Transformation Relaxation and Aging in a CuZnAl Shape-Memory Alloy Studied by Modulated Differential Scanning Calorimetry

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The reverse martensitic transformation and aging processes in a polycrystalline Cu-23.52 at. pct Zn-9.65 at. pct Al shape-memory alloy have been studied using the recently developed modulated differential scanning calorimetry (MDSC) technique, and some new findings are obtained. By separating the nonreversing heat flow from the reversing heat flow, MDSC can better characterize the thermodynamic, kinetic, and hysteretic features of thermoelastic martensitic transformations. Two kinds of exothermal relaxation peaks have been identified and separated from the endothermal reverse martensitic transformation: one is associated with the movement of twin interfaces or martensite-parent interfaces, and another is due to the atomic reordering in the parent phase *via* a vacancy mechanism. The martensite aging processes have been examined, and two stages of the aging process been distinguished: the first stage of aging is characterized by the stabilization of martensite, as manifested in the increase in the reversing enthalpy of the reverse martensitic transformation and in the transformation temperatures, and the second stage is, in fact, the decomposition of the martensite on prolonged aging, accompanied by a decrease in the transformation enthalpy. The results suggest that the mechanisms of the relaxation in the martensite and in the parent phase may be quite different.

I. INTRODUCTION

DIFFERENTIAL scanning calorimetry (DSC) is a very useful tool for analyzing various phase transitions in materials and has been extensively used to characterize the transformations, especially the forward and reverse martensitic transformations, in various shape-memory alloys.[1–4] However, traditional DSC does have some limitations. Since DSC measures only the sum of all the thermal events, the results are often confusing and misinterpreted if multiple transitions occur in the same temperature range. In addition, DSC results are always a compromise between sensitivity and resolution, so the sensitivity and resolution are not high enough to detect some weak transitions or to separate complex transitions. More recently, a greatly enhanced version of the DSC method called modulated differential scanning calorimetry (MDSC) was introduced and has now become available in the commercial differential scanning calorimeters of TA Instruments.[5,6] The MDSC method not only can incorporate the capability of conventional DSC by offering the same information, but also overcomes the limitations of DSC and provides significant and distinct advantages over it by providing new information that permits unique insights into the structure and behavior of materials; hence, MDSC has brought a new dimension to thermal analysis.[5,7]

In conventional DSC, the sample temperature is usually heated or cooled linearly at a constant rate. The measured heat flow is the total of all the thermal responses and can be simply expressed as[5]

$$\frac{dQ}{dt} = C_p \left(\frac{dT}{dt}\right) + f(t, T) \qquad [1]$$

where dQ/dt is heat flow, C_p the sample heat capacity, dT/dt is the heating rate, t is the time, T is the absolute temperature, and $f(t, T)$ is a function of time and temperature which governs the kinetic response of any physical or chemical transitions observed in DSC.[5] Accordingly, the measured heat flow is, in fact, a combination of two components: (1) the reversing heat flow, which is dependent on the heat capacity and directly follows the heating rate; and (2) the nonreversing heat flow, which depends on the rate of any kinetically driven process and does not follow the heating rate. The former is called the thermodynamic component, while the latter one is called the kinetic component. Unfortunately, it is impossible to separate the two components in conventional DSC.

In the updated MDSC method, a small temperature oscillation or perturbation, say, a sine wave, is superimposed on the normal isothermal, linear heating/cooling or other steps of the temperature program. By using a discrete Fourier transformation algorithm, the total calorimetric response to the perturbation is then deconvoluted into the reversing quantity and the nonreversing quantity. Accordingly, MDSC is an invaluable tool for characterizing the thermodynamic and kinetic features of a transition and may provide some information which cannot be obtained from traditional DSC. The benefits of MDSC, including the higher resolution and ability to separate complex transitions, improved sensitivity to weak transitions, simplicity in measuring heat capacity, and so on, have been well documented in the literature.[8,9,10] Some excellent reviews on MDSC can be found in References 5 and 6.

The martensitic transformations in Cu-based shape-memory alloys are thermoelastic, *i.e.*, the martensite exhibits a thermal reversibility on heating and cooling. In addition,

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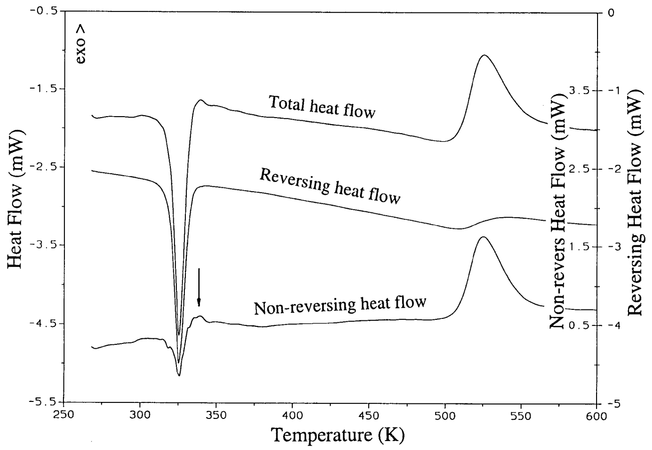

Fig. 1—The MDSC heating curves of the as-quenched CuZnAl alloy. Experimental parameters: underlying heating rate, 5 K/min, modulation amplitude, ± 1 K; and modulation period, 60 seconds. The arrow indicates an exotherm, which is amplified in Fig. 2.

the alloys are susceptible to postquench aging effects in both the ordered parent phase and in the martensite state, accompanied by substantial changes in various properties.[11–15] The complicated aging effects may deteriorate the technical reliability of the alloys and, hence, adversely impact the commercial applications of the alloys. It is well known that the aging effects originate from thermally activated relaxation processes wherein atoms rearrange themselves to tend to reach a more stable configurational state.[13,14,16] Despite a rich variety of experimental results, the mechanisms of the relaxation processes leading to the complex aging effects in the alloys remain not well understood so far. For instance, it remains an unresolved question regarding martensite aging as to whether atomic (re)ordering or atomic disordering occurs. Also, it has not yet been clarified whether there is any difference in the mechanisms of the kinetic relaxation processes in the martensite state and in the parent-phase state. Modulated differential scanning calorimetry seems to be a unique and powerful tool for analyzing the phase transformations in the alloys. The objectives of the present work are, therefore, to characterize the aging processes and examine the (reverse) martensitic transformations in a polycrystalline CuZnAl alloy by applying the advanced calorimetric technique.

