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Isothermal Martensitic Transformation as an Internal-Stress-Increasing Process

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Abstract. Based on the results that the magnitude of the stabilization of retained austenite increases with increasing the amount of martensite transformed, it has been assumed that the martensitic transformation is accompanied with an increase in internal resisting stress which subsequently results in the stabilization of retained austenite. By simplifying this internal resisting stress to be a type of hydrostatic compressive stress acting on retained austenite due to surrounding martensite plates, a thermodynamical analysis for an isothermal martensitic transformation under applied hydrostatic pressure has been performed. The calculated results, to some extent, show a good agreement with the experimental data.

1. INTRODUCTION

Experimental observations often show that an athermal martensitic transformation can proceed with either lowering temperature or releasing externally applied hydrostatic pressure at low holding temperatures. The continuous transformation of austenite into martensite suggests that austenite has not transformed into martensite completely at M_s temperature. Rather, the retained austenite is stabilized after partial martensitic transformation, and a higher chemical driving force is needed for a further transformation to occur [1–4]. X-ray diffraction results [5, 6] have shown that, in Fe-Ni-C and Fe-Mn-C alloys, during martensitic transformation the lattice parameter of austenite decreases drastically. If eliminating the temperature effect, the austenite lattice parameter decreases with increasing the amount of martensite curvilinearly, and meanwhile the austenite diffraction peak widens. This effect has been attributed to an overall compressive stress acting on the austenite phase due to formation of martensite. However, the reason of this phenomenon has not been carefully studied and thoroughly understood. So far, there is neither systematic research performed concerning this inhibition effect nor theoretical analysis made concerning the amount of martensite formed as a function of externally varying parameters, *e.g.* temperature, pressure, *etc.*, while taking into account the internally induced resisting stresses.

In the present study, a preliminary attempt has been made to examine the isothermal martensitic transformation behaviour under applied hydrostatic pressure from a thermodynamical point of view by simplifying the internal resisting stress to be a type of hydrostatic compressive stress. Since only experimental data for Fe-21.5Ni-0.95C single crystal specimens are available, we will perform the calculations for this alloy. The calculated amounts of martensite as a function of applied hydrostatic pressure at constant temperatures will be compared with the experimental results.

2. EXPERIMENTAL

The experimental procedure was to 1) raise the hydrostatic pressure surrounding the specimen to 1.5 GPa at room temperature, 2) lower the temperature to an isothermal holding temperature under constant pressure, 3) release the hydrostatic pressure to 0 GPa isothermally, and 4) warm up the whole system to room temperature. Several isothermal holding temperatures were chosen. Alloy Fe-21.5Ni-0.95C (wt.%) was used for the study. The martensitic transformation behaviour of this alloy was recorded in-situ by measuring its magnetic susceptibility during the whole experiment as shown in Ref. [7]. The amount of martensite transformed during the experiment was determined with an optical image analyser. The detailed experimental procedures and the heat treatments of the specimens are presented in [7].

3. RESULTS AND DISCUSSIONS

The effect of applied hydrostatic pressure on the martensitic transformation starting temperature has been studied by several researchers [7–9]. The results have shown that the applied hydrostatic pressure tends to inhibit the martensitic transformation, *i.e.*, lowers the M_s temperature of the specimen. Figure 1 displays the typical results of martensitic transformation during releasing the hydrostatic pressure at three different isothermal holding temperatures [7]. It can be seen that the martensitic transformation starting temperature was influenced by a combined effect of both applied hydrostatic pressure and undercooling. At lower holding temperatures, *i.e.* higher undercooling, the martensitic transformation started at a higher pressure and proceeded continuously while releasing the pressure.

The aim of this study is to thermodynamically describe the transformation process shown in Fig. 1 via proposing a plausible mechanism for the stabilization of retained austenite. As has been proposed earlier [3, 4] that the stabilization of retained austenite during martensitic transformation process is due to the internal compressive stress acting on retained austenite phase due to surrounding martensite plates. If we simplify the internal stress to be a type of internal hydrostatic compressive stress and assume that the inhibition effects of the martensitic transformation due to both the internal resisting stress and the hydrostatic pressure are additive, then the martensitic transformation behaviour of an alloy under applied hydrostatic pressure can be analysed as follows.

