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6 PRINCIPLES OF PHASE TRANSFORMATIONS

Fourth Partial Report

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Watertown Arsenal Laboratory
Report Number WA 310/37-3
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PRINCIPLES OF PHASE TRANSFORMATIONS

Fourth Partial Report

OBJECT

To investigate the stability of the tetragonal structure of martensite.

SUMMARY

Two conflicting theories have been proposed in the literature to explain the mechanism whereby martensite loses its tetragonality. According to one theory the loss of tetragonality is due to the diffusion out of certain preferred interstitial positions to neighboring interstitial positions. The initial cubic ferrite has the same carbon concentration as the parent tetragonal martensite. According to the second theory, the loss in tetragonality is due to the gradual reduction in amount of carbon in solid solution through some sort of precipitation.

In this report the two mechanisms are critically examined. It is found that both mechanisms are operative. The tetragonality initially decreases, because of some sort of precipitation, until the carbon content in solid solution has been reduced to about 0.2 weight per cent. Thereafter the lattice changes to a cubic structure with the same carbon content (0.2%) as the prior slightly tetragonal martensite.

In this examination it was necessary to determine the stability of tetragonal vs. cubic lattice with super-saturated carbon. It was found that a critical temperature exists below which the stable structure is tetragonal, above which the cubic structure is stable. When the carbon content is 0.2 weight per cent, this critical temperature is about 0° C.

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INTRODUCTION

Freshly formed martensite has a tetragonal structure.¹ This tetragonality is gradually lost upon aging at room temperature, is rapidly lost upon heating to 100°C, the martensite acquiring a cubic structure.

Two mutually exclusive theories have been proposed to explain this loss of tetragonality. According to one theory, proposed by Honda and Nishiyama,² the loss of tetragonality is due to the transfer of the carbon atoms from their initial to neighboring interstitial positions within the same crystal. According to the second theory, proposed by Hagg³ and adopted by Cohen and his co-workers,⁴ the gradual reduction in tetragonality is a consequence of the gradual diminution of carbon in solid solution arising from some sort of precipitation. These two theories were examined in detail by the author in his Third Partial Report⁵ of this series. He analyzed the problem in terms of the two types of interstitial positions. All the interstitial positions have tetragonal symmetry. One third of these positions, the p type, have tetragonal axes* parallel to the lattice tetragonal axis. Two thirds of the positions, the n type, have tetragonal axes normal to the lattice tetragonal axis. When the "ferrite" lattice is first formed by a shearing process from austenite, all the carbon atoms are in only the p positions, since only these positions originate from interstitial positions in the austenite. The tetragonality of

*The tetragonal axis refers to the axis with a four-fold rotational symmetry.

the freshly formed "ferrite", or martensite, may therefore be regarded as arising from the initially preferred distribution of the carbon atoms. Since the first stage of tempering must consist of the migration of the carbon atoms to neighboring interstitial positions, the conclusion appeared to the author unavoidable that the first stage of tempering must be associated with a loss of the preferred carbon distribution, and hence with a loss in tetragonality.

In a current report⁶ the author shows that from the anelastic behavior of iron and steel one may deduce that the average time a carbon atom remains in one interstitial position before migrating to another is of the order of tenths of a second at room temperature. If the first theory above discussed were correct, the life-time of tetragonal martensite would therefore be less than one second at room temperature, in place of the observed life-time of the order of years.

It is possible that a resolution of the above dilemma may be that the potential energy of a carbon atom is less when it is in a p position than when in an n position. In such a case the carbon atoms would reside longer in the former type of interstitial positions than in the latter, thereby preserving a preferred distribution and therefore preserving the tetragonality of the lattice. This resolution can be correct if, and only if, the preferred distribution is thermodynamically stable. The purpose of

the present report is to examine the precise conditions under which the preferred distribution is stable.

