

## Reversion of Martensite in 304 Stainless Steel Studied by Dilatometry and Calorimetry

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### Abstract

Dilatometry has been used to confirm that the reversion of deformation-induced martensite in Type 304 stainless steel occurs principally in the temperature range 425 to 650°C, and to show that the reversion is a thermal or not diffusion controlled. An attempt to correlate the change in length of cold-drawn 304 wire samples on heating to 800°C with the martensite content determined from the measured saturation magnetization was only qualitatively successful. The heat of reversion of martensite in cold-drawn wire samples was found by differential scanning calorimetry to be in the range 1800 to 2200 J/mol in cold-drawn 304 wires, in reasonable agreement with values for the heat of formation of martensite in 4340 steel determined by a completely different method. We also observe an exothermic reaction near 650°C of a few hundred J/mol which we ascribe to the recrystallization of cold-worked austenite.

**Keywords:** Dilatometry; Permeability; Magnetization; Calorimetry; Thermomechanical

### Introduction

AISI Type 304 stainless steel in the annealed condition is nominally face-centered cubic or austenitic. This phase is paramagnetic, with an unusually high magnetic permeability. When plastically deformed at a sufficiently low temperature, part of the deformation occurs by the formation of body-centered cubic (or slightly tetragonal) martensite, which is ferromagnetic. The density of the deformation-induced martensite is significantly lower than that of the austenite, so that in principle the volume fraction of martensite can be determined from a density measurement, and the reversion of martensite to austenite can be followed by dilatometry.

We have used dilatometry to follow the reversion of martensite in 304 stainless steel, finding that in samples deformed in tension at 0°C it occurs over the temperature range 425–625°C and is a thermal, implying that the martensite reverts to austenite by a reverse shear mechanism, not by a diffusion process. We have also tried to correlate the volume fraction of martensite in cold-drawn 304 wires, measured by the change in length that results from heating to 800°C, with the volume fraction of martensite measured by the saturation magnetization. The correlation was only qualitatively successful.

We have also used differential scanning calorimetry to measure the latent heat of transformation associated with the reversion of martensite in a number of different samples. We are unaware of any previous such measurements. Our results are discussed in connection with measurements of the heat of reversion of martensite in AISI 4340 steel, using a completely different technique [1].

### Dilatometry

Standard tensile test bars, 0.505 inch in diameter with a gage length of 2 inches, were elongated at 0.1 inch/minute until the first sign of load drop, with the sample held in an ice bath at 0°C. Total elongation was about 55%, resulting in a final diameter of 0.4 inch and a uniform diameter length of 3 inches. The saturation magnetization of the samples was measured with an integrating fluxmeter and was found to be 8.0 kG or 80 emu/g, corresponding to a martensite content of 55 ± 6%.

(There is no agreed value for the saturation magnetization of 100% martensite in 304 stainless. It is not possible to produce 100% martensite by deformation. Trygve Angel [2] working in the 1950s, plotted saturation magnetization against % martensite as determined by X-ray diffraction, and found a value of 160 emu/g for 100% martensite. Childress, Liou and Chien [3] produced a thin film of bcc phase by sputtering from a 304 stainless target, and measured a saturation magnetization of 130 emu/g. The value may be composition-dependent, and the composition limits of stainless steels are notoriously lax. We choose to use an average value of 145 emu/g, noting that it is uncertain by ±10%, to give the volume fraction of martensite knowing the saturation magnetization.)

Four cylindrical samples, each about 0.75 inch long, were cut from each bar using a water-cooled abrasive wheel. These samples were used for dilatometer measurements.

There are relatively few published values for the lattice parameters of austenite and martensite in 304 stainless, but a number of papers show X-ray diffraction patterns from which the lattice parameters may be deduced. We have also measured the lattice parameters of some of our samples, as described later. There is good agreement that the parameter for fcc austenite is 3.60 Å and for bcc martensite is 2.88 Å. None of the published diffraction patterns show any evidence of tetragonality in the martensite.

Using these lattice parameters, plus the knowledge that the martensite and austenite must have identical composition if the martensite forms by a shear transformation, and taking the density

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of fcc austenite as the commonly published value of 8.0 g/cm<sup>3</sup>, we calculate the room-temperature density of martensite as 7.81 g/cm<sup>3</sup>. This is substantially larger than the value of 7.35 calculated using a hard-sphere model.

