Phase transformations in $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ shape memory alloy

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Abstract

Thermal expansion characteristics of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy have been measured in the temperature range of 25 to 370 °C. The influence of the heating/cooling rate on the transient temperatures and hysteresis has been studied in the temperature range of the phase transformations. The transformation temperatures do not depend on the heating/cooling rates. The phase transformation martensite↔austenite occurs at the same temperature at heating and cooling. Hysteresis is a consequence of the latent heat. The sample temperature depends on the complicated process of the heat conduction and the phase transformation that take places in cooperation.

Key words: SMA, martensitic phase transformations

1. Introduction

Martensitic transformation is diffusionless structural transformation that occurs between a high-temperature cubic phase and a lower-temperature phase with a lower symmetry. The lattice strain is a transformation parameter that determines the physical states of an initial phase and a product phase, as well as local intermediate states of the alloy during the phase transformation. The free energy ΔF due to formation of a crystal of a product phase in the thermoelastic equilibrium is given by relation [1]

$$\Delta F = -\Delta f V + E_{\mathrm{el}} + \Gamma S \ , \tag{1}$$

where Δf is the driving force, V is the volume, S is the surface area, E_{el} is the elastic energy, and Γ is the specific interface energy of a martensite crystal. The gradual relaxation of the elastic energy during the phase transformation leads then to complex polydomain structure of the martensite.

The martensitic transformation is referred to as athermal transformation [2]. This transformation appears to be instantaneous at any temperature, and the amount of transformed material depends only on the temperature. The transient temperatures and hysteresis do not appear to be rate dependent. The path followed by the system during the phase transformation is influenced by the existence of disorder (dislocations and further crystalline disorder). During the martensitic phase transformation, the system passes through a sequence of metastable states. The transition from one metastable state to another occurs in a very short time [3].

The martensitic phase transformation is the first-order phase transformation. The first-order transformations are characterized by a discontinuous change in volume at a constant temperature and pressure. The release of the elastic energy during the martensitic phase transformation is connected with the macroscopic deformation of the material. Dilatometry determines not only deformations connected with thermal vibrations of the material, but all deformations occurring in the material during thermal loading. Dilatometry can therefore give important information about the development of elastic energy in the shape memory alloys during heating and cooling. In this work, we present the results of measurement of the expansion characteristics of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy. These characteristics are analysed in connection with an influence of the latent heat on the sample temperature.

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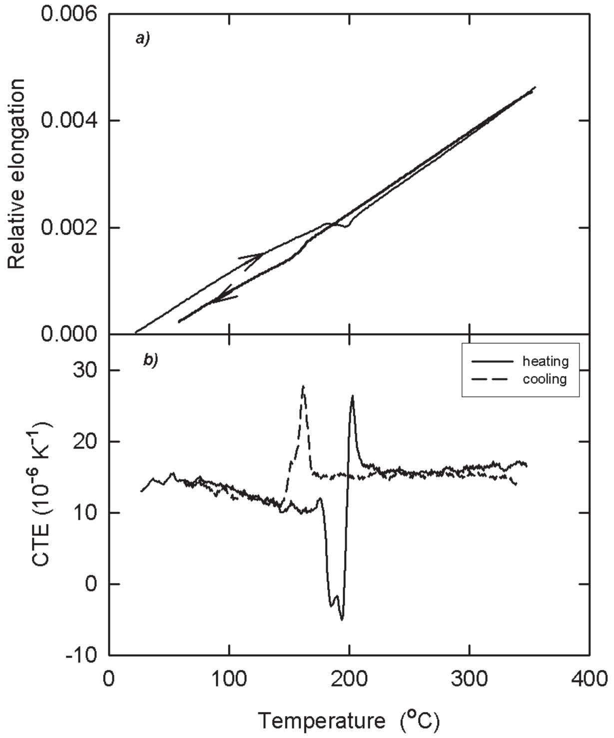

Fig. 1. Temperature dependence of the relative elongation (a) and the CTE (b) for the first thermal cycle (5 K min^{-1} in Ar).

