

Lattice changes in the martensitic phase due to ageing in 18 wt% nickel maraging steel grade 350

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Changes in the lattice parameter of martensite phase in a maraging steel is measured as a function of ageing temperatures. A decrease in the lattice parameter is observed when aged between 400–650°C which is attributed to the depletion of alloying elements in the martensite matrix as a consequence of precipitation and austenite formation. An increase in the lattice from 650 to 710 °C was characteristic of enrichment of alloying elements in the martensite matrix due to dissolution of austenite phase. A minimum value of the lattice parameter of martensite is observed at 650 °C which coincides with the maximum vol % of retained austenite. Electrical resistivity, hardness measurements, and *in situ* high temperature dilatometry was also carried out to delineate various precipitation reactions that occur in this steel.

1. Introduction

Maraging steels contain a very low percentage of carbon but exhibit ultra high strength combined with good fracture toughness. These steels consist of both, a 100% b.c.c. soft martensite phase in solution annealed condition, and a dual phase microstructure i.e. austenite and martensite which can coexist at room temperature if aged at a certain temperature range [1]. The strengthening effect in these steels is achieved by the precipitation of substitutional elements such as Ni, Ti, and Mo, which occurs during the ageing process. The precipitates which are responsible for their exceptionally high strength have been identified as Ni₃Mo [2], Ni₃Ti [3], Fe₂Mo [4], and FeTi [5]. During the precipitation process, the solute solubility of precipitate forming elements in the matrix decreases with the increase in the volume fraction of the precipitates according to the Gibbs–Thompson effect. As a consequence, changes in the lattice parameter of the matrix may result. Similarly, in the dual phase microstructure, a variation in the lattice parameters of martensite matrix may be expected with increasing volume % of austenite phase.

It is well known that electrical and magnetic properties of metals and alloys depend on the arrangement of atoms in the unit cell and any change in the lattice parameter may influence the electrical and magnetic properties of materials, such as in maraging steels where these properties are of prime importance in certain applications [6]. As far as the present authors are concerned, no published data are available on the changes in the lattice parameters of the martensite phase in maraging steel grade 350 during ageing, which is the subject of the present investigation. This paper reports the lattice parameter

changes in the martensite phase in 18% Ni maraging steel grade 350 as a result of ageing process. The observed changes in the lattice parameter of martensite phase are explained on the basis of various precipitation reactions and varying amounts of volume % austenite that forms in this steel. Various phase transformations that occur at high temperatures are also monitored by *in situ* dilatometry and are discussed in the light of observed changes in the electrical resistivity and hardness values measured over a wide range of ageing temperatures.

2. Materials and methods

The material used in this investigation is 18% Ni maraging steel whose composition is given in Table I.

The as received material was in the form of extruded bar from which samples measuring 20 × 15 × 5 mm³ were sectioned for various heat treatments. Samples were solution annealed at 820 °C in a vacuum furnace before any ageing treatment was given. Ageing at various temperatures was also carried out in a vacuum furnace keeping a constant heating and cooling rate of the order of 25 °C min⁻¹ and 45 °C min⁻¹ respectively. Cooling from ageing temperature to the room temperature was carried out in an inert gas atmosphere. Samples for X-ray analysis were prepared by grinding successively on 600 and 1200 grit SiC emery papers, followed by chemical polishing to remove approximately 20 μm of surface layer. Quantitative analysis of constituent phases was carried out by X-ray diffractometry [7] using CoKα radiation. All the possible diffraction lines were step-scanned with an interval of 0.02 degrees in 2θ,

TABLE I Chemical composition of 18% maraging steel grade 350

Ni	Co	Mo	Ti	C	S	Al	Fe
18.14	12.5	3.96	1.65	0.02	0.01	0.1	Balance

and the peak positions were determined by processing the numerical data using a computer program [8]. The lattice parameter of martensite phase was calculated from three peaks i.e. (1 1 0), (2 0 0), and (2 1 1), the accuracy of which was found of the order of $\pm 4 \times 10^{-5}$ nm.

For dilatometry experiments, cylindrical specimens of 6 ± 0.01 mm diameter and 50 ± 0.01 mm length were made from the extruded bar. A high temperature dilatometer was used with a resistive furnace supported by quartz rods enclosed in a test chamber. A vacuum of 1.333×10^{-1} Pa was kept in the furnace to avoid any oxidation of the sample. The length change of the sample was monitored by a transducer. Further details of the experimental set up is given elsewhere [9].