II. EXPERIMENTAL

The chemical composition of the alloy used was Cu-23.52 at. pct Zn-9.65 at. pct Al. The alloy was prepared by induction melting the commercially pure metals in a graphite crucible. The alloy ingots were homogenized at 1123 K for 8 hours and then forged into sheets of about 10 mm in thickness. All the specimens used were cut from the sheets or strips. The CuZnAl alloy samples were solution treated at 1123 K for 5 minutes and then subjected to different quenching. Much care was taken to avoid introducing any thermal or mechanical stresses into the samples after quenching. The as-quenched samples were slightly cleaned and then immediately taken to perform the MDSC measurements or held to undergo isothermal aging at the temperatures of interest.

The MDSC measurements were employed using a DSC 2910 MDSC* with a liquid nitrogen cooling accessory and an argon gas DSC cell purge. The system allows heating or cooling scans in the modulated or standard DSC regime. The calorimeter was calibrated for cell constant, baseline slope, and temperature readings using a standard sample of high-purity indium, and the heat capacity was calibrated with a standard sapphire sample using the same experimental parameters in the temperature of interest. Since the MDSC results of the alloys were found to be very sensitive to sample size and surface effects, the geometrical configuration and weight of samples were kept as closely identical as possible. The sample sizes were about 2.0 mm in diameter and 0.8 mm in thickness. The samples were weighed and placed into standard Al sample pans with crimped lids. A matching empty sample pan with crimped lid was used as the reference. The heating scan was performed by first cooling the samples from room temperature down to about 223 K and then starting the heating ramp. In order to obtain accurate and reproducible results, three experimental parameters, *i.e.*, underlying heating rate, modulation amplitude, and modulation period were carefully selected. The modulation period was 60 seconds. The modulation amplitudes of ± 1 and ± 2 K and various underlying heating rates, from 1 to 10 K/min, were selected in the present work to obtain various average and instantaneous heating-rate schemes. Trial scans with empty pans verified that, under the selected experimental parameters, the sine waves generated in the modulated heat-flow signals were symmetrical without any distortion.

III. RESULTS

A. *The MDSC of as-Quenched Samples*

Figure 1 shows the MDSC heating curves obtained from the room temperature–quenched sample, using a modulation period of 60 seconds, a modulation amplitude of ± 1 K, and an underlying heating rate of 5 K/min. The MDSC result consists of three curves, representing the total heat flow, the reversing heat flow, and the nonreversing heat flow, respectively, as depicted in the figure. The total heat-flow curve shows the sum of all the thermal responses of the sample and provides almost the same information as that obtained from the traditional DSC result at the same underlying heating rate. In the temperature range from 250 to 600 K, the total heat-flow curve exhibits two evident peaks. Evidently, the endothermic peak at around 325 K is due to the transformation from martensite to parent β phase. The exothermic peak, with a peak temperature of about 525 K, may either stem from the precipitation of bainite in the ordered β phase or result from the $D0_3 = B2$ transition in the alloys, which was found to take place within that temperature range. Because the bainitic transformation usually exhibits an exothermal peak, while the disordering transition is a second-order transition, if there arises any thermal event, it should exhibit an endotherm rather than an exotherm.[17,18,19] Actually, the critical temperature of the $D0_3 = B2$ transition can be determined by combined employment of DSC and MDSC, and the details of the characterization of the weak transitions in the alloys will be described elsewhere. Accordingly, the exothermic peak around 525 K

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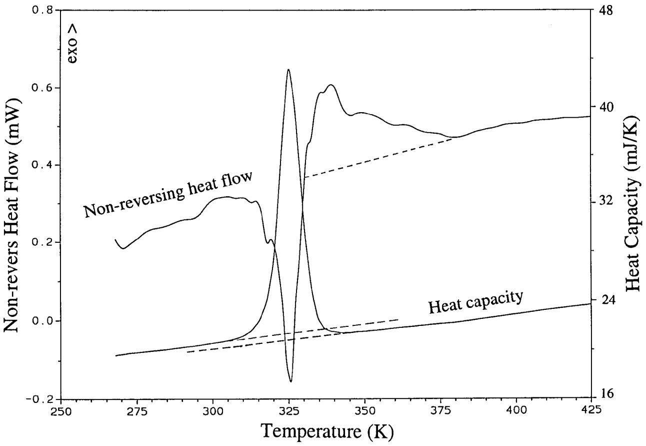

Fig. 2—The amplified exotherm in the nonreversing heat flow curve and the heat capacity of the alloy as a function of temperature. The dashed lines are added to guide readers.

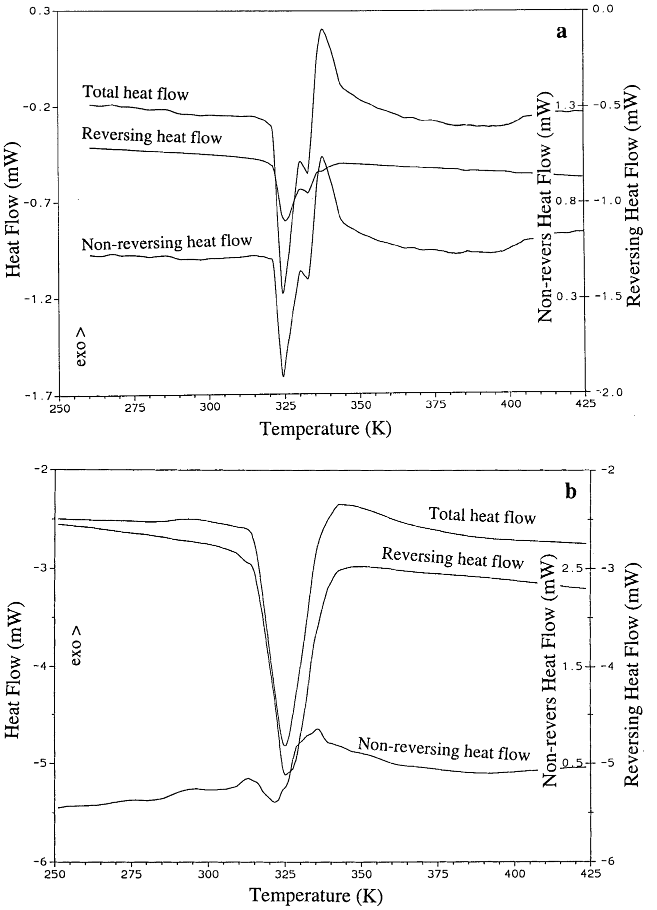

Fig. 3—The MDSC heating curves with improved resolution and sensitivity by modifying the experimental parameters: (*a*) modulated ±2 K every 60 s, with a underlying heating rate of 3 K/min; (*b*) modulated ±2 K every 60 s, with a underlying heating rate of 10 K/min.

should be ascribed to the formation of bainite. Similar exothermic peaks, due to the bainitic transformation and other weak transitions in a modified CuAlNi alloy, have been characterized in a previous article using conventional DSC.[17] It is well known that the bainitic transformation in the CuZnAl alloys is a diffusion-controlled process and that the bainite does not show any thermoelastic reversibility, although the mechanism of the nucleation of bainite remains controversial.[20,21] This point is clearly evidenced by the fact that the exotherm observed in the total heat flow is mainly contributed from the kinetic component, that is, the nonreversing heat flow. Meanwhile, only a small step is observed in the reversing heat-flow curve, due to the change in the heat capacity. This result is, in itself, a persuasive example demonstrating the advantages of MDSC over traditional DSC in the characterization of phase transformations.