Figure 1: Volume fraction of martensite as a function of externally applied hydrostatic pressure at different isothermal holding temperatures for single crystal specimens of an Fe–21.5Ni–0.95C alloy.

In the general case, according to the thermodynamics of martensitic transformation [10, 11], the critical condition for an athermal martensitic transformation to occur is determined by a free energy balance between martensite and austenite phases at M_s temperature. At M_s temperature, the chemical driving force for martensitic transformation, *i.e.*, the Gibbs chemical free energy change (cal/mol) accompanying the austenite-to-martensite transformation, $\Delta G_c^{\gamma \rightarrow \alpha'}$, is balanced by the non-chemical free energy change accompanied with the transformation, $\Delta G_{nc}^{\gamma \rightarrow \alpha'}$, consisting of the elastic strain energy, the austenite/martensite interfacial energy, and energies associated with the formation of other types of defects during transformation. This energy balance can be expressed as follows:

$$\left(\Delta G_c^{\gamma \rightarrow \alpha'} + \Delta G_{nc}^{\gamma \rightarrow \alpha'} \right) \Big|_{T=M_s} = 0 \quad (1)$$

However, under the applied stresses, the free energy balance is modified by a mechanical work term, U , either positively or negatively depending on the direction and mode of the stress, which in turn results in the shift of the transformation temperature from M_s to M_s' as schematically shown in Fig. 2. In the presence of the hydrostatic compressive stress, p , the transformation free energy balance is modified by a mechanical work, $p \epsilon_0 V_m$, as proposed by the earlier researchers [8, 12]. Here ϵ_0 is the volume change associated with the transformation of a unit volume of austenite to martensite and V_m is the molar volume of martensite phase. Hence, the M_s temperature is lowered to M_s' as follows:

$$(\Delta G_c^{\gamma \rightarrow \alpha'} + \Delta G_{nc}^{\gamma \rightarrow \alpha'} + p \epsilon_0 V_m) \Big|_{T=M_s'} = 0 \quad (2)$$

Figure 2: Schematic diagram showing the chemical free energy of austenite and martensite phases as a function of temperature, and the effects of applied mechanical work on the martensitic transformation starting temperature.

If considering that the non-chemical free energy change is about the same per molar volume of martensite phase transformed at both M_s and M_s' for the same alloy, the complex term of non-chemical free energy change can then be avoided in the calculation by combining Eq. (1) and Eq. (2) as follows:

$$\Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{T=M_s', P} - \Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{T=M_s, 0} + p \epsilon_0 V_m = 0 \quad (3)$$

The terms of Gibbs chemical free energy change accompanying the transformation in Eq. (3) can be calculated according to Kaufman and Hillert [13]:

$$\Delta G_c^{\gamma \rightarrow \alpha'} = \sum_i x_i (G_i^{bcc} - G_i^{fcc}) + (EG^{bcc} - EG^{fcc}) + \Delta G_c^{\alpha \rightarrow \alpha'} \quad (4)$$

where x_i is the atomic fraction of element i , G_i^{bcc} and G_i^{fcc} are the Gibbs free energies of bcc and fcc phases of pure element i , respectively. EG^{bcc} and EG^{fcc} are the excess Gibbs free energies of mixing of bcc and fcc phases, respectively, and they can be calculated according to the Redlich-Kister equation [13]. $\Delta G_c^{\alpha \rightarrow \alpha'}$ is the Gibbs chemical free energy difference between the bct martensite (α') and the bcc ferrite (α) and it can be calculated according to Fisher [14] and Kaufman *et al.* [15]:

$$\Delta G_c^{\alpha \rightarrow \alpha'} = -50000 \frac{x_C^2 Z^2}{1 - x_C} + 0.7 x_C T \phi(Z) \quad (\text{cal/mol}) \quad (5)$$

where x_C is the atomic fraction of carbon, Z is the Zener's order parameter which is a function of the ratio between temperature T and the ordering temperature T_C , $\phi(Z)$ is a numerical function of the order parameter Z , and T_C is related to the carbon content by $T_C = 28000 x_C (1 - x_C)$. In the present calculation, Z and $\phi(Z)$ were taken as their maximum values tabulated by Fisher [14]: $Z = 1$ and $\phi(Z) = 3.295$. Under applied hydrostatic pressure, and taking into consideration the internally induced resisting stress, σ_i , due to partial martensitic transformation, Eq. (3) can also be written as follows:

$$\Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{T, P} - \Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{M_s, 0} + (p + \sigma_i) \epsilon_0 V_m = 0 \quad (6)$$

