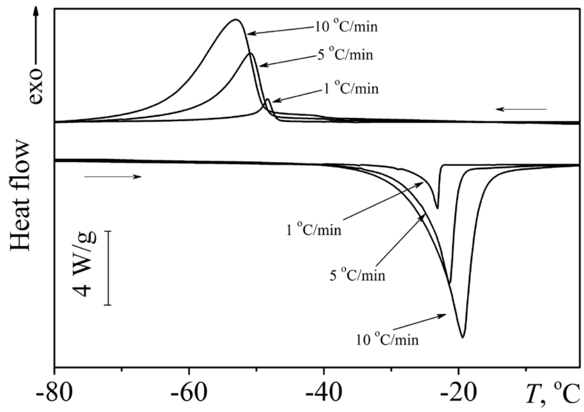


Fig. 2. Calorimetric curves obtained on cooling and heating of the $Ni_{51}Ti_{49}$ alloy with different cooling/heating rates.

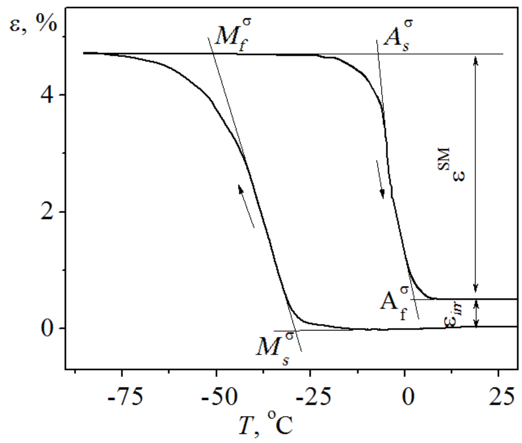


Fig. 3. Strain vs temperature curve obtained on cooling and heating of the $Ni_{51}Ti_{49}$ alloy under a stress of 100 MPa with a rate of 5°C/min.

According to ASTM F-2004, the recommended temperature variation rate for calorimetric studies of phase transformations is 10°C/min, which is why for further consideration, the difference between the transformation temperatures measured on cooling and heating at 1 or 5°C/min and the temperatures determined at 10°C/min have been analysed. Fig. 4 shows the dependencies of the temperature increments of the martensitic transformations compared to cooling and heating at 10°C/min on the temperature rate (*dT*/*dt*). First of all, it is found that at zero stress, the cooling/heating rate influences the M_s and M_f temperatures of the forward transformation (Figs. 4 a and b), with a decrease in *dT*/*dt*, the M_s and M_f temperatures increase. This is caused by the forward transformation that might occur athermally, as well as isothermally, in the quenched $Ni_{51}Ti_{49}$ alloy. Moreover, in [6, 9–11], it was found that the isothermal transformation might occur during holding at a temperature larger than M_s. Thus, it may be assumed that the less the *dT*/*dt*, the larger the contribution of the isothermal transformation to the heat release peak and the higher the temperatures of the forward transformation.

The analysis of the data shown in Fig. 4 demonstrates that the influence of the *dT*/*dt* on the transformation temperature depends on the stress that acts on cooling and heating. An increase in the stress suppresses the influence of the *dT*/*dt* parameter on the M_s and M_f temperatures. For instance, a decrease in *dT*/*dt* from 10 to 1°C/min leads to an increase in the M_f temperature by 13°C if the cooling and heating are realised without stress, and by 5°C if the stress is equal to 250 MPa. This is due to the isothermal transformation is associated with the observation of the pre-martensitic phenomenon, i. e., the formation of the strain nanodomains on cooling in some temperature range prior to the forward martensitic transition [14]. At the same time, according to the Clausius-Clapeyron-like relation, the temperatures of the martensitic transformation increase with stress. In this case, on cooling of the sample under stress, the athermal martensitic transformation starts at higher temperatures than the formation of the strain nanodomains. As a result, the isothermal transformation does not occur and the variation in the cooling/heating rate does not affect the transformation temperatures.