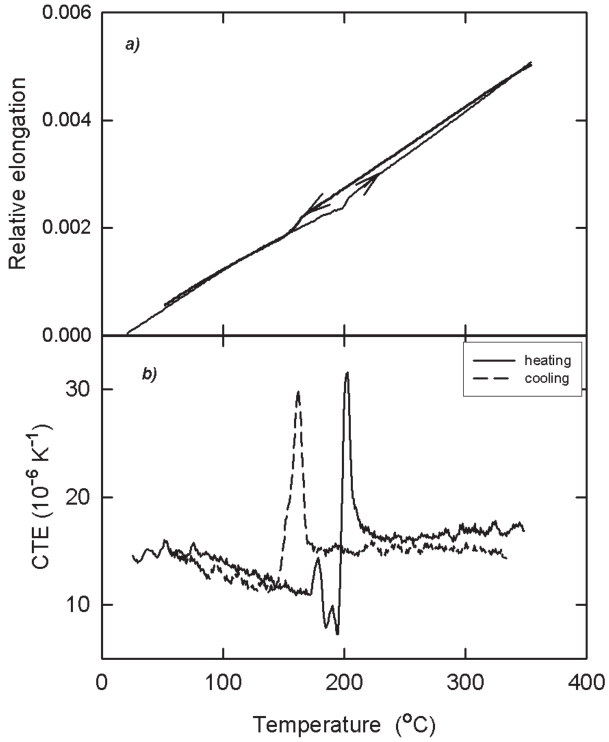

Fig. 2. Temperature dependence of the relative elongation (a) and the CTE (b) for the second thermal cycle (5 K min^{-1} in Ar).

2. Experiment

A polycrystalline ingot of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy was prepared by arc melting of the elements under argon atmosphere. The samples prepared were annealed for four days at 850 ℃.

The linear thermal expansion of the samples was measured in argon and helium atmosphere using Netzsch 402 C/4/G dilatometer at room temperature of 370 ℃. Heating and cooling rates were 0.5, 2, 5, and 7 K min^{-1}. The samples were 6 mm in diameter and 25 mm in length. The accuracy of the measuring apparatus was checked by determining the coefficient of thermal expansion (CTE) of pure Mg and comparing it with the data available from literature. The agreement between the measured values and the values in literature is in the range ± 1 %. The material was predeformed by compression up to 1% using an Instron type deformation machine.

3. Results

Figure 1 shows how relative elongation and CTE of the alloy depend on the temperature of the sample after heat treatment. The phase transitions are distinctly perceptible on both heating and cooling branches. The martensite→austenite transition is connected at first with the decrease of both dilatation characteristics, which is immediately followed by an increase. The reverse transition, austenite→martensite, takes place in one step. After the first thermal cycle reduction of the sample, the length was 24 μm. Figure 2 reveals the dilatation characteristics obtained in the second thermal cycle. No shortening of the sample was found after this thermal cycle. A negative peak on the heating branch of the temperature dependence of the CTE practically disappears, and a new positive peak occurs at the beginning of the transient temperature range of the martensite→austenite. The dilatation in the third and the fourth thermal cycles already had the same shape. The temperature dependence of the CTE obtained in the fourth thermal cycle is shown in Fig. 3a. The rate of heating and cooling was 5 K min^{-1} in all experiments presented so far. Figure 3b shows the temperature dependence of the CTE obtained in the thermal cycle with the heating and the cooling rates of 0.5 K min^{-1} (the second thermal cycle made with this heating/cooling rate; also the fifth run). No sample shortening was found even after the third and the fourth thermal cycles; further reduction of the sample length after the fifth thermal cycle was found to be 10 μm. The reduction of the sample after the thermal cycle is connected with

