139. An Interpretation of Hysteresis Loops in A_3 and A_4 Transformations of Pure Iron.

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It is well known that the dilatation curve of pure iron can be represented schematically as in Fig. 1. In this diagram $abdefg$ is the heating curve, while $ghkmna$ is the cooling curve. These curves form two hysteresis loops, $bdmn$ and $efhk$, i.e. the length of the specimen changes irreversibly at the A_3 and A_4 points. One¹⁾ of the present authors suggested the irreversibility at A_1 point was due to the large internal stresses set up by the transformation. These stresses are tensile during the transformation $\alpha \rightarrow \gamma$, while they are compressive during the transformation $\gamma \rightarrow \alpha$. At that time, the author supposed the transformation to begin from several centres of nuclei and to grow gradually into full-sized crystals under the assumption that the specimen was spherical.

Usual dilatation experiments, however, are made with cylindrical specimens and it seems reasonable, in this case, that the transformation starts from the periphery of the cylinder and proceeds inwardly. If this is true, the cylinder will develop internal stresses as the outer hull of the specimen works against the inner core from which it follows that stress accompanying the transformation may be calculated by means of the usual theory of a thick walled cylinder under hydrostatic pressure.

If no stress acts during the A_3 transformation, it may be supposed²⁾ that a sharp transformation point T actually exists because of the reversible character of transformation. Such a point is indicated by the vertical line bm in Fig. 1, and enlarged view of the loop at A_3 point. In this figure, ab represents normal dilatation, bm , a sudden contraction and md , normal dilatation. If, however, this contraction is accompanied by tension, the transfor-

Fig. 1. Schema of hysteresis loops at A_3 and A_4 points.

1) K. Honda: Proc. Japan Acad., **25** (1949), No. 1, 11.

2) Here the authors wish to express their cordial thanks to Professor Dr. Carl Benedicks of Stockholm for his valuable suggestion given by his personal communication.

mation will start at higher temperatures following the line bd, and then from d, normal dilatation will take place along a line de. On cooling, normal contraction occurs along a line em, until the temperature m is reached, at which point the transformation will start. Under successively increasing pressure the curve follows a line mn. From n, normal contraction takes place along a line na. Thus, if a transformation is accompanied by tension and pressure, a hysteresis loop will be obtained during cyclic heating and cooling. The stored energy is assumed to be dissipated in the surrounding media after each cycle of transformation.

The same is true for the A_1 transformation, but in this case a transformation on heating is accompanied by an expansion, while transformation on cooling is accompanied by a contraction, thus forming a hysteresis loop in the opposite direction as in the case of the A_3 point.

In the present case, it is assumed that transformation starts from the periphery of a cylindrical specimen and proceeds inwardly.

Fig. 2. Thick walled cylinder under hydrostatic pressures.

It is thus necessary to calculate the stress due to the volume change accompanying the transformation. Fig. 2 shows the outer hull of the cylinder to be α -iron and the inner one γ -iron. The same figure may be taken as representing any stage of the reverse transformation, by replacing α and γ by γ and α respectively. In the case of the $\gamma \rightarrow \alpha$ transformation, a radial pressure should act at the interface, while in the case of the $\alpha \rightarrow \gamma$ transformation, a radial tensile stress should exist at the α and γ -iron interface. Such a stress may be calculated by the elastic theory of a thick walled cylinder under hydrostatic pressure. An expression for the magnitude of such a stress, p , is³⁾

$$p = \frac{3}{8} K \frac{\Delta v}{v} \frac{1 - \left(\frac{r_1}{r_2}\right)^2}{1 + \frac{3}{8} \left(\frac{r_1}{r_2}\right)^2},$$

where K is the bulk modulus of elasticity, $\Delta v/v$ the volume change per unit of volume and r_1 and r_2 are the radii of two coaxial cylinders as shown in Fig. 2. If r_2 is very large compared with r_1 , then p takes on its maximum value

3) M. Satô und Y. Tino: Jour. Sci. Res. Inst., **44** (1949), 59.

$$p_0 = \frac{3}{8} K \frac{\Delta v}{v}.$$

Thus the value of p depends on r_1 , being zero when $r_1 = r_2$ and increasing at first rapidly and later slowly as r_1 decreases tending to the maximum value p_0 at $r_1 = 0$, as shown in Fig. 3.

Fig. 3. Stress distribution as a function of r_1/r_2 .