Contrary to the forward transformation temperatures, a decrease in the cooling/heating rate decreases the reverse transformation temperatures if the stress is larger than 100 MPa. The observed phenomenon cannot be caused by the isothermal transformation, because the reverse transformation does not occur in the quenched $Ni_{51}Ti_{49}$ alloy under isothermal conditions [10]. It is well known that the start temperature of the reverse thermoelastic transformation

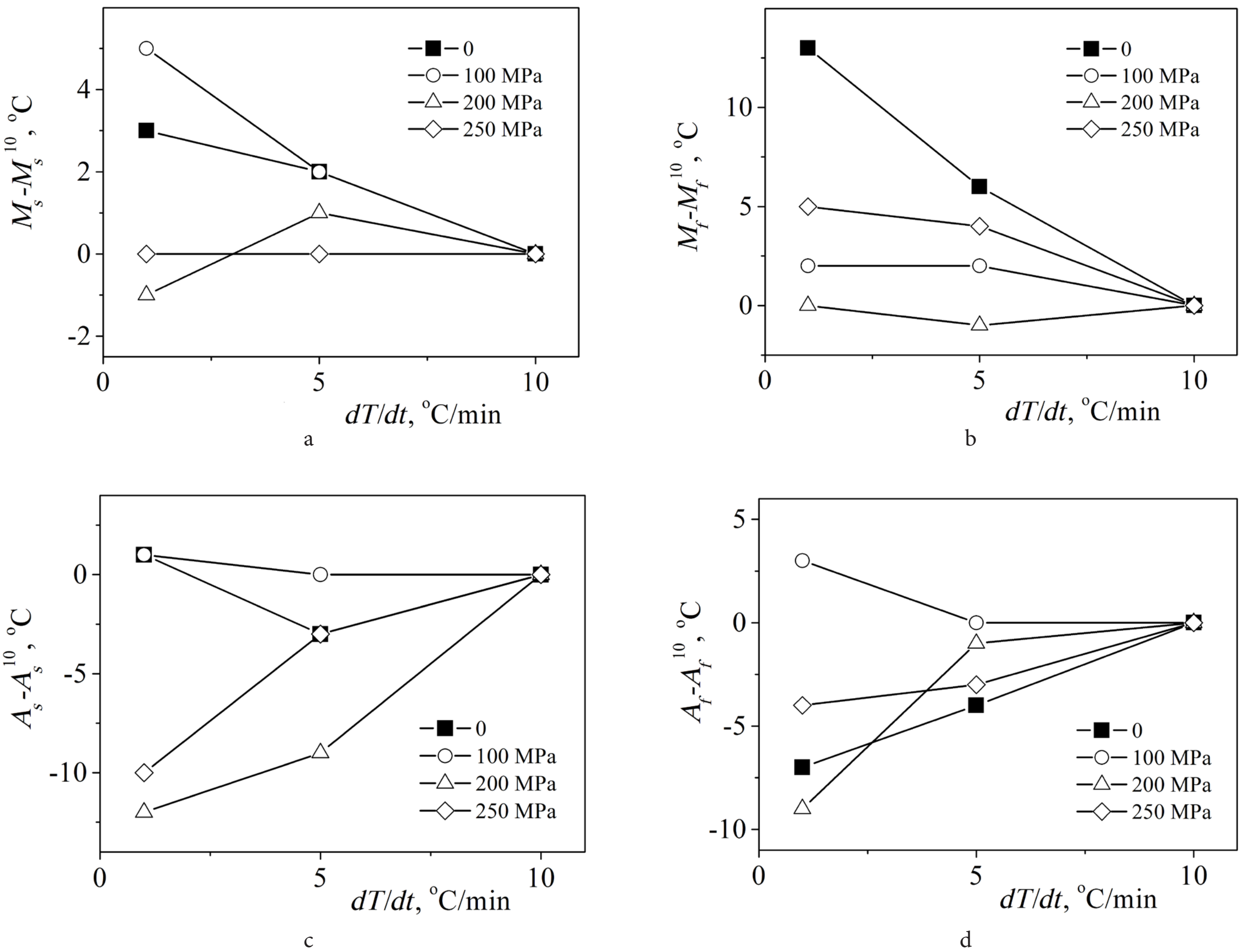


Fig. 4. Influence of cooling/heating rate on the increment in the martensitic transformation temperatures M_s (a), M_f (b), A_s (c) and A_f (d) in relation to the temperatures measured during cooling and heating with a rate of 10°C/min. The transformation temperatures were determined on cooling and heating under different stresses.