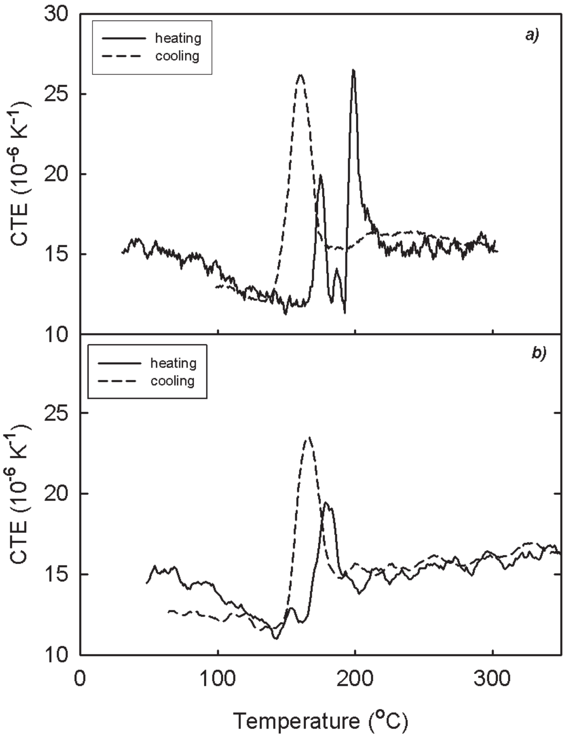

Fig. 3. Temperature dependence of the CTE (a) for the fourth thermal cycle measured by heating/cooling rate 5 K min^{-1} (b) for the second thermal cycle measured by rate 0.5 K min^{-1} (in Ar).

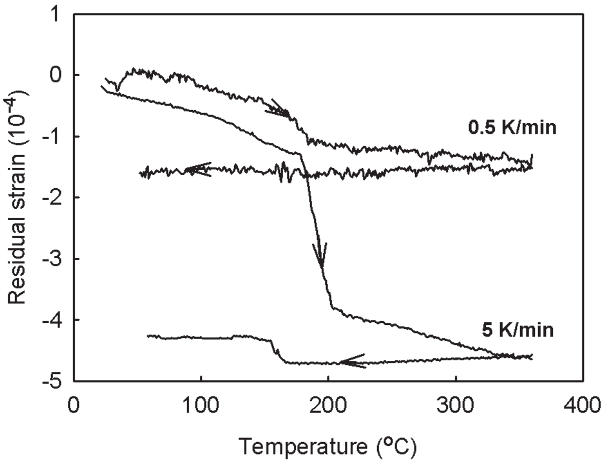

Fig. 4. Temperature dependence of the residual strain.

the release of the residual strain. The temperature dependence of the residual strain may be obtained by subtracting the relative elongation of the first and the second thermal cycles. The residual strain for the heating and the cooling rates 5 K min^{-1} and 0.5 K min^{-1} is shown in Fig. 4.

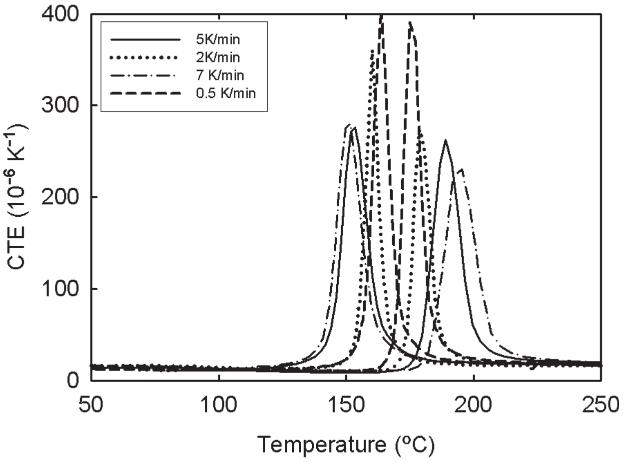

Fig. 5. Temperature dependence of the CTE for pre-deformed sample (in Ar).

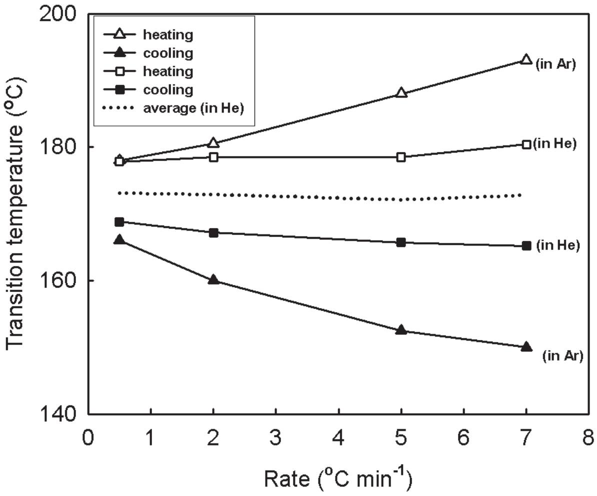

Fig. 6. Dependence of the transformation temperature on heating/cooling rate.