From Kaufman data bank, the chemical driving force for martensitic transformation of Fe-21.5Ni-0.95C alloy can be calculated as shown in Fig. 3, and the least-square fitting of the data gives:

$$\Delta G_c^{\gamma \rightarrow \alpha'} = -417.05 - 9.8775 \times 10^{-2} T - 9.1823 \times 10^{-4} T^2 + 2.137 \times 10^{-5} T^3 - 3.7175 \times 10^{-8} T^4 \quad (\text{cal/mol}) \quad (7)$$

(0 < T < 300 K)

If assuming that the internal resisting stress acting on the retained austenite phase by the surrounding

martensite plates can be simplified as a hydrostatic compressive stress, the relationship between internal resisting stress, σ_i , and the volume fraction of martensite formed in the specimen, $f(T)$, can then be obtained by comparing the experimental results shown in Refs. [4] and [7], in which the magnitudes of the stabilization of retained austenite due to applied hydrostatic pressure [7] and the amount of prior formed martensite [4] are obtained experimentally. By using the approximate values of $\epsilon_0 = 0.0298$ and $V_m = 7.11 \text{ cm}^3/\text{mol}$ [7], the relationship between the hydrostatic compressive stress, p , and the change in the martensitic transformation starting temperature, ΔM_s , can be calculated as demonstrated in Refs [3, 4]. Comparing this result with the experimental results of ΔM_s as a function of $f(T)$, the relationship between the internal resisting stress, σ_i , and the volume fraction of martensite, $f(T)$, can be established. In the case of Fe-20Ni-0.73C alloy, the least-square fitting of the experimental data by using a quadratic relationship between the internal resisting stress, σ_i , and the volume fraction of martensite, $f(T)$, gives:

$$\sigma_i = 0.1011f(T) + 2.4727 f(T)^2 \quad (\text{GPa}) \quad (8)$$

The coefficients in the above formula vary with varying magnitude of ϵ_0 and V_m . Since the lattice parameters are function of temperature, ϵ_0 and V_m are thus also function of temperature. By means of X-ray diffraction measurement, the lattice parameters of martensite and austenite phases in Fe-20Ni-0.73C alloy as a function of temperature between 10 K and 300 K can be obtained [16]. By using the X-ray diffraction results, a more precise formula can be obtained as follows:

$$\sigma_i = 0.39172 f(T) + 1.3278 f(T)^2 \quad (\text{GPa}) \quad (9)$$

Figure 3: Chemical free energy change associated with martensitic transformation in an Fe-21.5Ni-0.95C alloy.

Since an exact formula for the Fe-21.5Ni-0.95C alloy has not been obtained yet, we may try to use Eq. (9) obtained for a similar alloy, *i.e.*, Fe-20Ni-0.73C, for an approximate calculation. Combining Eqs (6) and (9), we obtain:

$$f(T, P)^2 + 0.295 f(T, P) + p/1.3278 + A (1.3278 \times 0.239 \times 10^9 \times \epsilon_0 V_m)^{-1} = 0 \quad (10)$$

$$A = \left(\Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{T, P} - \Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{M_s, 0} \right)$$

where p is the applied hydrostatic pressure. For an isothermal experimental mode, both $\Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{T, P}$ and $\Delta G_c^{\gamma \rightarrow \alpha'} \Big|_{M_s, 0}$ are constants. Solving above equation one obtains the amount of martensite as a function of applied hydrostatic pressure:

$$f(T, P) = 0.5 \times \left\{ -0.295 - \left[(0.295^2 - 4/1.3278 \left(p_i + A (0.239 \times 10^9 \times \epsilon_0 V_m)^{-1} \right))^{1/2} \right] \right\} \quad (11)$$