If the deformation of a sample consisting initially of 100% austenite produced a material consisting of 100% martensite, the sample density should decrease by 2.38%, and if the volume change is isotropic, the linear expansion should be 0.80%. Note, however, that these values are quite sensitive to the values of the lattice parameters. If the martensite parameter is 2.87 instead of 2.88, the calculated expansion becomes 0.46 instead of 0.80%.

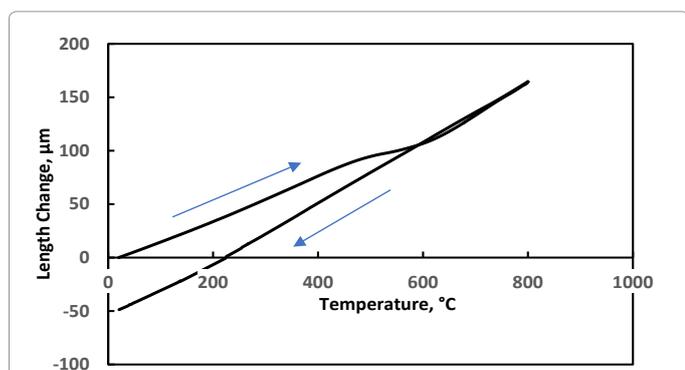
The measured expansion should be directly proportional to the martensite content, and should be reversible as the martensite reverts to austenite on annealing.

Dimensional change vs. temperature was measured using a TA 500 instrument thermomechanical test apparatus. Preliminary experiments determined that slow heating and cooling rates were necessary to minimize hysteretic effects, and the data reported here were obtained using a heating and cooling rate of 1°C/minute.

Figure 1 shows dilatometer data for continuous heating to 800°C followed by cooling to near room temperature. The reversion of martensite begins very gradually at about 400°C and appears to be complete at about 600°C. The difference in thermal expansion coefficient between the two-phase bcc + fcc mixture during heating and the single phase fcc structure during cooling is clearly seen in the difference between the two slopes. The slope of the cooling curve is in good agreement with published values for the thermal expansion of annealed 304 stainless steel.

Analysis of the kinetics of the phase change is difficult, since several effects are occurring simultaneously. As the sample increases in temperature, both the austenite and the martensite are undergoing thermal expansion while the relative fraction of the two phases is changing due to the reversion of martensite. In addition, the reversion itself produces a volume contraction. However, because the cooling curve is recorded down to room temperature, we can measure at room temperature the total contraction of the sample as a result of heating to 800°C.

The sample contraction after annealing is 0.34%, implying an original martensite fraction of 0.34/0.80 equal to 0.43, less than the value of 0.55 suggested by the measured saturation magnetization. The reason for this discrepancy is not clear, but at least two possibilities exist:



**Figure 1:** Dilatometer trace at 1°C/min on AISI 304 stainless steel elongated 55% at 0°C. Reversion of martensite to austenite occurs in the range 400-650°C.

1. The chosen lattice parameters are slightly in error.
2. The assumption that the volume change is isotropic is invalid. The deformation of the sample was directional, so the martensite formation may have been directional.

We are aware of just one previously published dilatometer result for the reversion of martensite in 304 stainless steel by Stalder et al. [4]. It shows reasonable agreement with Figure 1.

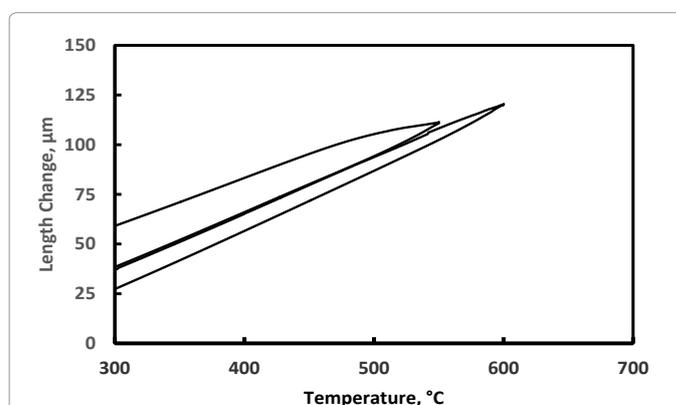
Several dilatometer runs were made in which a deformed sample was heated at 1°C/min to a temperature in the martensite reversion range of 425 to 625°C, held there for 10 minutes, and then cooled at 1°C/minute to near room temperature before being reheated to a higher temperature and again held at temperature and cooled. One such run is shown in Figure 2. From these runs, we conclude that the reversion of martensite is a thermal – the amount of martensite transformed to austenite depends only on the maximum temperature reached by the sample, and not on time. This implies that the mechanism of reversion is the reverse shear of martensite, and not any kind of diffusion-controlled nucleation and growth of austenite.