Specific electrical resistivity (later on termed as electrical resistivity) was measured at room temperature by standard a four probe method [10] using samples measuring $25 \times 2.5 \times 0.1$ mm. Hardness was measured on Vickers hardness scale using a 30 kg load.

3. Results

Fig. 1 depicts the changes in the lattice parameters of martensite, and the volume percent of austenite phase that forms as a function of ageing temperatures.

Martensite phase exhibits a sharp reduction in the lattice parameter values from 400 to 460 °C which is attributed to the formation of A_3B types of precipitates. The lattice parameter values continue to decrease from 460 to 650 °C with increase in ageing temperatures. The inflection points observed on the lattice parameter curve are marked with the corresponding temperatures (Fig. 1). These inflection points are mainly due to change in the precipitate types, or the increasing amounts of austenite phase that is formed at higher ageing temperatures. A small quantity of austenite (<2 vol %) is observed between 530–570 °C which could not be assessed quantitatively, and hence is presented with the dotted line in Fig. 1. A minimum value of the lattice parameter is observed at 650 °C which corresponds to the maximum volume % austenite that is formed at this ageing temperature. This minimum value of the lattice parameter is probably due to the maximum depletion of the solute elements in the martensite matrix. With further increase in ageing temperature from 650 °C, an increase in the lattice parameter of martensite phase is observed with the corresponding decrease in the volume % of austenite phase. Such an increase may be related with the enrichment of the solute elements in the martensite matrix as a result of dissolution of austenite phase.

The relative change in length observed during the high temperature dilatometry experiment is plotted in

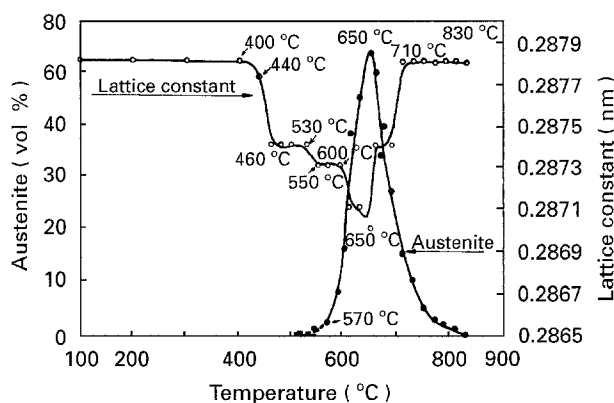


Figure 1 Variation in the lattice parameters of martensite phase and the amount of austenite phase that forms as a function of ageing temperatures.

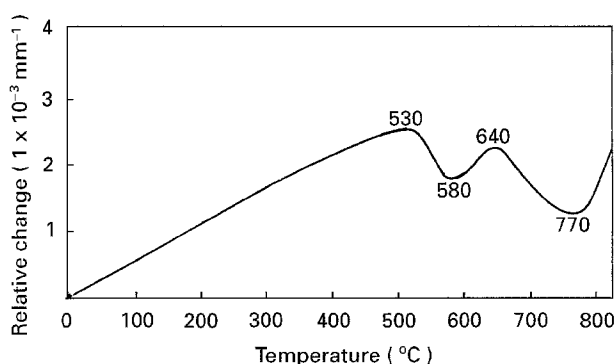


Figure 2 Relative changes in length observed during *in-situ* high temperature dilatometry.

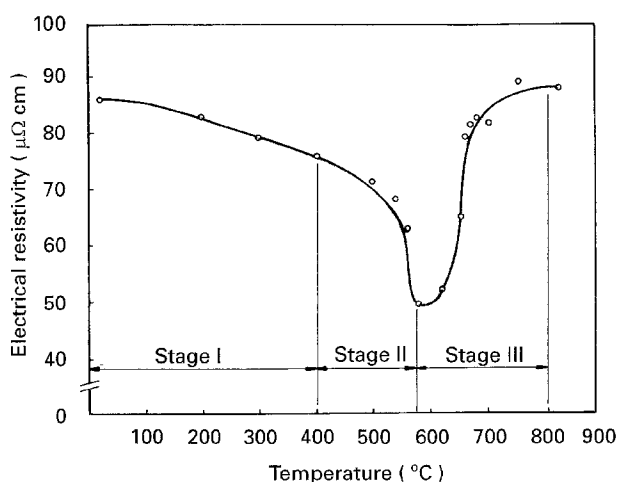


Figure 3 Changes in the electrical resistivity as a function of ageing temperature.