As regards the reverse martensitic transformation, both the reversing and nonreversing heat-flow curves exhibit an endotherm, comprising the endotherm in the total heat-flow curve. It's easy to understand the larger endotherm in the reversing heat-flow curve because the martensite is thermoelastic. However, the martensite hardly exhibits a perfect instaneous reversibility for the dissipation of some chemical free energy due to some irreversible lattice defects, and, therefore, a certain amount of driving force, *i.e.*, supercooling or overheating, is needed to trigger the forward or reverse transformation. As a result, there always exists a thermal lag or hysteresis between the forward and the reverse transformation. Thereby, the endotherm in the nonreversing heat-flow curve, however small, stems from the kinematical feature of the transformation, including the contribution from the nonreversible frictional energy dissipated during the transformation and the contribution from the martensite, whose thermal hysteresis cannot be covered by the minor rapid temperature perturbation. We'll discuss this point in more detail in the following section.

Very interestingly, careful examination of the nonreversing heat-flow curve revealed that the endotherm that appeared during the reverse martensitic transformation is actually followed by a sluggish exotherm with a temperature span of more than 30 K, as indicated by the arrow in Figure 1 and amplified in Figure 2. A advantage of MDSC is its simplicity in determination of the heat capacity: the heat capacity and the heat flow can be measured in a single heating ramp. The measured heat capacity of the alloy is also presented in Figure 2. A small difference in the heat capacity can be found between the martensite and the parent phase. From the figure, it is evident that the endotherm in the nonreversing heat-flow curve is associated with the reverse martensitic transformation process, but the sluggish exotherm seems to be related to a kinetic relaxation process in the ordered β phase. This can be seen from the fact that the heat capacity or the reversing heat flow exhibits no substantial changes within the temperature range corresponding to the exotherm.

The exothermic peak becomes more evident and remarkable and can be clearly separated from the endothermic peak by changing the underlying heating rate and the amplitude of modulation to further increase the sensitivity or resolution. Figures 3(a) and (b) show the MDSC results measured at an underlying heating rate of 3 and 10 K/min, respectively, using a larger modulation amplitude of ±2 K with a period of 60 seconds. The measured data, especially the peak areas roughly (transformation enthalpy), were found to show remarkable dependence on the experimental parameters. Although the relaxation peak becomes more

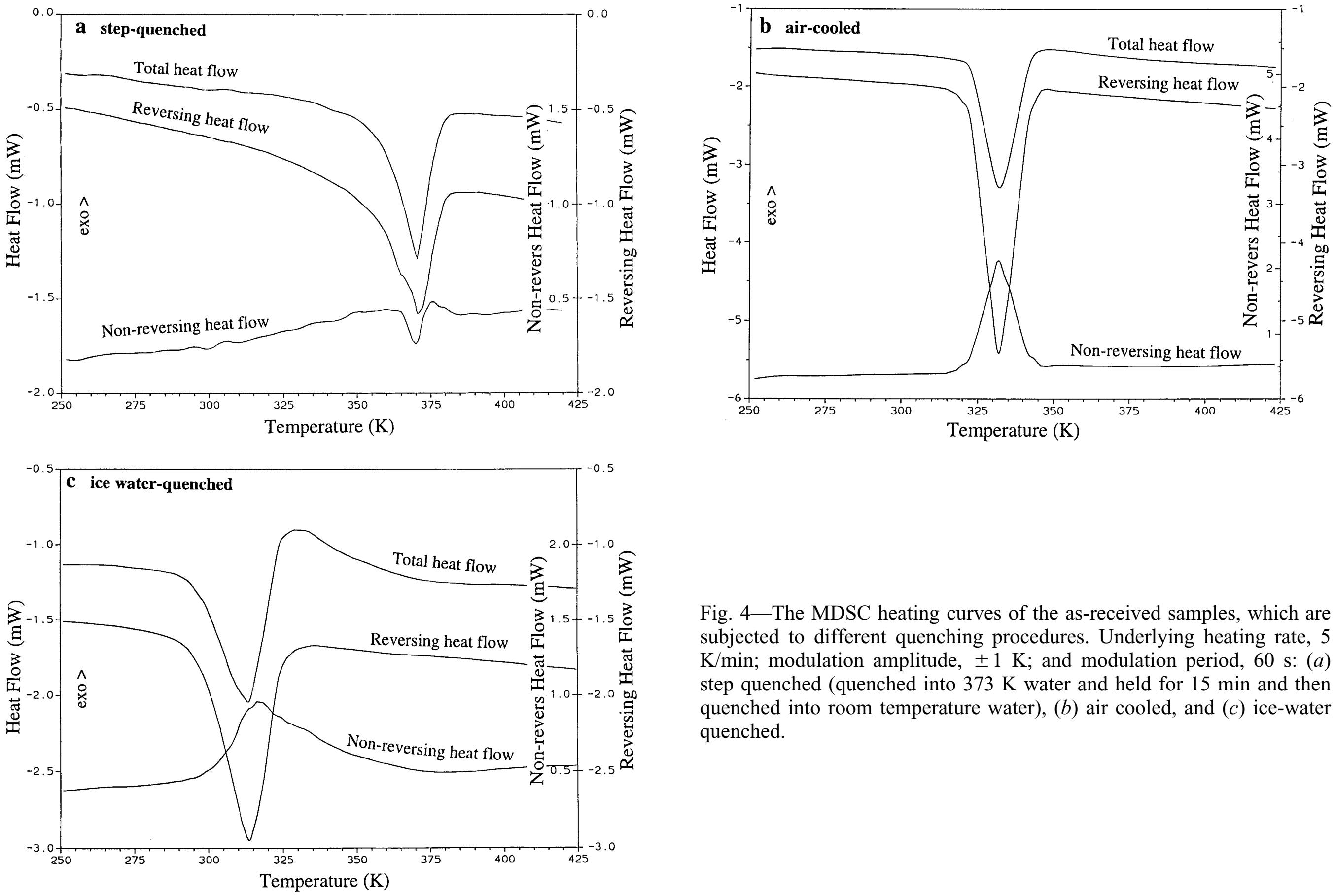

Fig. 4—The MDSC heating curves of the as-received samples, which are subjected to different quenching procedures. Underlying heating rate, 5 K/min; modulation amplitude, ± 1 K; and modulation period, 60 s: (*a*) step quenched (quenched into 373 K water and held for 15 min and then quenched into room temperature water), (*b*) air cooled, and (*c*) ice-water quenched.

sharp when using a lower underlying heating rate, we found that the rate of 10 K/min can better characterize the relaxation. Since only atomic ordering or reordering is an exothermic relaxation process in the temperature range of interest, the exotherm is suggested to be due to the relaxation leading to atomic reordering in the parent phase *via* a vacancy mechanism.