Measuring the volume fraction of martensite in a deformed 304 sample is an experimental challenge. X-ray diffraction is often used, but in our experience it is subject to error because it samples only a thin surface layer of the sample, and the surface may not be representative of the bulk, primarily because of local heating or local deformation during sample preparation. Determination of phase fractions from the areas of diffraction peaks is also somewhat inexact.

Measurement of the saturation magnetization should give a good value for the martensite content of a sample, but as noted above there is no agreed value for the saturation magnetization of martensite.

Having established that the reversion of martensite is essentially complete at 625°C it is no longer necessary to use high-temperature dilatometry to measure the volume fraction of martensite by dimensional change. A direct measurement of the change in density, or volume, or length of a sample before and after annealing should give the volume fraction of martensite.

We tested this idea by measuring the length of a series of 5.5 inch long cold-drawn 304 stainless steel wires before and after heating to 800°C. The length measurements were made with a 6-inch micrometer modified to detect electrically the first contact between the ends of the



**Figure 2:** Same as Figure 1, with heating stopped at two temperatures and sample held for 10 minutes before cooling and reheating. Note no visible change in length during the holding period. This is an example of several similar runs.

sample wire and the measuring anvils of the micrometer. The saturation magnetization of each wire was determined using a vibrating-sample magnetometer with a maximum applied field of 20.5 kOe.

Figure 3 is a plot of fractional change in length vs. saturation magnetization for the wire samples. The trend, as expected, is that samples with higher magnetization have higher fractions of martensite and show a larger length and volume change. However, the distribution of the data indicates that this is not a reliable method for determining the volume fraction of martensite. Improving the resolution of the length measurement would not improve the result.

There have been several investigations of the reversion of martensite in 304 stainless with magnetic measurements [5-7]. They are in broad agreement with the results reported here, but magnetic methods are always difficult to interpret because the effect of temperature on the magnetic properties of the martensite cannot be separated from the effect of temperature on the amount of martensite.

### Calorimetry

There appears to be little published information on the thermal effects of martensite formation and reversion, either in conventional or in stainless steels. A fairly recent paper (ref 1) approaches this subject in AISI 4340 steel by an indirect technique, assigning the difference between a measured and a calculated cooling curve to the heat of formation of martensite. In the extensive literature on shape memory alloys, however, it is common to find calorimeter measurements of martensite formation and reversion [8].

We have made calorimeter measurements using a TA Q500 instrument on samples from two sources:

1. A 0.5 inch thick bar held at  $22 \pm 2^\circ\text{C}$  and rolled in small steps to a maximum of about 50% reduction in area [9].
2. The cold-drawn wires mentioned above. These were purchased in the cold-drawn state, and the degree of deformation is unknown. We have no reason to think the temperature was controlled during wire drawing, and it is likely that the wire was heated well above room temperature by the deformation.

The clearest results were obtained from the cold-drawn wire samples. Figure 4 shows a calorimeter run at  $50^\circ\text{C}/\text{minute}$ . A rapid heating rate was chosen because the anticipated thermal effects were small. The first negative peak in Figure 4 is the start-up transient of the

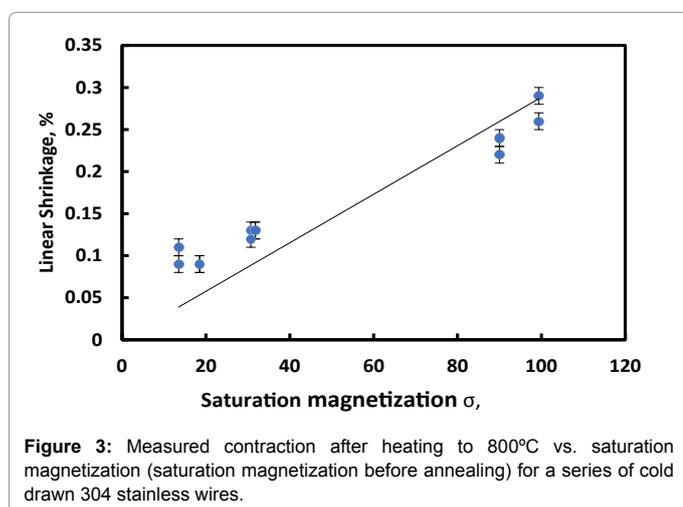


Figure 3: Measured contraction after heating to  $800^\circ\text{C}$  vs. saturation magnetization (saturation magnetization before annealing) for a series of cold drawn 304 stainless wires.