Figure 3 shows substantial influence of heating/cooling rate on the transient temperature of the austenite↔martensite transformation. The influence of the heating/cooling rate was studied in further experiments. The dilatation characteristics were determined on the sample predeformed by compression up to 1 %, where larger transformation deformation than in previous samples existed. The residual strain after predeformation was removed by heating/cooling thermal cycle (5 K min^{-1}; 370 ℃). The dilatation characteristics were then measured using the heating/cooling rates of 0.5, 2, 5, and 7 K min^{-1}. The temperature dependences of the CTE for these rates are presented in Fig. 5. It can be seen that with increasing heating/cooling rate the transient temperature increases/decreases, and hysteresis increases. The transient temperature is the temperature when the max-

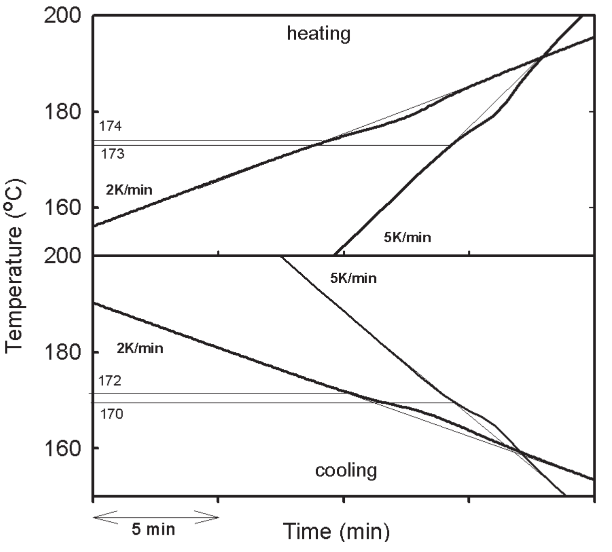

Fig. 7. Time dependence of the temperature for heating/cooling rate 2 and 5 K min^{-1} (in He).

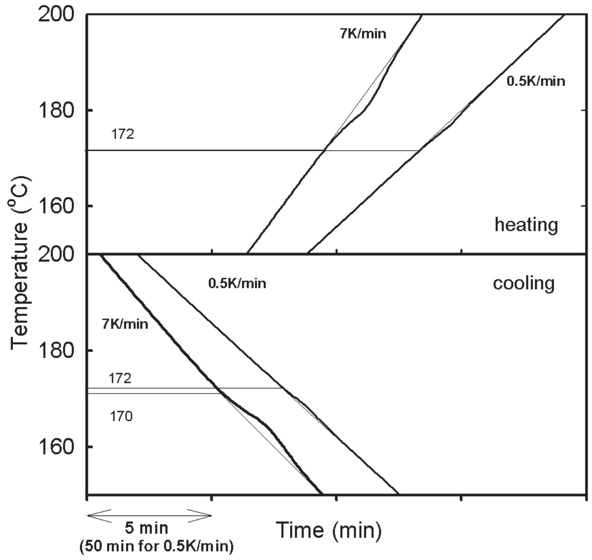

Fig. 8. Time dependence of the temperature for heating/cooling rate 0.5 and 7 K min^{-1} (in He).

imum value of the CTE was reached. The temperature dependence of the transient temperatures is revealed in Fig. 6. All results obtained so far were measured in argon atmosphere. In this figure, the transient temperatures obtained in helium atmosphere are also presented. All other experimental details are the same as in the previous arrangement. It can be seen that quite different results were obtained. Hysteresis does not depend on the heating/cooling rate.

Figures 7 and 8 show the time dependence of the temperature measured in the arrangement where the thermocouple was located directly on the sample. It was measured in helium atmosphere. The influence of the latent heat is obvious; during heating/cooling the latent heat decreases/increases temperature. Figure 9 displays the influence of latent heat on the temperature during measurement of the thermal diffusivity.