In the case under consideration, α -iron grows from the periphery towards the inside, subjecting the γ -iron to successively increasing pressure. The pressure at the α and γ -iron interface may be assumed to be identical to the result calculated above. The mean value of this pressure, $\bar{p}$, during complete transformation can be found by integration to be

$$\bar{p} = \int_0^1 p \, dr = p_0 \int_0^1 \frac{1 - \left(\frac{r_1}{r_2}\right)^2}{1 + \frac{3}{8}\left(\frac{r_1}{r_2}\right)^2} dr = p_0 \times 0.624$$

or

$$\bar{p} = 0.234 K \frac{\Delta v}{v}.$$

The mean pressure is thus about 40% less than the maximum value p_0 .

The shift in transformation temperature, δT , caused by applied hydrostatic pressure or tension p is given by the Clapeyron-Clausius' equation

$$\delta T = T p \frac{\Delta v}{v} / \rho \lambda,$$

where T , $\Delta v/v$, ρ and λ are the transformation temperature, the volume change, the density and the latent heat of transformation respectively. If the external pressure or tension is replaced by p_0 , the change of transformation point due to the maximum pressure or tension accompanying the transformation can be calculated by

$$\delta T_{\max} = \frac{3}{8} K T \left(\frac{\Delta v}{v}\right)^2 / \rho \lambda,$$

while the same change caused by the mean pressure or tension is

$$\delta T_{\text{mean}} = 0.234 K T \left(\frac{\Delta v}{v}\right)^2 / \rho \lambda.$$

Thus it is seen that $\delta T_{\max}$ or δT_{mean} is a square function of $\Delta v/v$ and therefore independent of its sign. During heating λ is always positive and during cooling it is negative, and so the sign of $\delta T_{\max}$ or δT_{mean} depends solely on that of λ . It is, therefore, convenient to represent the expression of $\delta T_{\max}$ to be

$$\delta T_c = \frac{3}{8} K_c T \left(\frac{\Delta v}{v} \right)_c^2 / \rho_c \lambda \quad \text{and} \quad \delta T_r = -\frac{3}{8} K_r T \left(\frac{\Delta v}{v} \right)_r^2 / \rho_r \lambda.$$

Normally, the A_{c3} point is represented as the position at which the change on heating occurs most rapidly, while the A_{r3} point corresponds to the same position on cooling. It is difficult to define such a position physically. If the above theory is valid, the cause of irreversibility is due to the presence of a tension and a pressure, whose effects on the transformation temperature depends upon the proportion of α and γ -phase, as seen from the expression of transformation stresses. When the whole mass is just transformed, the effect of transformation stresses is a maximum. It seems reasonable to define positions, d and n in Fig. 1, representing these conditions to be A_{c3} and A_{r3} point respectively. In the same figure, s indicates the point at which the mean tension acts, while q indicates the position at which the mean pressure acts. These positions however, are close to the A_{c3} and A_{r3} points as usually defined whence it is convenient to take the horizontal distance between A_{c3} and A_{r3} points in usual sense.

The slope of a line bd can be determined immediately, if the position of d is found by means of the above calculation. The same is true for a line mn. Since the horizontal distance between bm and d or n increases with increasing tension or pressure respectively, then the width and the inclination of loop to the vertical coordinate are increased.

The above considerations can be applied to the case of A_4 transformation.

The shift in A_3 . To calculate the shift in A_3 for pure iron, the following values may be taken⁽²⁾:

$$\frac{\Delta v}{v} = 8.46 \times 10^{-3}, \quad \rho = 7.8 \text{ gr/cm}^3, \quad K = 0.667 \times 10^6 \text{ kg/cm}^2,$$

$$\lambda = 5.6 \times 4.2 \times 10^7 \text{ erg/gr}, \quad T = 900^\circ\text{C} = 1173^\circ \text{ abs.}$$

These values of $\Delta v/v$ and K give

$$\text{Max. stress: } p_0 = \frac{3}{8} K \frac{\Delta v}{v} = 2115 \text{ kg/cm}^2,$$

$$\text{Mean stress: } \bar{p} = 0.624 p_0 = 1320 \text{ kg/cm}^2.$$

For pure iron, the difference between A_{c3} and A_{r3} points is small, so that the following relation exist, that is,

$$K_c \doteq K_r = K, \left(\frac{Jv}{v}\right)_c \doteq \left(\frac{Jv}{v}\right)_r = \frac{Jv}{v}, \quad \rho_c \doteq \rho_r = \rho.$$

Hence, the elevation and the depression of A_3 point due to maximum stress are calculated to be

$$\delta T_c \doteq -\delta T_r = \frac{3}{8} K T \left(\frac{Jv}{v}\right)^2 / \rho \lambda = 11.1^\circ$$

or
$$\delta T = |\delta T_c| + |\delta T_r| = 22.2^\circ.$$

Thus the total shift of A_3 point during heating and cooling becomes 22.2°C (40°F). This is larger than the temperature difference between A_{c3} and A_{r3} points as usually defined, because in the present case, the maximum stress was taken for calculation.