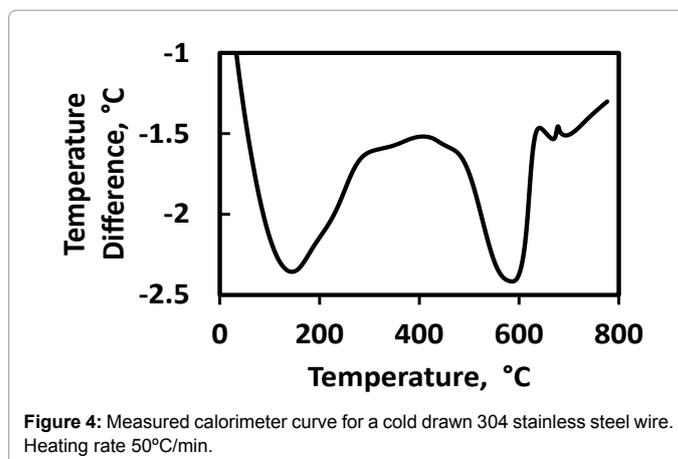


Figure 4: Measured calorimeter curve for a cold drawn 304 stainless steel wire. Heating rate  $50^\circ\text{C}/\text{min}$ .

apparatus that is similar for all samples and has no physical significance. The second negative peak, with a minimum slightly below  $600^\circ\text{C}$ , is the endothermic reversion of martensite to austenite. The very small positive peak at  $670^\circ\text{C}$  is the melting of a small aluminum contaminates in the reference pan and is unrelated to the stainless steel sample.

We suggest that the behavior in the temperature range  $600$  to  $650^\circ\text{C}$  can be interpreted as shown in Figure 5. The dashed line shows the curve required to make the reversion peak symmetrical. Then the area A + C is the endothermic reversion of martensite, and the area B + C is an exothermic process which we attribute to the recrystallization of deformed austenite. Note that the area C is counted twice, once as a contribution to the endothermic reversion of martensite and once as an equal contribution to the exothermic recrystallization of austenite.

### Results

The calorimeter was calibrated by melting and freezing 11.0 mg of aluminum with heat of fusion taken as  $10,700 \text{ J/mol}$ . On this basis the heat of reversion of martensite is  $1,100 \text{ J/mol}$ , and the exothermic heat of recrystallization of austenite is  $130 \text{ J/mol}$ . These values are per mole of sample, but the sample before heating consists of a mixture of martensite and austenite. The sample wire of Figures 4 and 5 had a saturation magnetization of  $90 \text{ emu/g}$  in the cold-drawn state, suggesting a volume fraction of about 0.6 martensite, 0.4 austenite. Using these fractions, we arrive at the heat of reversion of martensite as  $1,800 \text{ J/mol}$  and the heat of recrystallization of austenite as  $320 \text{ J/mol}$ . The heat of recrystallization will of course depend on the degree of cold work, which is unknown for this sample.

A second heating of the same sample showed minimal thermal effect in the temperature range  $400$ - $650^\circ\text{C}$ , confirming that martensite reversion and austenite recrystallization were complete after the first heating.

An identical measurement on a second sample of the wire in Figures 4 and 5 gave the same value of  $1,800 \text{ J/mol}$  for the reversion of martensite, but a significantly larger value of  $450 \text{ J/mol}$  for the recrystallization of austenite.

A second similar 304 stainless wire sample with saturation magnetization of  $100 \text{ emu/g}$  and martensite content of about 0.7, gave values of  $2,200 \text{ J/mol}$  of martensite for reversion and  $640 \text{ J/mol}$  of austenite for recrystallization.

These heats of reversion are comparable to those proposed for AISI 4340 steel [1]. We will return to this reference in the Discussion section below.

None of the samples deformed at controlled temperatures showed the exothermic peak that we have attributed to the recrystallization of deformed austenite. The maximum deformation of these samples was about 50% reduction in area, presumably much less than the reduction imparted to the wire samples by drawing. All the controlled-temperature samples showed negative (endothermic) peaks in the 400-700°C range, but the peaks are shallow and their areas are difficult to define with precision. An example is shown in Figure 6.