(A_s) is determined by the elastic energy that is stored during the forward transformation and the larger the energy the lower the A_s temperature. Thus, it may be assumed that a decrease in the cooling/heating rate leads to an increase in the elastic energy that is stored in the sample on cooling under a high stress (larger than 100 MPa), which decreases the A_s temperature.

The results of the study show that the influence of the cooling/heating rate on the transformation temperatures depends on whether the transformation occurs under zero stress or not. Thus, during the design of the Ni-rich NiTi actuator, it is not possible to use the dependence of the transformation temperatures on the dT/dt that was measured in differential scanning calorimetry experiments (without stress). It is necessary to check the influence of the dT/dt on the temperatures of the strain variation measured on cooling and heating under stress.

In the study, it was found that the cooling/heating rate affected not only the transition temperatures, but also the deformation behaviour of the quenched $Ni_{51}Ti_{49}$ alloy. It is found that the value of reversible strain ε^{SM} does not depend on the dT/dt and this is determined by the value of the stress that acted on cooling and heating (Fig. 5a). However, the variation in irreversible strain ε_{irr} on the cooling/heating rate depends on stress (Fig. 5b). If the stress is equal to 100 MPa, a decrease in the dT/dt leads to an increase in the plastic strain, whereas if the stress is equal to 250 MPa, the plastic strain decreases. The different dependences of the plastic strain on the dT/dt under various stresses are probably due to the different processes that occur on cooling and heating under stress. Cooling under a stress of 100 MPa leads to the partial formation of the oriented martensite while the other part of the alloy transforms to non-oriented martensite which formation does not give a contribution to the strain variation. At the same time, cooling under a stress of 200 MPa and more results in the oriented martensite appearing in the entire volume of the alloy. This is confirmed by the value of the shape memory effect. This parameter is equal to 4.2% on cooling and heating under 100 MPa and 9% under 200 MPa and more.

It may be assumed that on cooling and heating under a stress of 100 MPa, the relaxation process may occur due to the coexistence of the oriented and non-oriented martensite and the smaller the heating rate, the more intensive the relaxation and the larger plastic strain appears. On cooling and heating under a stress of 200 MPa, the oriented martensite appears, but it may be realised by a different way. The oriented martensite may appear directly from the austenite phase on cooling or the oriented, as well as non-oriented, martensite may appear on cooling but the non-oriented martensite may be subjected to further orientation because the stress is larger than the stress needed for the reorientation. It is known that the orientation of the non-oriented martensite is accompanied by a larger plastic strain variation than the formation of the oriented martensite from the austenite state. It may be assumed that on cooling with a high rate and/or under a large stress (250 MPa), the second scenario is more preferable. In contrast, on cooling with a small rate and/or under a stress of 200 MPa, the first scenario occurs and it gives smaller plastic strain.

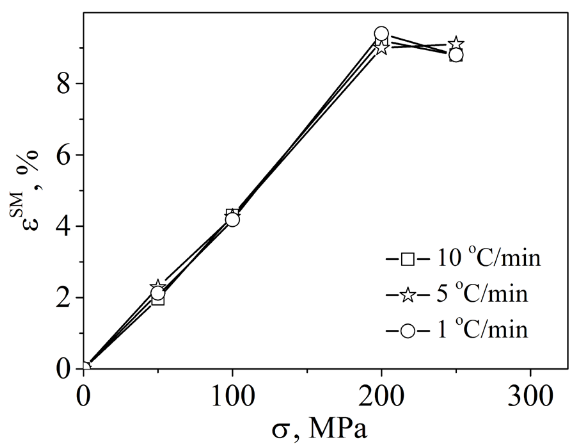
4. Conclusions

The results of the study may be summarised as follows.