In the aforementioned MDSC measurements, the samples were quenched into a room-temperature water bath. To examine the effect of the heat-treatment procedure on the MDSC results, three more cooling procedures were employed: ice-water quenching, air cooling, and step quenching (the samples were quenched in 373 K water, held for 15 minutes, and then quenched in room-temperature water). The MDSC results, especially the nonreversing heat-flow curves for the as-received CuZnAl samples, are quite different, as shown in Figure 4. From the nonreversing heat-flow curves, it can be found that in the step-quenched sample (Figure 4(a)) there exists only a small endotherm which is directly related to the reverse martensitic transformation. On the contrary, a sharp exotherm is observed in the air-cooled sample (Figure 4(b)). Meanwhile, in the rapidly cooled sample (Figure 4(c)), a very sluggish exotherm with a temperature span of more than 70 K appears, starting from the onset of the reverse martensitic transformation but exceeding the transformation range. Without question, the MDSC results reflect the effects of the quenched-in defects and the state of atomic order on the martensitic transformations. It is well established that, in the CuZnAl alloy, the next nearest-neighbor (NNN) atomic ordering can significantly increase the martensitic transformation temperatures.[22] In the step-quenched sample, the NNN atomic ordering is well developed; thereby, higher transformation temperatures are obtained and there is no kinetic relaxation process leading to atomic reordering in the β phase on postquench heating scan. On the other hand, since the long-range order (LRO) and short-range order (SRO) parameters cannot reach their equilibrium states during rapid quenching, atomic reordering will take place in the β phase in the rapidly cooled sample. Thus, lower transformation temperatures and an exothermic peak were observed on the heating scan. However, it should be noticed that the exotherm in the air-cooled sample may represent another kind of relaxation process. The exotherm seems to be more intimately related to some kind of relaxation process accompanying the reverse martensitic transformation rather than due to the atomic reordering in the β phase. This can be evidenced by the fact that the span of the exotherm corresponds almost exactly to that of the endotherm.

B. *Effects of Martensite Aging*

Of particular interest is the effect of martensite aging on the MDSC heat-flow curves. Figure 5 shows the MDSC results of some CuZnAl samples aged in the martensite state at room temperature for different periods. In agreement with the traditional DSC curve, the total heat-flow curve indicates that, on martensite aging, the peak temper-

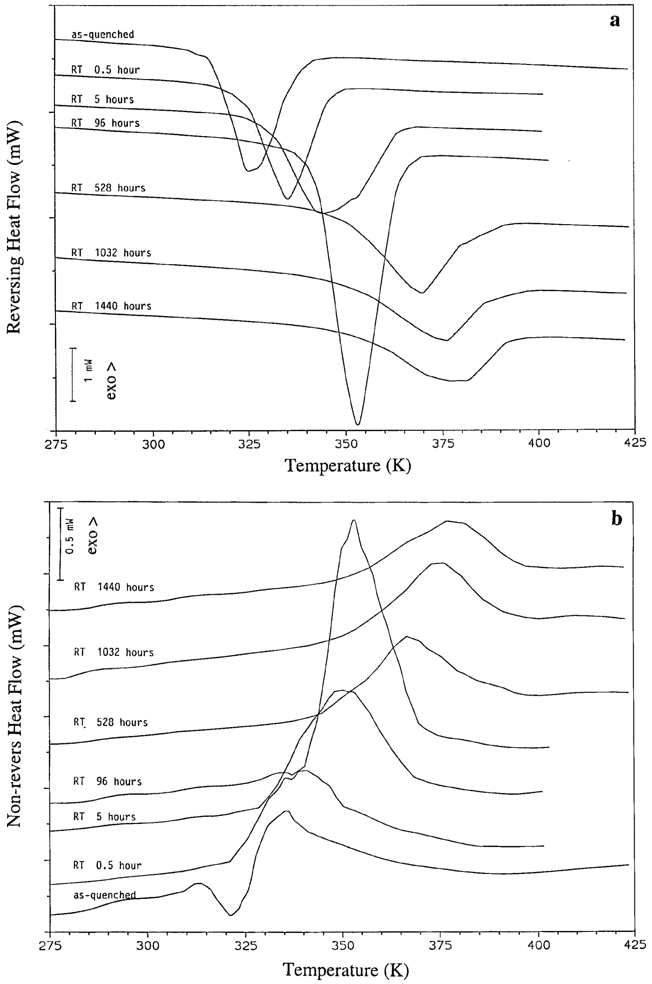

Fig. 5—The effect of martensite aging on the MDSC curves: (*a*) reversing heat flow and (*b*) nonreversing heat flow. Underlying heating rate, 10 K/min; modulation amplitude, ±2 K; and modulation period, 60 s.

ature shifts upward and the area of the peak, generally speaking, tends to decrease. Very importantly, the reversing and the nonreversing heat-flow curves provide clearer information which cannot be obtained from the traditional DSC. Once the alloy is aged in the martensite state, the endotherm in the nonreversing heat-flow curve is gradually superimposed by the exotherm and finally becomes hardly observable. Meanwhile, the exotherm becomes more significant, with an increase in the area of the peak with increasing aging time. Correspondingly, the area of the endothermic peak in the reversing heat-flow curve also increases significantly with increasing aging time. On prolonged aging in the martensite state, however, the areas of the endotherms in both the total heat-flow curve and the reversing heat-flow curve and that of the exotherm in the nonreversing heat flow curve all tend to diminish. The measurements using different underlying heating rates and modulation amplitudes were also performed, and similar results were obtained.

It is worth noting that once the as-quenched or aged martensite is transformed into the parent phase, the exotherm observed in the nonreversing heat-flow curve will partially or even completely disappear on the subsequent heating scan, depending upon the temperature and duration in the parent phase. With increasing holding time in the β-phase state, the area of the exotherm decreases and, finally, an endotherm can be seen in the nonreversing heat-flow curve after a certain period. The result can be easily understood because, as we have described previously, the relaxation leading to atomic reordering occurs in the parent phase. As a matter of fact, the step-quenched sample, as shown in Figure 4(a), already illustrates such an effect of parent-phase holding on the MDSC result. In addition, the difference in the heat capacity of the martensite and the parent phase was found to become smaller in the samples exposed to parent-phase holding.