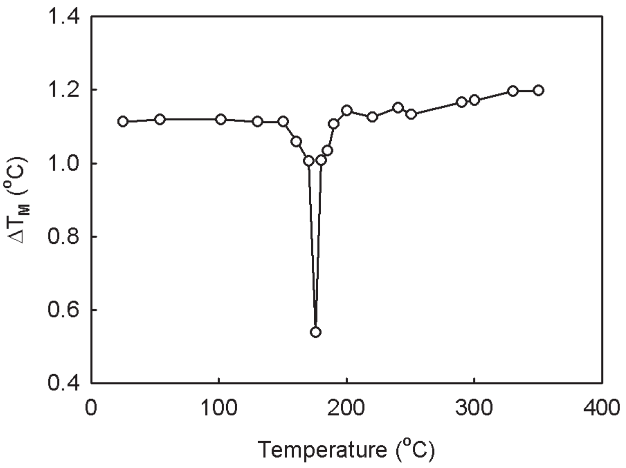

Fig. 9. Temperature dependence of the maximum temperature rise of the sample irradiated by pulse of energy in the flash method.

4. Discussion

It was mentioned in the introduction that phase transformation martensite↔austenite is a strain phase transformation. The macroscopic deformation of the alloy in the range of the phase transformations is a demonstration of the term of the elastic energy in Eq. (1). The peaks on the temperature dependence of the CTE represent release of the transformation deformation during thermal cycle.

The first three figures show development of the deformation in the alloy during the three thermal cycles following heat treatment. The negative peak on the heating branch of the temperature dependence of the CTE in the first thermal cycle can have two causes. The first cause of this effect may be removing the residual strain that occurs in the alloy during cooling from 850 ℃ (heat treatment). In this hypothesis, it is assumed that dislocations and further crystalline defects are bound in the coherent boundary in the martensite. During heating, when the martensite transforms into the austenite, all these defects are removed. The second cause may be removing the frozen austenite. Both effects would be connected with permanent reduction of the sample length that has been found. The first alternative is assumed to be more probable. The residual strain is expected in all cases where large amounts of the various interfaces exist in the material. The residual strain usually appeared in the as-cast composites [4] or in the as-cast alloys [5]. The release of this residual strain is always connected with a reduction of the sample length. Temperature dependence of the residual strain is shown in Fig. 4. In this figure, we can also find the temperature dependence of the residual strain for the same sample in the following run when the heating/cooling rate was 0.5 K min^{-1}. It can be seen that not all the residual strain was removed during heating at 5 K min^{-1}. The removal of the residual strain depends not only on the finish temperature of the thermal cycle but also on the heating rate. The results obviously show that thermal history influences behaviour of the alloy. Similar results were found by Pierge et al. [6] where the influence of the heat treatment on the transformation behaviour in polycrystalline NiMnGa based alloy was studied by DSC. Their results show that the transformation peaks of the heat-treated alloy are clearly defined, whereas those of the nonheat-treated alloy tend to be diffuse and extend on a wider temperature range.

Figure 3 shows that the dilatation characteristics of the alloy in the transient temperature range depend on the heating/cooling rate. For a study of influence of the heating/cooling rate on the dilatation characteristics, the predeformed sample in compression was chosen because deformation during martensite↔austenite transformation is more obvious here than in the nondeformed sample. Figure 5 shows the results obtained during measurement of the CTE for four heating/cooling rates (0.5, 2, 5, and 7 K min^{-1}). The transient temperature of the martensite→austenite increases with increasing heating rate and decreases with increasing cooling rate. Increasing heating/cooling rate increases the hysteresis of the phase transitions (Figs. 5, 6). Dependence of the transient temperature on the heating/cooling rate was also found by Kostov et al. [7] for copper-based shape memory alloys. Figures 5 and 6 show that the hysteresis strongly depends on the atmosphere that exists in the system where the temperature and the thermal expansion are measured. Helium has at about an order higher thermal conductivity than argon. The result that the hysteresis does depend on the heating/cooling rate is in agreement with general characteristics of the athermal phase transformation. On the other hand, it is in disagreement with majority of the experimental findings where the rate dependence of the physical parameters was found (for example [8, 9]).