ANALYSIS

In this section the conditions will be found under which a ferrite lattice with carbon dissolved interstitially will spontaneously acquire a tetragonal structure. The ferrite lattice will automatically acquire that structure which renders its free energy a minimum. The conditions are therefore to be found under which the free energy is less in the tetragonal than in the cubic structure, that is, less with a preferred than with a random distribution of carbon atoms. The free energy of a unit volume is

$$G = U - T S - e \sigma , \quad (1)$$

where U is the internal energy and S the entropy per unit volume, and e and σ are the tensile strain and stress, respectively. In the computation of the strain e , the reference configuration will be taken as that in which σ is zero and in which the distribution of carbon atoms is random. The condition that the free energy be a minimum may be expressed by the following equation

$$\delta G = 0 , \quad (2)$$

where the variation δ refers to any small change of internal parameters which leaves the stress σ unchanged. This variation will be taken as the transfer of a carbon atom from

an n to a p position. If N_n and N_p represent the number per unit volume of carbon atoms in these two types of positions, respectively, then the variation δ may be defined as

$$\delta N_p = 1, \delta N_n = -1 \quad . \quad (3)$$

The corresponding variation in energy U is given by

$$\delta U = u_p - u_n + \sigma \delta e \quad ,$$

where u_p and u_n refer to the energy of a carbon atom in a p and n position, respectively. The equilibrium Equation (2) therefore becomes

$$u_p - u_n = T \delta S \quad . \quad (4)$$

An estimation of the left hand member of Equation (4) may be made if it is assumed that it is a function of the tensile strain e irrespective as to how this strain is obtained, e.g. by a tensile stress or by a preferred distribution. We start with a random distribution and with no stress. The material is then subjected to such a tensile stress along a lattice principal axis as will produce the strain e , the distribution of carbon remaining random. The internal energy is thereby raised by the amount $(1/2) E_{100} e^2$. Next, keeping the strain constant, all the carbon atoms are moved to p positions. The change in internal energy associated therewith is $(2/3) N (u_p - u_n)$,

where N is the total number of carbon atoms per unit volume. The total change in energy is therefore

$$(1/2) E_{100} e^2 + (2/3) N (u_p - u_n) .$$

The final stress necessary to maintain the strain e will be zero if the derivative of this energy with respect to e is zero, i.e. when

$$E_{100} e + (2/3) N \delta(u_p - u_n)/\delta e = 0 .$$

Since, for small strains, $u_p - u_n$ may be taken as a linear function of the strain, this equation reduces to

$$u_p - u_n = - E_{100} \lambda e \quad (5)$$

where

$$\lambda = e/(2/3) N , N_p = N .$$

The quantity λ may be interpreted as the strain introduced by the transfer of one carbon atom per unit volume from an n to a p position. Equation (5) was derived for the case of complete order ($N_p = N$). Since $u_p - u_n$ is a linear function of e , it must be of general validity.

The right hand side of Equation (4), the change in entropy associated with the transfer of a carbon atom from an n to a p position, may be shown by the standard methods of statistical mechanics to be given by the equation

$$\delta S = -k \ln (2 N_p/N_n) .$$

It will be found more suitable to express the entropy change in terms of a parameter which changes from zero, in the case of random distribution, to unity, in the case where all carbon atoms are in p positions. Such a parameter is given by

$$z = (3/2) (N_p/N - 1/3) .$$

In terms of this order parameter

$$\delta S = -k \ln \left(\frac{1 + 2z}{1 - z} \right) . \quad (6)$$

Upon combining Equations (4) - (6) one obtains

$$E_{100} \lambda e = k T \ln \left(\frac{1 + 2z}{1 - z} \right) . \quad (7)$$

A. Case of Zero Tensile Stress.

When no tensile stress is present the strain is proportional to the order parameter,

$$e = (2/3) N \lambda z . \quad (8)$$

In this case the order parameter itself may be interpreted as the ratio of the actual tetragonality over the maximum tetragonality, which occurs in the case of complete order. Substitution of Equation (8) into Equation (7) leads to

$$(2E_{100} N \lambda^2 / 3 k T) z = \ln \frac{1 + 2z}{1 - z} . \quad (9)$$

The qualitative nature of this solution may be obtained from

an examination of the graph of the right hand side of this equation, presented as Figure 1. The abscissa of the intercept of this curve with the straight line $(2 N E_{100} \lambda^2 / 3 kT) \cdot z$ gives the value of the order parameter z at the temperature T . When T is above a certain critical value, T_c , the only intercept is at $z = 0$, corresponding to a random distribution of the carbon atom in the p and n positions. At this critical temperature the straight line is tangent to the curve at $z = 0.33$. Therefore, as the temperature is slowly lowered, the order parameter z suddenly changes from 0 to 0.33 when the critical temperature is reached. The gradual increase of z as the temperature is further lowered is shown in Figure 2, obtained by graphically solving Equation (9).