In order to examine the thermoelastic transformations, the martensite-aged samples were subjected to transformation cycling, typically between 223 and 433 K. Both the forward and the reverse martensitic transformations were traced by MDSC. The results clearly indicate that the martensite aging effects in the early stage of aging can be annealed out by heating to the parent-phase state: the transformation temperatures are shifted to the stable values and no exotherm peak can be seen on the second and third heating scan. However, the second and third scans of the well-aged samples show a gradual decrease in the area of the endothermic peaks in the three kinds of heat-flow curves, as compared to the MDSC results of the as-quenched samples and short term–aged samples. This result suggests that, on prolonged aging, more and more martensite plates become fully stabilized and, hence, lose their reversibility. Figure 6 shows the first, second, and third heating scans of two typical samples aged at room temperature (in the martensite state) for different times, as defined in the early stage and prolonged stage of aging, respectively. The variation of the peak temperatures and peak areas as a function of martensite aging time, derived from the first heating cycle and the second cycle, are presented in Figure 7. From the results, two stages of the aging process can be clearly distinguished.

In the first aging stage, the shift upward of the peak temperature and the remarkable increase in the reversible transformation enthalpy clearly indicate the stabilization of martensite. Meanwhile, the fact that the derived values from the subsequent scans remain essentially unchanged during this stage suggests that the aging process is dominated by kinetic relaxation rather than by thermodynamic decomposition. From the MDSC curves, we can find that the onset and peak temperatures of the exotherm in the nonreversing curve always fall behind the temperatures of the endotherm in the reversing curve, but may last an additional 20 to 30 K even when the endotherm ends. This fact strongly implies that the exotherm is related to the formation of the β phase and that the kinetic relaxation process occurs once the martensite is transformed into the parent phase. As we mentioned earlier, assuming the exotherm is ascribed to the relaxation process leading to the atomic reordering in the β phase, the increase in the peak area of the exotherm suggests that atomic disordering might have occurred during the previous martensite aging. If this is the case, a sluggish endotherm is expected to appear on martensite aging; otherwise, an exotherm should be observed if atomic reordering takes place during the martensite aging.

In order to examine the relaxation processes occurring in

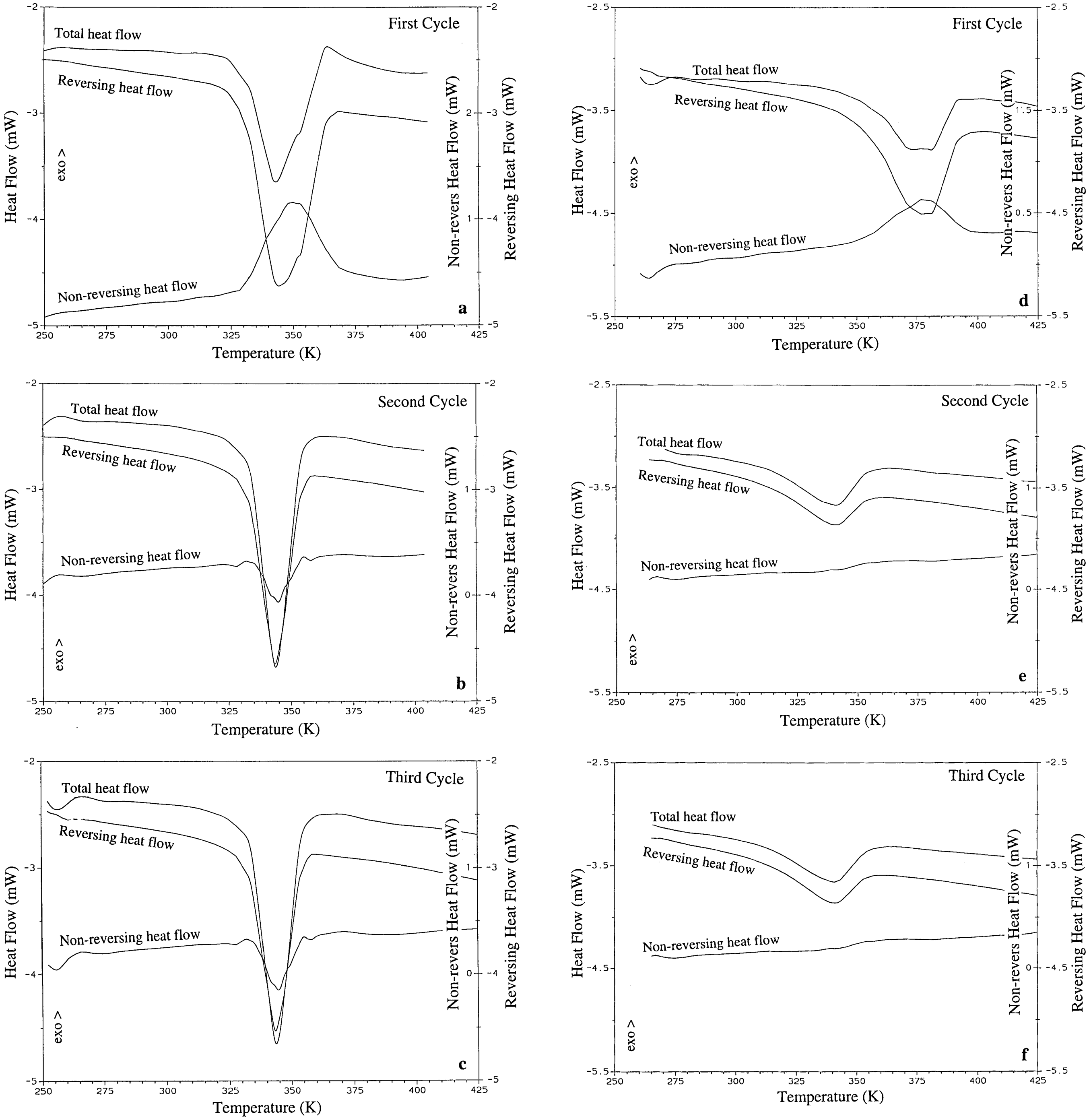

Fig. 6—The typical first, second, and third heating curves for the samples aged in the martensite state for different periods: (*a*) through (*c*) aged at RT for 5 h and (*d*) through (*f*) aged at RT for 1440 h. Underlying heating rate, 10 K/min; modulation amplitude, ±2 K; and modulation period, 60 s.

the martensite state, the as-quenched samples were scanned from 193 K using various underlying heating rates from 1 to 10 K/min and altering the modulation amplitude to increase the sensitivity or resolution. Very strangely, no noticeable endothermic or exothermic relaxation peaks were detected in the temperature range in the martensite state. This fact indicates that the relaxation in the martensite state is different from that in the parent phase and that similar atomic reordering on martensite aging can be denied. To further trace the martensite aging process, isothermal MDSC measurements were performed. The preliminary results reveal a clear, although weak and irregular, endothermal relaxation process on the martensite aging. More detailed investigations are underway.

