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Regular Article

Temperature memory effect in a magnetic shape memory alloy for monitoring of minor over-cooling

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ABSTRACT

Almost all previously reported temperature memory effect (TME) in shape memory materials is meant for the heating process. In this paper, we experimentally investigate the TME in the cooling process in a shape memory alloy. Experimental results reveal that the lowest cooling temperature, provided that it is within a temperature range of 15 °C between the original martensite start and finish temperatures, roughly has a linear relationship with the new martensite start temperature in the final cooling process. This finding may be utilized for temperature sensors to estimate the lowest cooling temperature with an accuracy of ±0.95 °C.

Shape memory alloys (SMAs) are well-known to be featured with the shape memory effect (SME), so that at the presence of the right stimulus, they are able to return their permanent shapes after being quasi-plastically deformed [1,2]. On the other hand, the temperature memory effect (TME), which, according to the current definition within the community of shape memory materials (SMMs) (including alloys and polymers, etc.), refers to the capability of a SMM to reveal the previous highest heating temperature [3–7], has been found as another interesting feature of many SMAs and shape memory polymers (SMPs) [1,3,6,8–13].

The standard procedure to reveal the TME in a SMA is via differential scanning calorimeter (DSC) test, which includes two steps. The first step is to heat a small piece of SMA sample to a temperature (T_s), which is between the austenite start temperature (A_s) and the austenite finish temperature (A_f), and then to cool it all the way to below the martensite finish temperature (M_f) at a constant heating/cooling speed. In the next step, the sample is heated to above A_f again at the same heating/cooling speed. The resulted heat flow vs. heating temperature curve in this heating process is distorted, when compared with the DSC curve of a complete thermal cycle. Since there is a kind of reasonably fixed relationship between the previous heating stop temperature (T_s) and the temperature corresponding to the newly formed feature (e.g., peak or trough) in the heat flow vs. heating temperature curve of the last heating process, T_s can be estimated accordingly. Hence, this phenomenon is termed the TME within the SMM community.

In order to get rid of the strict testing condition applied in above mentioned DSC process, i.e., to ensure the sample is cooled to below M_f in every thermal cycle, a modified approach is recently proposed in [14], so that the TME can be implemented as a cost-effective technology for over-heating monitoring using both shape memory alloy/polymer [6,13].

Indeed, so far, almost all mentioned TME in both SMAs and SMPs are meant for heating only. However, in some occasions, such as in transportation and storage of protein based vaccines [15,16], it is ideal to check whether any individual items have ever been over-cooled, and what the lowest temperature was if over-cooling did happen. The purpose of this paper is to investigate the feasibility of using SMA to monitor over-cooling via DSC test.

The SME in NiMnGa based magnetic alloys has been well documented [17–21]. The SMA used here is $(Ni_{56}Mn_{25}Ga_{19})_{98}Ag_2$, which was prepared from high purity elements by melting four times in an argon atmosphere in a vacuum arc furnace. Subsequently, the resultant ingot was sealed in a vacuum quartz ampoule and annealed at 900 °C for 10 h, followed by quenching in iced water. Small samples (less than 20 mg) were cut out of the ingot for DSC test using a TA-Q 200 A differential scanning calorimetry at a cooling/heating rate of 10 °C/min.

According to the gray solid line in Fig. 1(a), there is only one transition within the tested temperature range between 440.0 °C and 265.0 °C, i.e., one peak upon cooling (from austenite to martensite, which is the martensitic transformation) and one trough upon heating (from martensite to austenite, i.e., the reverse martensitic transition). The martensitic transformation temperatures may be determined by the standard tangent method as: $M_s = 358.1$ °C, $M_f = 335.7$ °C, $A_f = 396.1$ °C, and

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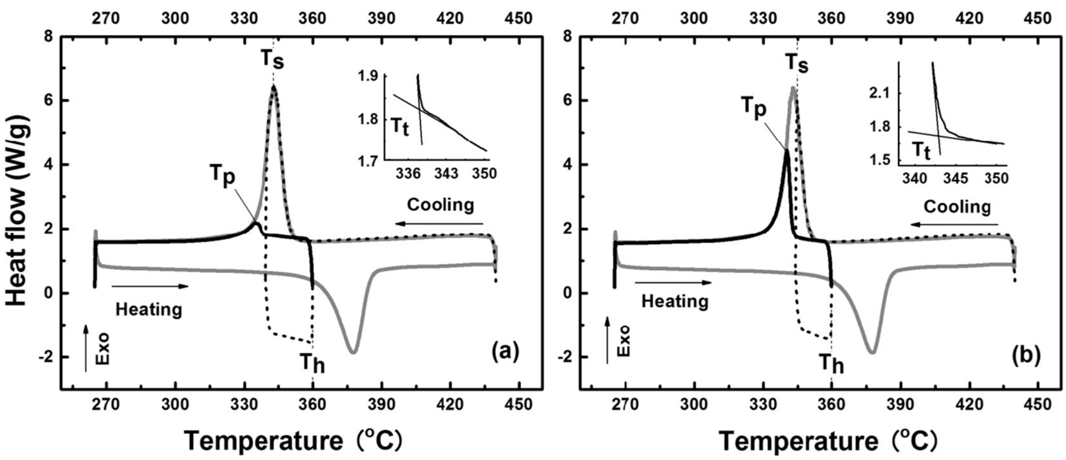

Fig. 1. Typical DSC curves of single-stop TME for $(Ni_{56}Mn_{25}Ga_{19})_{98}Ag_2$. (a) $T_s = 339.5$ °C; (b) $T_s = 344.0$ °C. Insets are zoom-in view to show how T_t is determined.