At the critical temperature the product $z^{-1} \ln \left\{ (1 + 2z) / (1 - z) \right\}$ may be computed as 2.75. Therefore the critical temperature is given by

$$T_c = 0.243 N E_{100} \lambda^2 / k \quad (9)$$

In order that T_c may be expressed in terms of the weight per cent of carbon, X_c , the following substitutions are made:

$$N = 3.92 \times 10^{21} X_c$$

$$E_{100} = 1.3 \times 10^{12} \text{ dyne/cm}^2$$

$$\lambda = 1.2 \times 10^{-23}$$

$$k = 1.39 \times 10^{-16} .$$

One obtains

$$T_c = 1,330 X_c \text{ } ^\circ\text{K} .$$

This equation is given graphically in Figure 3.

B. Case of Non-Vanishing Stress.

A tensile stress parallel to a lattice principal axis will lower the potential energy of carbon atoms in p positions with respect to n positions, and will therefore result in a preferred distribution of carbon atoms at all temperatures. The presence of microscopic residual stresses will therefore result in a smoothing out of the abrupt transition shown in Figure 2. The analysis of the preferred distribution in the presence of a tensile stress may be carried out by a slight modification of the analysis of the preceding section. Equation (8) must be replaced by the equation

$$e = (2/3) N \lambda z + E_{100}^{-1} \sigma ,$$

and therefore Equation (9) by

$$(2E_{100} N \lambda^2 / 3 k T) z + \sigma \lambda / k T = \ln \left(\frac{1 + 2z}{1 - z} \right) .$$

This equation has been solved graphically for several values

of the ratio σ/σ_m , where σ_m is the tensile stress which would have to be applied to produce the same strain as that produced by a transition of the order parameter from zero to unity. Thus

$$\sigma_m = E_{100} (2N/3) \lambda .$$

The solutions are presented as Figure 4.