The second stage of martensite aging is characterized by the irreversible thermodynamic decomposition of martensite, and the resulting aging effect cannot be annealed out by heating the alloy to the parent state. According to our observations, the two aging stages can hardly be separated in some cases, such as, for instance, in the rapidly-quenched alloy. Also worthy of mention is the effect of sample size and geometry. A thin sample with a large surface area usually promotes the decomposition of martensite and makes it impossible to distinguish the two stages.

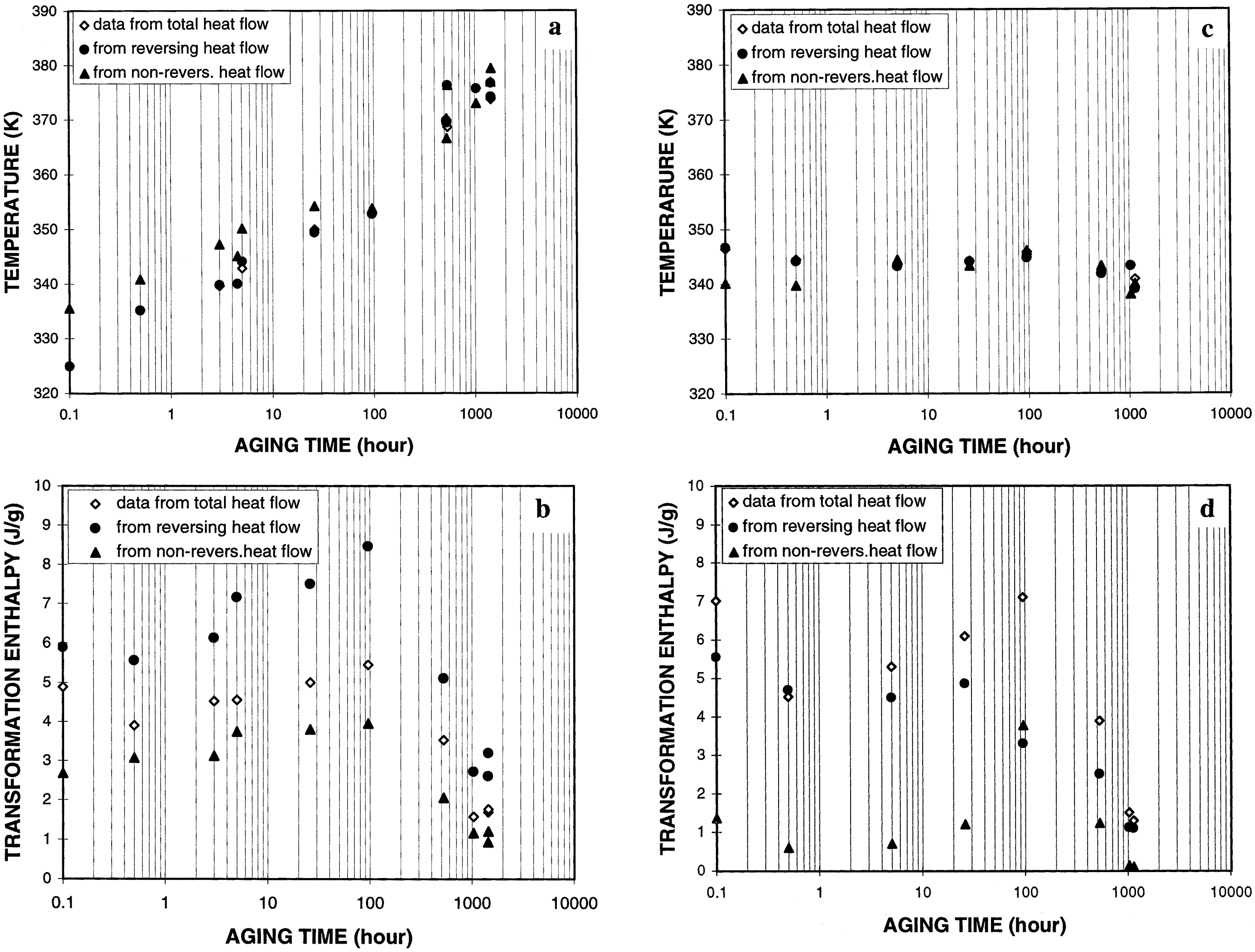

Fig. 7—The transformation peak temperatures and peak areas (transformation enthalpy) as a function of martensite aging time at RT (*a*) and (*b*) the first transformation cycle and (*c*) and (*d*) the second transformation cycle. See text for more details.

IV. DISCUSSION

A. *Interpretation of the MDSC Data*

Since MDSC is an updated calorimetric technique, the detailed interpretations of the MDSC data are still being discussed in the literature. The total heat flow is the only quantity that is available and, hence, it is the only quantity that is always measured in conventional DSC experiments.[7] Actually, in a calorimetric run of a thermally induced thermoelastic martensitic transformation, the heat measured in the conventional calorimeter is the sum of three components.[1]

For the forward transformation,

$$-Q_f = -\Delta H_{ch}^{p-m} + \Delta H_{el}^{p-m} + E_{fr}^{p-m} \qquad [2]$$

For the reverse transformation,

$$Q_r = \Delta H_{ch}^{m-p} - \Delta H_{el}^{m-p} + E_{fr}^{m-p} \qquad [3]$$

where Q_f and Q_r are the measured heat during the forward transformation and the reversion, respectively; ΔH_{ch} the chemical enthalpy change (latent heat of the transformation); ΔH_{el} is the stored elastic strain enthalpy change; and E_{fr} is the energy dissipated in the form of frictional work. Here, the positive sign is used when the system absorbs heat or energy, and *vice versa*. Evidently, the transformation enthalpy is only a part of the measured heat and, therefore, it is only a rough approximation to equal the measured heat to the transformation enthalpy. Also, the heat capacity obtained from the conventional DSC measurements is only the "apparent heat capacity" or "total heat capacity." In the MDSC measurements, the measured heat capacity is associated with the reversible heat flow only and, hence, represents a more accurate interpretation of heat capacity.[7]