$A_s = 374.5$ °C. Here, M_s is the martensite start temperature. Note that the gray solid line, i.e., the result of full thermal cycle, is always included in DSC plot as a reference for comparison.

As reported, e.g., in [22], the actual cooling/heating speed could have strong influence on the obtained DSC result, unless it is very slow. In the intended application of temperature monitoring, a SMA is expected to undergo thermal fluctuation in a random manner together with the item, which is subjected to temperature monitoring. Therefore, unless the mass of the item is very small, the actual cooling/heating speed should be relatively slow. Hence, a cooling/heating rate of 10 °C/min might be reasonable. Consequently, this speed was applied in all experiments reported herein.

Note that all samples were pre-thermally cycled twice from below M_f to above A_f to remove the possible influence from the previous thermo-mechanical history. The actual testing process for the TME is as following:

(1) Cooling from above A_f to T_s ($M_f < T_s < M_s$);
(2) Heating to a prescribed temperature, namely T_h ($M_s < T_h < A_s$);
(3) Cooling to below M_s.

Similar to the modified approach to monitor over-heating using SMA reported in [14], in over-cooling tests reported here, the highest temperature in all incomplete thermal cycling (T_h) was fixed as 360.0 °C, so that $M_s < T_h < A_s$ is largely satisfied. Steps (1) and (2) might be repeated up to three times with different T_ss in each incomplete thermal cycle. For convenience, in all DSC curves presented herein, solid gray line is meant for the result of a full range thermal cycling between 440.0 °C and 265.0 °C, and solid black line represents the result of the final cooling process, while dashed, dash-doted, and doted black lines are for the heating processes with different T_Ss.

Fig. 1(a) presents the typical curve of a TME test with single stop, in which the applied T_s was 339.5 °C. As shown, the temperature corresponding to the peak in the final cooling process is defined as T_p, while the inset in Fig. 1(a) shows how the start temperature of the peak in the final cooling process (T_t) is determined by the standard tangent method. In this particular test, T_t and T_p are 338.3 °C and 334.7 °C, respectively. Fig. 1(b) is the result of another single-stop test with a relatively higher T_s of 344.0 °C, and the corresponding T_t and T_p are identified as 342.5 °C and 340.3 °C, respectively. Testing parameters (T_s and T_h) and results (T_p and T_t) of other nine single-stop tests are listed in Table 1.

In addition to above mentioned single-stop tests, a series of triple-stop tests were carried out as well Fig. 2(a) is a special case, in which three T_ss (namely, $T_{s,1}$: 347.0 °C, $T_{s,2}$: 342.5 °C, and $T_{s,3}$: 338.0 °C) follow a descend order, and the corresponding T_t and T_p in the final cooling process are 336.6 °C and 333.0 °C, respectively. Fig. 2(b) is another special case, in which the three stop temperatures (namely, $T_{s,1}$: 344.0 °C, $T_{s,2}$: 345.5 °C and $T_{s,3}$: 347 °C) follow an ascend order. The resultant T_t and T_p are 341.7 °C and 339.3 °C, respectively.

It should be pointed out that a close look of the final cooling process in both tests reported in Fig. 2 reveals some small fluctuations before the remarkable turning point. Such a phenomenon can be observed in many other tests as well. The previous incomplete cooling, in which the cooling stop temperature(s) is higher, should be the underline mechanism for the fluctuation, since the actual solid to solid phase transformation propagation process within a material can be unavoidably affected by the actual thermal process. However, unlike that in the previously reported TME tests in a heating process [3,14], where more than one significant peaks can be found after multiple incomplete thermal cycles, such a kind of fluctuation in the cooling process is minor and is rather difficult to quantitatively link to a particular cooling stop temperature, so that we may ignore it. It is clear that there is only one peak in the final cooling process in both tests, which is unlike that in the previously reported TME tests in a heating process [3,14], where more than one peaks may be found after multiple incomplete thermal cycles. In other triple-stop tests (refer to Table 1 for their testing parameters and results), where the three T_ss do not follow any particular order (i.e., in a random manner), same phenomenon is observed.

Table 1
Summary of key testing parameters and results (temperature unit: °C).

		$T_{s,1}$	$T_{s,2}$	$T_{s,3}$	T_h	T_t	T_p
Single-stop	I	338.0			360.0	336.5	332.7
	II	339.5			360.0	338.3	334.7
	III	341.0			360.0	339.7	336.6
	IV	342.5			360.0	341.1	338.9
	V	344.0			360.0	342.5	340.3
	VI	345.5			360.0	343.5	341.3
	VII	347.0			360.0	344.3	342.4
	VII	348.5			360.0	345.8	342.7
	IX	350.0			360.0	346.8	342.9
	X	351.5			360.0	347.6	342.6
	XI	353.0			360.0	347.9	342.7
Triple-stop (ascend)	I	338.0	342.5	347.0	360.0	336.7	332.7
	II	339.5	341.0	342.5	360.0	337.3	333.2
	III	341.0	342.5	347.0	360.0	339.3	335.4
	IV	342.5	344.0	347.0	360.0	340.7	337.5
	V	344.0	345.5	347.0	360.0	341.7	339.3
	VI	345.5	348.5	350.0	360.0	343.0	340.6
	VII	347.0	350.0	351.5	360.0	344.6	342.3
Triple-stop (descend)	I	347.0	342.5	338.0	360.0	336.6	333.0
Triple-stop (random)	I	347.0	338.0	342.5	360.0	336.8	332.8
	II	338.0	347.0	342.5	360.0	336.7	332.8
	III	342.5	347.0	338.0	360.0	336.8	333.1
	IV	342.5	338.0	347.0	360.0	336.7	333.3