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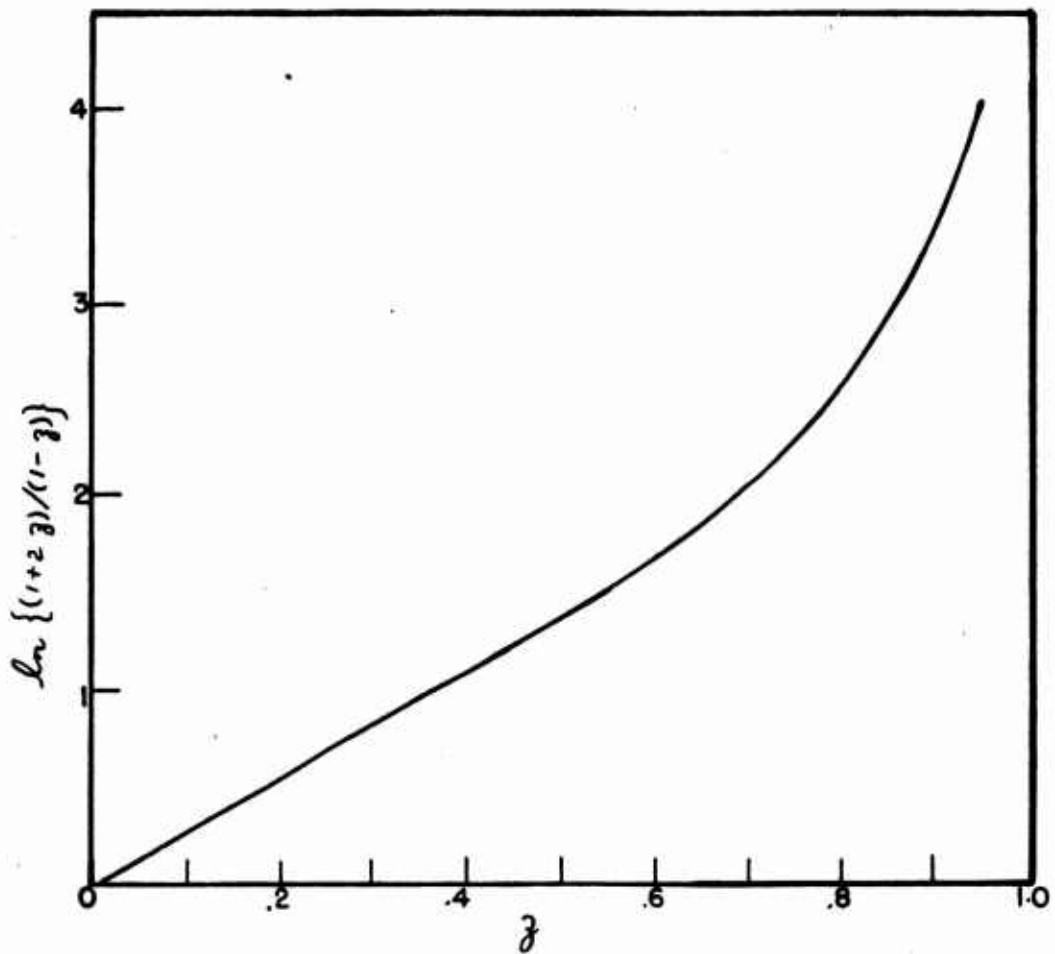