If no irreversible contributions had to be taken into account in the nonchemical free energy change, the thermoelastic martensitic transformation would be ideally reversible and an already existing martensite plate would grow and shrink without any hysteresis in temperature. Owing to the presence of irreversible contributions to the nonchemical free energy, significant thermal hysteresis is at play even for already existing martensite plates.[1] In principle, a local thermoelastic equilibrium must be reached at individual parent-martensite interfaces, resulting in a null change in the energy balance. Usually, the change in the chemical free energy ΔH_{ch} is homogeneous, but the change in the stored elastic energy ΔH_e and the frictional work E_{fr} are quite inhomogeneous. As a result, different martensite plates or even different parts of the same martensite plate may exhibit different thermal hysteresis. Within a given temperature modulation amplitude, some martensite plates may show a reversible feature while the others may be irreversible. For instance, once a small positive temperature perturbation, say, ΔT_1, is produced, some martensite plates will transform into the parent phase. Within the negative temperature perturbation $-\Delta T_2$ (ΔT_2 is always smaller than ΔT_1 on heating scans), only part of the parent phase is transformed into martensite again; the other part may need a larger negative temperature change to retransform into martensite. Therefore, the reversing heat flow reflects the thermodynamically reversible quantity of the thermoelastic transformation, whereas the nonreversing signals include not only the irreversible frictional work dissipated during the transformation, but also the contribution of some thermoelastic transformation with larger hysteresis. If no additional relaxation processes are involved, the nonreversing heat flow should always show an endotherm on the reverse martensitic transformation. The dependence of the measured data on the MDSC experimental parameters can be used to analyze the kinetics and hysteretic features of the martensitic transformations. This is an important area worthy of future exploration.

Although there still remain some uncertainties in the analysis and interpretation of the data, the reversing and nonreversing heat-flow signals provide more rich information which is not available in the total heat flow. For instance, previous DSC measurements of the transformation enthalpy in aged martensite revealed a decrease in the transformation enthalpy with increasing aging time.[23,24] This result cannot explain the fact that the martensite is being stabilized. Our MDSC measurements clearly show that the reversible transformation enthalpy increases with the aging time, indicating that the martensite becomes more difficult to transform into parent phase. Tsuchiya *et al.*[25] have found that there is a good agreement between the kinetics of the rubber-like effect and that of the stabilization of martensite, and a clear rubberlike behavior was observed within 10^5 seconds when the martensites in CuZnAl alloys were aged at ambient temperatures. This is just within the first aging stage, as we observed. It seems that the mechanism of the rubberlike behavior may be associated with the remarkable change in the reversing transformation enthalpy or entropy. The rubberlike behavior on prolonged (second-stage) aging, however, has not been reported. According to our results, it can be deduced that the rubber effect will gradually diminish with prolonged aging.

B. *Mechanisms of the Relaxation Processes*

As we described previously, two kinds of relaxation peaks have been observed: one is associated with the reverse transformation, while the other is due to the atomic reordering in the parent phase. To be more specific, the former one, *i.e.*, the relaxation peak observed in the air-cooled sample, may originate from the movement of the twin interfaces and the martensite-parent interfaces. It has been observed that, in the water-quenched CuZnAl alloys, the martensitic transformations start progressively, whereas the slow-cooled samples show a burst type of transformation and transmission electron microscopy (TEM) observations revealed some differences in the fine substructures of the martensite plates.[26,27] It seems that the interfaces in the martensites are pinned by some obstacles and the relaxation is related to the characteristic anelastic effect. As is known, the pinning effect of the interfaces has been widely observed in the stabilized martensites.[14] Thus, it is expected that a similar relaxation process may appear in the stabilized martensites. Figures 5 and 6 clearly show that, on martensite aging, the exotherm becomes more sharp and closely related to the transformation. The exotherms observed in the aged martensites may be the combination of the two kinds of relaxation processes.

According to the thermodynamic assessments based on the Bragg–Williams approximation, the A2 = B2 and B2 = $D0_3(L2_1)$ ordering transitions in the ternary CuZnAl shape-memory alloys are second-order transitions,[19] and neutron diffraction experiments have confirmed the point.[18] Therefore, it is incorrect to assume that the B2 = $D0_3(L2_1)$ ordering transition is depressed on quenching and will develop further on postquench aging. However, although the NNN atomic ordering transition cannot be suppressed by rapid cooling, the kinetic evolution of the LRO parameters en route to the final equilibrium state at a given temperature is a typical first-order transition and, hence, can be greatly affected by factors such as the cooling rate and holding temperature and time. In the as-quenched alloys, a relaxation process will take place on aging, wherein atomic reordering proceeds through the diffusion of atoms *via* the vacancy mechanism. In order to increase the degree of SRO and LRO, the atoms will rearrange between different sublattice, as well as within the same sublattice, sites. Usually, a long-range diffusion mechanism is operative in such a relaxation process and an exotherm can be observed

As regards the mechanism of martensite aging, there have been some controversial interpretations. Previously, it was suggested that the incomplete $D0_3(L2_1)$ atomic order would tend to be more complete on martensite aging, giving rise to the stabilization of martensite.[24,28] On the contrary, Ahlers and his co-workers[29,30] suggested that atomic disordering between Cu and Zn atoms on nearest-neighbor sites takes place, leading to a decrease in long-range order. Atomic location by channeling-enhanced microanalysis (ALCHEM) measurements, performed by Nakata *et al.*,[31] and other experiments, including TEM observations,[32] electron and proton irradiation,[33,34] electrical resistivity, and thermoelectric power measurements,[35,36] have confirmed the occurrence of atomic disordering on martensite aging.

Considering that MDSC has improved sensitivity and resolution over traditional DSC, the fact that no relaxation peaks were detected on the scanning in the martensite state implies two possibilities: (1) the kinetics of martensite aging is too slow or the resulting thermal response is too weak to be detected by the heating scans; and (2) the mechanism of the kinetic relaxation process resulting in martensite stabilization is different from that of the relaxation process in the parent phase. From Figures 5 to 7, we can see that the kinetic evolution of the martensite aging is not very slow, as manifested by the shift of about 10 K in the peak temperature and a significant increase in the area of the exotherm after aging at room temperature for only about 30 minutes. If the same diffusion mechanism as that in the parent phase is operative, such a thermally activated relaxation process of martensite must yield some noticeable thermal effect, which could be observed when measured at a very low underlying heating rate. The unexpected failure suggests that the mechanisms of the relaxation processes in the martensite state and in the β phase may be quite different. Most probably, the relaxation in the martensite is accomplished *via* a short-range diffusion mechanism, which may result in smaller thermal events. More work is needed in this area.