At a constant temperature, the term A in Eq. (10) is mostly determined by the value of the chemical driving force at M_s temperature under externally applied pressure. The values of ϵ_0 and V_m for the Fe-21.5Ni-0.95C alloy at the testing temperatures are presented in Ref. [7]. In the present study, it was found that the M_s temperature of the single crystal specimens varies from 196 to 209 K, which may be due

to segregation of alloying elements. If taking $M_s = 205$ K for the calculation using Eq. (11), the results can be plotted as in Fig. 4 compared with the experimental data. From Fig. 4 it can be seen that the calculated result for the isothermal holding temperature of 96 K fits well with the experimental data. However, for the other two experimental temperatures, the calculated results show both lower transformation temperatures and lower amounts of transformed martensite.

Figure 4: Comparison of the experimental and calculated results of the amount of transformed martensite while releasing the applied hydrostatic pressure at three isothermal holding temperatures shown.

Figure 5: Calculated amount of martensite as a function of isothermal holding temperature under several applied hydrostatic pressures indicated.

It needs to be kept in mind that, although the calculated results show a better correlation to the experimental data for the 96 K isothermal holding temperature, several uncertain factors are involved in the calculation. One is the form of the relationship between the magnitude of the internal resisting stress and the amount of martensite which was that of the alloy Fe-20Ni-0.73C and which may be different for the present Fe-21.5Ni-0.95C alloy. It was found that the coefficients of the formula affect the calculated amount of martensite. Another factor is that the M_s temperature of 205 K was used for the calculation, which is within the range of the experimentally determined data. However, variation of M_s temperature will affect the value of A and in turn changes the transformation starting temperature of the calculated results. The third factor is that there may be inaccuracies in the calculation of chemical free energies due to neglecting the contributions from the other alloying elements than Fe, Ni and C. In the case of the other two calculated results, the poor correlation with the experimental data may also come from the inaccurate determination of the experimental parameters in addition to the above mentioned three factors. The variation of the temperature during the experiments may be a major factor against obtaining an ideal experimental result.

If plotting the calculated amounts of martensite as a function of isothermal holding temperature for several chosen values of applied hydrostatic pressure in Fig. 5, one can find that under the same pressure the amount of martensite increases with lowering the isothermal holding temperature. This agrees qualitatively with the experimental results shown in Fig. 1, and is analogous to the results in an athermal transformation mode [4].

In the calculations, several assumptions were made, *i.e.*, 1) the internal resisting stress acting on retained austenite was simplified as a hydrostatic compressive stress in order to simplify the term of mechanical work for the calculation; 2) the relationship between the amount of martensite and the internal resisting stress was assumed to obey a quadratic relationship. However, at very low temperature range this relationship may need to be slightly modified, when the rate of the stabilization of retained austenite slows down.

4. SUMMARY AND CONCLUSIONS

The isothermal martensitic transformation under applied hydrostatic pressure can be simulated thermodynamically by taking into account the influencing factors on the stabilization of retained austenite. One of the most predominant factors considered here is the internal resisting stress induced by the formation of martensite plates, which is acting on the retained austenite phase and inhibits its further transformation. The mode of the internal resisting stress may be complex. However, based on the X-ray diffraction results [5,6], this stress might be mainly a compressive stress since the austenite lattice parameter decreases with increasing the amount of martensite, although the literature data might not be feasible to be used quantitatively due to an unideal experimental procedure. The broadening of the austenite diffraction peaks suggests that the real internal stress may not be simple. If assuming that the internal stress can be simplified to be a type of hydrostatic compressive stress, the martensitic transformation process can somehow be simulated based on thermodynamical principles. Comparing the calculated results with the experimental data, one can conclude that the calculated results, to some extent, fit well with the experimental data. The difference between the calculated results and the experimental data may be due to several factors, *e.g.*, 1) the internal resisting stress might not be a simple one; 2) the inaccuracy in thermodynamical treatment and the simplification in the calculation; 3) the formula for the relationship between the magnitude of internal stress and the amount of martensite needs to be determined more accurately with ideal experimental methods and procedures. 4) The small variations of temperature during the present experiments may have affected for obtaining ideal experimental results.

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