If the surface of the sample reaches the transient temperature and the phase transformation starts the sample, temperature decreases/increases during heating/cooling. The sample temperature is strongly influenced by the latent heat of the phase transformation. Figures 7 and 8 show the surface temperatures that are the highest in the sample. Inside the sample, a very complex process occurs in which the heat is conducted in cooperation with the phase transformation. The interface between the austenite and the martensite propagates progressively into the sample as the interior sample temperature reaches the transient temperature. The transformation is complete when the temperature in the whole sample is the same or higher than the given transformation temperature. In our measurements, the transformation temperature range is spread into range 20–30 ℃.

Table 1. Temperature dependence of the transformation temperatures determined from Figs. 7 and 8

Rate (K min^{-1})	Transient temperature (℃)	
	heating	cooling
0.5	172	172
2	174	170
5	173	172
7	172	170

The time dependences of the temperature in the transient temperature range allow to determine the temperature when the phase transformation starts (it is the temperature where the measured temperature starts to deviate from a linear interpolated temperature as seen in Figs. 7 and 8). These temperatures are presented in Table 1. It can be seen that there is practically no difference between heating and cooling. No hysteresis exists for the transformation temperatures determined by this manner. It is assumed that this transformation temperature has not yet been influenced by the latent heat. The complicated process cooperation of the heat conduction and the phase transformation (absorption or release of the latent heat) in the sample causes the temperature to which the thermal expansion is related to be higher (heating) or lower (cooling) than the real temperature in the sample. Hysteresis (not dependent on the heating/cooling rate) is a consequence of the latent heat and the thermal diffusivity of the material. Our results clearly show agreement with the thermodynamic conclusions that the phase transformation martensite↔austenite occurs at the same temperature for heating and cooling 172 ℃ ± 2 ℃. The transient temperature can be also obtained as average value of the transient temperatures obtained during heating and cooling when measurement was made in He (Fig. 6). This value 172.1 ± 1.3 ℃ is the same as the previous value. From the presented results, it is obvious that heat conduction plays a dominant role in the transformation process.

The latent heat always influences the measured temperature. If this fact is not respected during measurement of certain physical parameters, then wrong results are obtained. For example, during measurement of the specific heat, Cesari et al. [10] did not find any peak typical for the martensitic phase transformation in Ni-Mn-Ga alloy. Kuo et al. [11] measured the thermal conductivity of the NiMnGa alloy by the direct-pulse technique also in the transient temperature range. They found a peak that was interpreted as "phonon peak". However, this peak is a consequence of the influence of the latent heat on measured temperature. Storage of energy occurs in this case in the sample because input energy is used for the calculation of the thermal conductivity. Influence of the latent heat on measured temperature is displayed in Fig. 9. These data were obtained in the flash apparatus for the measurement of the thermal diffusivity. The sample is irradiated from one side and the time dependence of the temperature rise is measured on the opposite side. The maximum increase of the temperature is shown in Fig. 9. The results concerning the thermal diffusivity of the Ni-Mn-Ga alloy will be published. The present analysis of the phase transformations shows the thermal diffusivity and the thermal conductivity of the martensite and the austenite as the parameters determining the system state during the nonstationary process of the phase transformation. Both parameters are strongly dependent on the chemical and the physical properties of the system.

5. Conclusion

The phase transformation martensite↔austenite of $Ni_{53.6}Mn_{27.1}Ga_{19.3}$ alloy was studied by dilatometry. During the first thermal cycle after heat treatment, residual strain is released, and this process is connected with the permanent sample reduction. Dilatation characteristics depend on the heating/cooling rate if measurement of the dilatation characteristics is made in argon atmosphere. If measurement is made in helium atmosphere (He has at about an order higher thermal conductivity than Ar), the transformation temperatures and hysteresis do not depend on the heating/cooling rate. Generally hysteresis of the various physical properties during thermal cycle is a consequence of the latent heat. The latent heat reduces the sample temperature during heating and increases it during cooling.

Analysis of the time dependence of the temperature on the sample surface shows that phase transformation occurs at 172 ℃ ± 2 ℃ and that this temperature is the same for heating and cooling. The phase transformation martensite→austenite takes place firstly on the sample surface where the temperature is the highest. The austenite-martensite interface propagates progressively into the sample in the direction of the decreasing temperature gradient. The temperature in the interior of the sample depends on the complicated process of the heat conduction and the phase transformation that takes place in cooperation.

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