V. CONCLUSIONS

The MDSC technique has been employed to characterize the martensitic transformations, kinetic relaxation processes, and aging effects in a CuZnAl shape-memory alloy. The results demonstrate that MDSC is a unique and powerful tool for analyzing phase transformations in the shape-memory alloy. In particular, the reversing and nonreversing heat flows can provide more useful information than that which is available from conventional DSC measurements.

Two kinds of exothermal relaxation peaks have been found in the CuZnAl alloys on heating. One is mainly associated with the movement of twin interfaces and martensite-parent interfaces, observed in the air-cooled sample and martensite-stabilized samples. The other one is due to the atomic reordering in the parent phase, which appeared in the water-quenched and martensite-aged samples. The two kinds of relaxation processes may coexist in some aged samples, and both of them can be annealed out when heating to the parent phase.

Two stages of martensite aging are distinguished the first stage is characterized by the stabilization of the martensite and the second stage is the decomposition of the martensite. Our MDSC measurements clearly reveal that the martensite stabilization is not only reflected by the increase in the reverse transformation temperatures, but is also represented by the increase in the reversible transformation enthalpy. The stabilization of martensite also gives rise to an increase in the enthalpy for the exothermal relaxation process. The mechanism of the relaxation process in the martensite state is suggested to be quite different from that in the parent phase.

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REFERENCES

1. J. Ortin and A. Planes: *Acta Metall.*, 1988, vol. 36, pp. 1873-89.
2. V. Torra and H. Tachoire: *Thermochimica Acta*, 1992, vol. 203, pp. 419-44.
3. J. Ortin: *Thermochimica Acta*, 1987, vol. 121, pp. 397-412.
4. C. Picornell, C. Segui, V. Torra, C. August, L. Manosa, E. Cesari, and R. Rapacioli: *Thermochimica Acta*, 1986, vol. 106, pp. 209-17.
5. M. Reading: *Trends in Polymers*, 1993, vol. 1, pp. 248-53.
6. M. Reading, D. Elliott, and V.L. Hill: *J. Thermal Analysis*, 1993, 40, pp. 949-56.
7. T. Wagner and S.O. Kasap: *Phil. Mag. B*, 1996, vol. 74, pp. 667-80.
8. A. Toda, T. Oda, M. Hikosaoa, and Y. Saruyama: *Polymer*, 1997, vol. 38, pp. 231-33.
9. D.J. Hourston, M. Song, A. Hammiche, H.M. Pollock, and M. Reading: *Polymer*, 1997, vol. 38, pp. 1-7.
10. I. Okazaki and B. Wanderlich: *J. Polymer Sci. B: Polymer Phys.*, 1996, 34, pp. 2941-52.
11. D.P. Dunne and N.F. Kennon: *Met. Forum*, 1981, vol. 4, pp. 176-83.
12. M.H. Wu: in *Engineering Aspects of Shape Memory Alloys*, T.W. Tuerig, K.N. Melton, D. StÖkel, and C.M. Wayman, eds., Butterworth-Heinemann, London, 1990, pp. 69-88.
13. D.Z. Yang and Z.G. Wei: in *Shape Memory Materials 94*, Y. Chu and H. Tu, eds., International Academic Publishers, Beijing, 1994, pp. 319-23.
14. M. Ahlers: *Proc. ICOMAT'86*, JIM, Nara, 1986, pp. 786-93.
15. M. Chandrasekaran, E. Cesari, J. Wolska, I. Hurtado, R. Stalmans, and J. Dutkiewicz: *J. Phys. IV*, 1995, vol. 5-C2, pp. 143-52.
16. K. Bhattacharya, R.D. James, and P.J. Swart: *Acta Mater.*, 1997, vol. 45, pp. 4547-61.
17. Z.G. Wei, H.Y. Peng, and D.Z. Yang: *Acta Mater.*, 1996, vol. 44, pp. 1189-99.
18. A. Planes, L. Manosa, E. Vives, J.R. Carvajal, M. Morin, G. Guenin, and J.L. Macqueron: *J. Phys.: Condens. Matter*, 1992, vol. 4, pp. 553-59.
19. Z.G. Wei: Ph.D. Dissertation, Dalian University of Technology, Dalian, China, 1996.
20. A. Nagasawa: *Mater. Trans. JIM*, 1991, vol. 32, pp. 774-82.
21. H.I. Aaronson, J.P. Hirth, B.B. Rath, and C.M. Wayman: *Metall. Trans. Mater. A*, 1994, vol. 25A, pp. 2655-73.
22. J. Vinals, V. Torra, A. Planes, and J.L. Macqueron: *Phil. Mag.*, 1984, vol. 50, pp. 653-66.
23. Y. Murakami, S. Morito, Y. Nakajima, K. Otsuka, T. Suzuki, and T. Ohba: *Mater. Lett.*, 1994, vol. 21, pp. 275-78.
24. G. Scarsbrook, J.M. Cook, and W.M. Stobbs: *Metall. Trans A*, 1984, vol. 15A, pp. 1977-86.
25. K. Tsuchiya, K. Tateyama, K. Sugino, and K. Marukawa: *Scripta Metall. Mater.*, 1995, vol. 32, pp. 259-64.
26. R. Rapacioli and M. Ahlers: *Scripta Metall.*, 1979, vol. 11, p. 1147.
27. F.J. Gil and J.M. Guilemany: *Thermochimica Acta*, 1992, vol. 205, pp. 75-85.
28. G. Scarsbrook, J. Cook, and W.M. Stobbs: *J. Phys.*, 1982, vol. C4, pp. 703-08.
29. A. Arab and M. Ahlers: *Acta Metall.*, 1988, vol. 36, pp. 2627-38.
30. F. Saule and M. Ahlers: *Acta Metall. Mater.*, 1995, vol. 43, pp. 2373-84.
31. Y. Nakata, O. Yamamoto, and K. Shimizu: *Mater. Trans., JIM*, 1993, vol. 34, pp. 429-37.
32. M.H. Wu and C.M. Wayman: *Mater. Sci. Forum*, 1990, vols. 56–58, pp. 553-58.
33. A. Tolley, M.P. Macht, M. Muller, C. Abromeit, and H. Wollenberger: *Phil. Mag.*, 1995, vol. 72, pp. 1633-47.
34. K. Tsuchiya and K. Marukawa: in *Shape Memory Materials '94*, Y. Chu and H. Tu, eds., International Academic Publishers, Beijing, 1994, pp. 314-18.
35. L. Cooreman, J. Van Humbeeck, and L. Delaey: *Acta Metall. Mater.*, 1990, 38, pp. 2663-66.
36. Z.G. Wei and D.Z. Yang: *Acta Metall. Sinica*, 1996, vol. 32, pp. 578-84.