Figure 7 shows the heat of reversion of martensite vs. measured

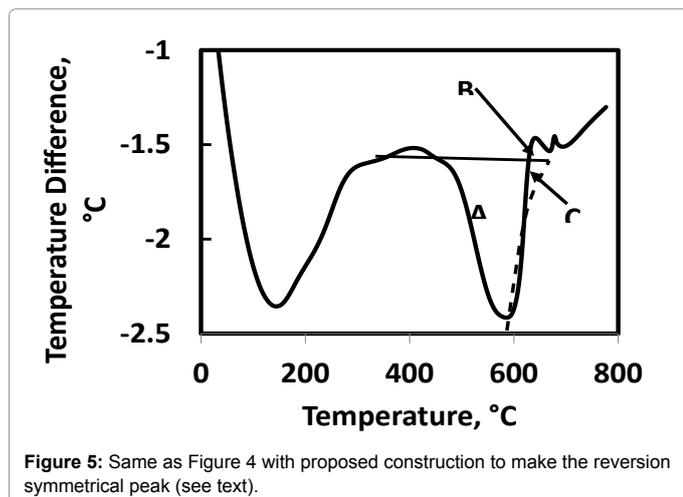


Figure 5: Same as Figure 4 with proposed construction to make the reversion symmetrical peak (see text).

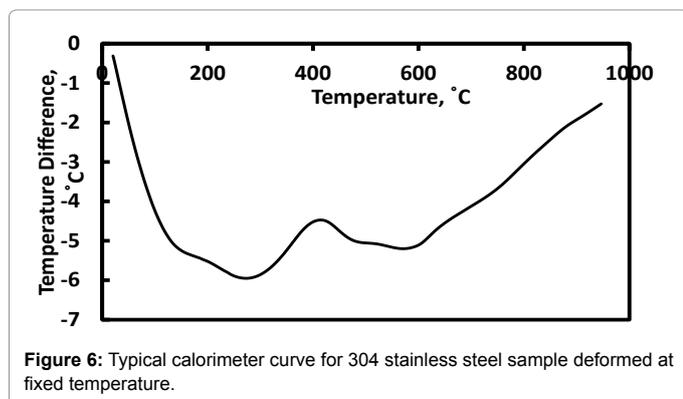


Figure 6: Typical calorimeter curve for 304 stainless steel sample deformed at fixed temperature.

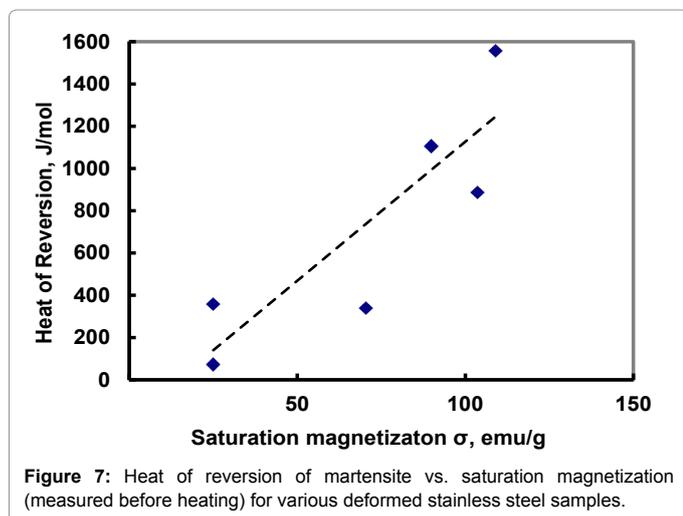


Figure 7: Heat of reversion of martensite vs. saturation magnetization (measured before heating) for various deformed stainless steel samples.

saturation magnetization for all of the samples measured. Although there is considerable scatter, the samples with higher magnetization contain more martensite and show higher heats of reversion.

## Discussion

The authors of ref 1 found, perhaps surprisingly, that the best fit to their measured cooling curve resulted when the heat of formation of martensite in 4340 steel was assumed to be strongly temperature dependent, rising sharply from 2,000 J/mol at 270°C to 5,000 J/mol at 0°C. Note that ref 1 reports values for the heat of formation of martensite, while we report values for the heat of reversion. The two values should of course be equal in magnitude but opposite in sign for a given material. Our measurements provide no direct information on possible temperature dependence of the heat of reversion of martensite in 304 stainless, but we note that our measured heats of reversion are consistently higher in the wire samples that were deformed without temperature control and were presumably heated during deformation.

Because in 304 stainless the martensite is produced by deformation and the temperature of deformation can be controlled, it should be possible to use differential calorimetry to look for a temperature-dependent heat of reversion of martensite.

## Acknowledgements

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