FIGURE 1

GRAPH FOR SOLUTION OF EQUATION 9

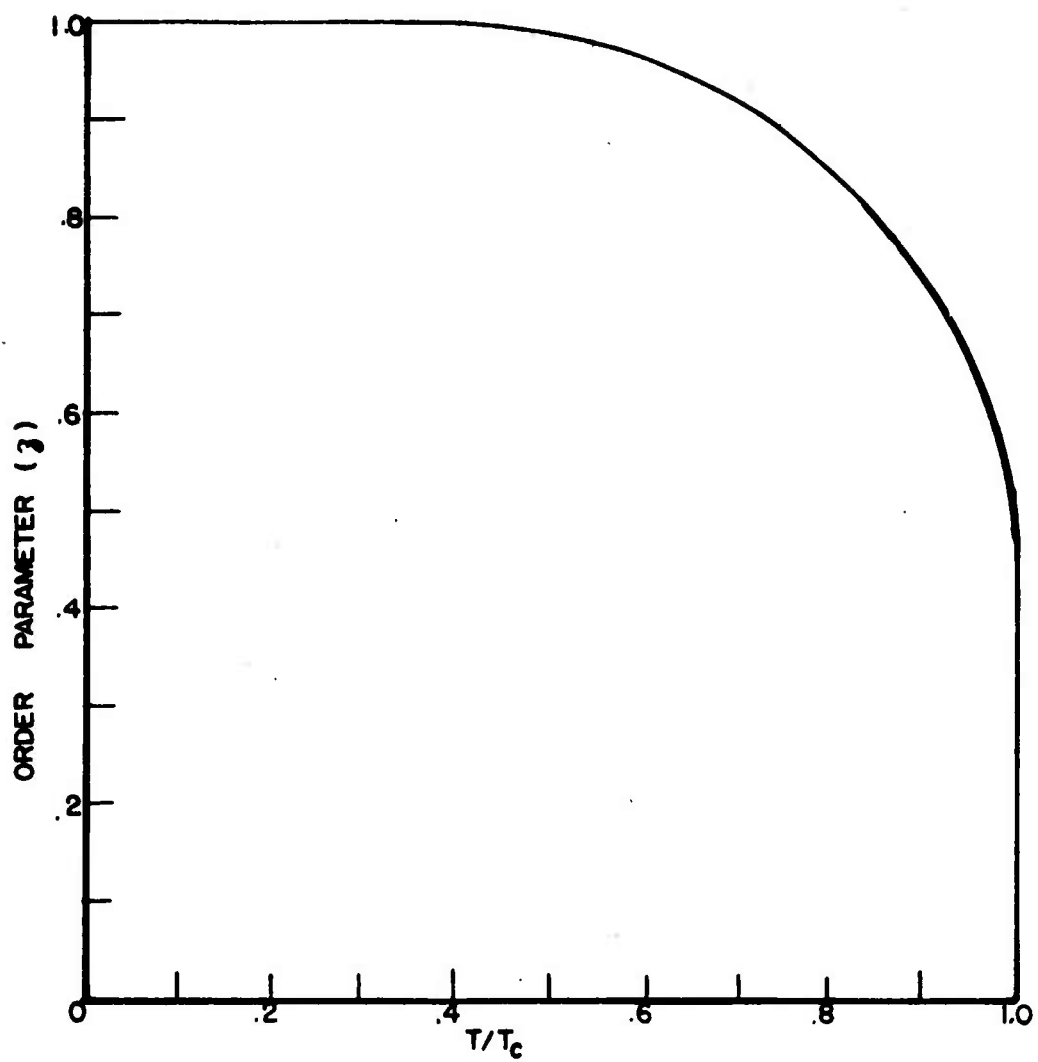


FIGURE 2

DEPENDENCE OF PREFERENTIAL DISTRIBUTION
UPON TEMPERATURE, CASE OF ZERO STRESS