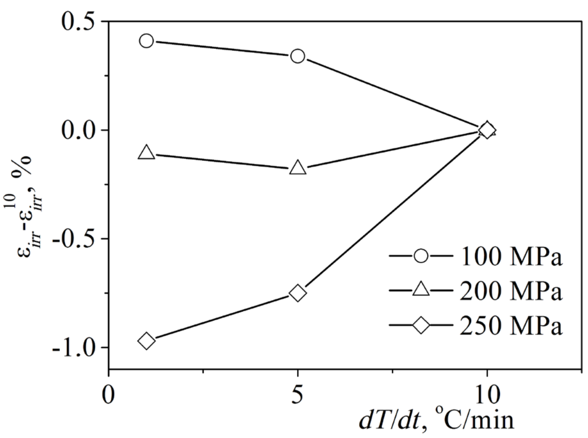
1. In the quenched $Ni_{51}Ti_{49}$ alloy, a decrease in the cooling rate from 10 to 1°C/min leads to an increase in the forward martensitic transformation temperatures under zero stress. This is caused by the forward transformation, which occurs under isothermal conditions.

2. An increase in the stress that acts on cooling and heating decreases the sensitivity of the transformation temperatures to the cooling/heating rate. The larger the stress, the less the shift in the transformation temperatures on a decrease in the cooling/heating rate. This is due to the Clausius-Clapeyron-like relation, where the stress increases the transformation temperatures that exceed the temperatures of the pre-martensitic phenomenon that is responsible for the isothermal transformation. In this case, the isothermal transformation does not occur and the cooling/heating rate does not affect the transformation temperatures.

3. The start temperature of the reverse transformation (A_s) decreases with a decrease in the cooling/heating rate. This is not caused by the isothermal transformation and may be due to a decrease in the elastic energy that is stored in the sample on cooling.



a



b

Fig. 5. Influence of the stress on the reversible strain measured on different cooling/heating rate (a). The influence of cooling heating rate on irreversible strain compared to the strain measured on cooling and heating with a rate of 10°C/min measured under different stresses (b).

4. The cooling/heating rate does not influence the reversible strain (ε^{SM}), but affects the irreversible strain (ε_{irr}) that is measured after cooling and heating under stress through the martensitic transformation temperature range. Depending on the stress, ε_{irr} can increase or decrease on a decrease in the dT/dt value, and this may be due to various mechanisms of the oriented martensite formation.

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References

1. D. Stoeckel. Mater. Des. 11, 302 (1990). Crossref
2. J. Mohd Jani, M. Leary, A. Subic, M. A. Gibson. Mater. Des. 56, 1078 (2014). Crossref
3. K. Otsuka, X. Ren. Prog. Mater. Sci. 50, 511 (2005). Crossref
4. S. Kustov, I. Golovin, M. L. Corró, E. Cesari. J. Appl. Phys. 107, 053525 (2010). Crossref
5. S. Kustov, D. Salas, E. Cesari, R. Santamarta. J. Van Humbeeck. Acta Mater. 60, 2578 (2012). Crossref
6. T. Fukuda, S. Yoshida, T. Kakeshita. Scripta Mater. 68, 984 (2013). Crossref
7. T. Fukuda, S. Yoshida, T. Kakeshita. Scripta Mater. 69, 239 (2013). Crossref
8. Y. Ji, D. Wang, X. Ding, K. Otsuka, X. Ren. Phys. Rev. Lett. 114, 055701 (2015). Crossref
9. N. Resnina, S. Belyaev, A. Shelyakov. Scripta Mater. 112, 106 (2016). Crossref
10. N. Resnina, S. Belyaev, E. Demidova, A. Ivanov, V. Andreev. Mater. Lett. 228, 348 (2018). Crossref
11. E. Demidova, S. Belyaev, N. Resnina, A. Shelyakov. J Therm Anal Calorim. (2019). Crossref
12. S. Xue, W. Wang, D. Wu, Q. Zhai, H. Zheng. Mater. Lett. 72, 119 (2012). Crossref
13. H. Fang, M. Wong, Y. Bai, R. Luo. Constr. Build Mater. 101, 447 (2015). Crossref
14. N. Resnina, S. Belyaev, A. Shelyakov, V. Rubanik, V. Rubanik Jr., R. Konopleva, V. Chekanov, E. Ubyivovk, M. Krzhizhanovskaya. Intermetallics. 67, 69 (2015). Crossref