If the elevation and the depression caused by the mean stress are taken, then

$$\delta T_c \doteq -\delta T_r = 0.234 K T \left(\frac{Jv}{v}\right)^2 / \rho \lambda = 6.9^\circ$$

or
$$\delta T = |\delta T_c| + |\delta T_r| = 13.8^\circ,$$

which agrees well with S. Satô's⁴⁾ observed temperature difference 20°C (36°F) between A_{c3} and A_{r3} points as usually defined. If the shape of specimen had been assumed spherical, we find²⁾ the total shift⁵⁾ of A_3 point due to the mean stress to be 22.0°C (40°F).

The shift in A_4 . Appropriate values of constants may be taken as follows⁶⁾:

$$\frac{Jv}{v} = 6.03 \times 10^{-3}, \quad \rho = 7.4 \text{ gr/cm}^3, \quad K = 3.33 \times 10^7 \text{ kg/cm}^2,$$

4) S. Satô: Sci. Rep., **14** (1925), 513.

5) According to experiments, the width of the loop or the temperature difference between A_{c3} and A_{r3} points depends on the heating and cooling velocities, decreasing with decreasing velocities. T. Satô has found the temperature differences for electrolytic iron to be 40°C with a heating or cooling rate of $20^\circ\text{C}/\text{minute}$, 20°C with a rate of $10^\circ\text{C}/\text{minute}$ and 8°C with a rate of $2^\circ\text{C}/\text{minute}$. T. Satô: Jour. Soc. Mech. Eng. Japan, **31** (1928), 915. The bulk modulus K_t at any moment can be expressed as follows:

$$K_t = K_\infty + (K_0 - K_\infty) e^{-\frac{t}{\tau}},$$

where K_0 and K_∞ are the initial value of K at $t = 0$ and the final value of K at $t = \infty$; τ means the time of relaxation. If heating or cooling is slow, the bulk modulus is smaller than K_0 . The transformation stress, therefore, depends on heating or cooling rate. Thus, the rigidity or the bulk modulus to be inserted in the formula for transformation stress should be taken for the same conditions as the dilatation experiment; since this is too difficult in actual cases, a slight disagreement between theory and experiment may be expected.

6) Landolt-Börnstein's Table, *Ergänzungsband 1* (1927), 15.

H. E. Cleaves and J. G. Thompson: *The Metal-Iron, Alloys of Iron* (Monographs published by McGraw Book Company, 1935), 149, 165, 273.

$$\lambda = 2.21 \times 4.2 \times 10^7 \text{ erg/gr, } T = 1400^\circ \text{C} = 1673^\circ \text{ abs.}$$

Thus the maximum stress and the mean stress become

$$\text{Max. stress: } p_0 = \frac{3}{8} K \frac{\Delta v}{v} = 754 \text{ kg/cm}^2,$$

$$\text{Mean stress: } \bar{p} = 0.624 p_0 = 470 \text{ kg/cm}^2.$$

Hence, the elevation and the depression of A_1 point due to the maximum stress can be calculated to be

$$\delta T_c \doteq -\delta T_r = \frac{3}{8} K T \left(\frac{\Delta v}{v} \right)^2 / \rho \lambda = 12.6^\circ$$

$$\text{or } \delta T = |\delta T_c| + |\delta T_r| = 25.2^\circ.$$

If the mean stress is taken, it follows that

$$\delta T_c \doteq -\delta T_r = 0.234 K T \left(\frac{\Delta v}{v} \right)^2 / \rho \lambda = 7.9^\circ$$

$$\text{or } \delta T = |\delta T_c| + |\delta T_r| = 15.8^\circ.$$

According to S. Satô⁴⁾, the temperature difference between A_{c4} and A_{r4} as usually defined is 20° which agrees well with the above theoretical value. If the shape of specimen is assumed spherical, the total shift in the A_1 point due to the mean stress is 21.0° which is very close to the above S. Satô's value.

Conclusion.

1. The irreversibility of A_3 and A_4 transformations of pure iron is caused by the presence of internal stress accompanying the transformation.

2. The elevation of A_3 point on heating and the depression of A_4 point on cooling are due to the tension engendered by the transformation.

3. The depression on A_3 point on cooling and the elevation of A_4 point on heating are due to the pressure set up by the transformation.

4. The width and the inclination of hysteresis loop to the vertical coordinate increase with increasing internal stress accompanying the transformation.

5. The A_{c3} , A_{c4} and A_{r3} , A_{r4} points may be defined as the positions at which the whole mass has just transformed under the transformation stress on heating and cooling respectively.

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