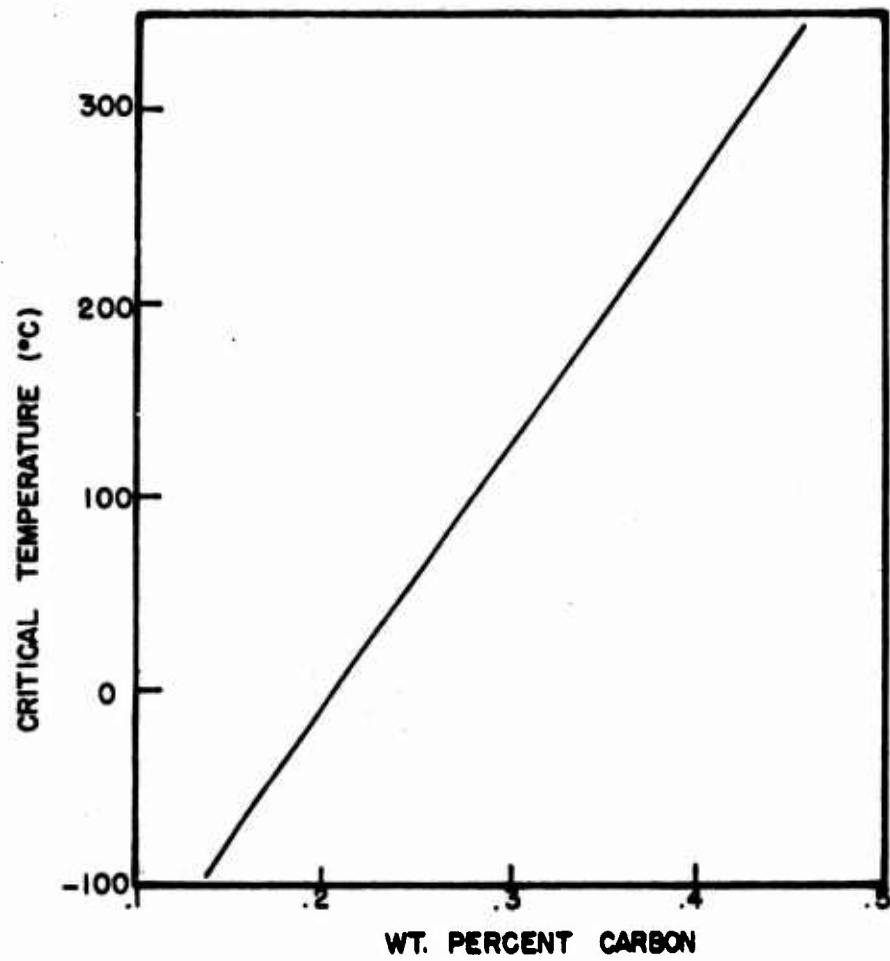


FIGURE 3

CRITICAL TEMPERATURE

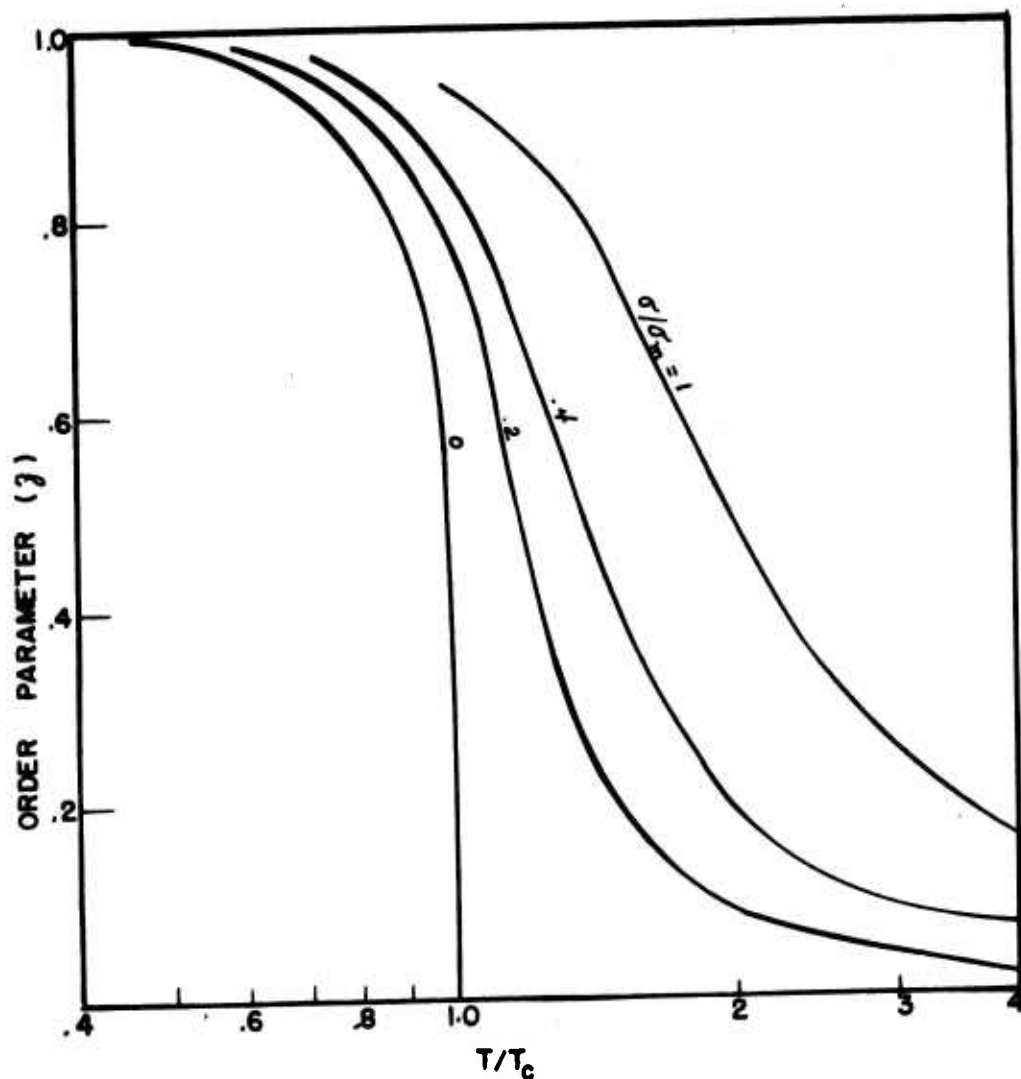


FIGURE 4

DEPENDENCE OF PREFERENTIAL DISTRIBUTION
UPON TEMPERATURE, CASE OF NON-ZERO STRESS