Fig. 2. The onset of contraction at 530 °C is taken as austenite start temperature. A dilation hump observed between 580–640 °C may be speculated as a result of the change of A_3B types of precipitates to A_2B types. The austenite finish temperature was taken at 770 °C, which corresponds to the temperature where the dilation curve resumes linearity.

The changes in the electrical resistivity as a function of ageing temperatures are shown in Fig. 3.

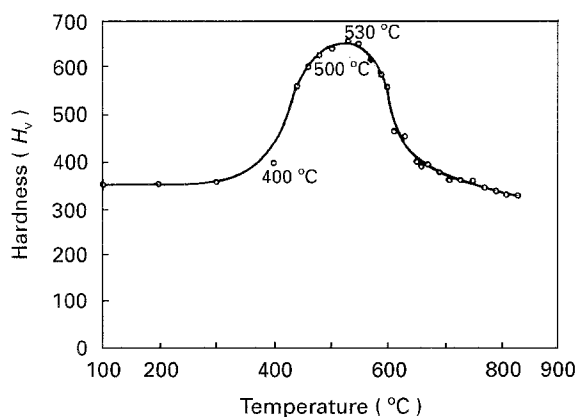


Figure 4 Hardness variation as a function of ageing temperatures.

The resistivity curve can be divided into three stages: (I) A small initial decrease up to 400 °C which may be due to the accumulation of solute elements such as Ni, Ti, and Mo from the solid solution. (II) A sharp decrease from 400 °C until a minimum is reached around 570 °C which may be associated with the formation and coarsening of hardening precipitates. (III) Finally an increase from 570 °C until it levels off around 800 °C which may be directly related to the amount of austenite phase that is formed between these ageing temperatures.

The hardness curve plotted in Fig. 4 as a function of ageing temperatures exhibits an initial slow increase of the hardness values up to 400 °C which may be attributed to the accumulation of solute elements, while the rapid increase from 400 to 500 °C is the result of the formation of hardening precipitates. The decrease in hardness from 530 °C may be attributed to the dissolution of hardening precipitates.

4. Discussion

The variation in the lattice parameter of martensite phase can be best interpreted in view of a variety of precipitation reactions that these steels undergo at different ageing temperatures. Numerous studies have been conducted to study the precipitation reactions in these steels [11–13], however, there exists a considerable difference of opinion about the nature of precipitates that are formed during the ageing process. This discrepancy stems from the close similarity in the structure and d-spacing of these precipitates, which are further aggravated due to the complexity of the alloy system. As a consequence, several different types and often more than one kind of precipitate have been reported [2–5]. However, a general consensus on the precipitation sequence can be drawn on the basis of reported literature which forms the basis of interpretation of changes in the lattice parameter of martensite phase observed in this study.

When aged in the temperature range between 400–500 °C, Ni₃Ti and Ni₃Mo precipitates are formed in the martensite matrix [11, 12]. Higher ageing temperatures or longer ageing times leads to a gradual increase in coherency stresses and Ni₃Mo and Ni₃Ti

are replaced by more stable Mo-containing precipitates, such as Fe₂Mo or FeMo [14]. As a consequence of the formation of precipitates, the single phase b.c.c. martensite matrix becomes depleted in the precipitate forming elements such as Ni, Ti, and Mo which results in the decrease of the lattice parameter of the martensitic matrix. Cheng *et al.* [15] have found a similar decrease in the lattice parameter of the iron matrix due to the depletion of the nitrogen atoms in an iron–nitrogen martensite.

Changes in the lattice parameter of martensite phase in Fig. 1 is indicative of the fact that more than one precipitation process is taking place if the variation of lattice parameter changes are related to the precipitation process alone. Peters and Cupp [16] on the basis of electrical resistivity measurements have observed that the ageing process in these steels occurs in three stages, during which partitioning of alloying elements between martensite and austenite phase is expected [17]. The decrease in lattice parameter observed between 400 to 460 °C may be attributed to the depletion of alloying elements in the martensite phase as a consequence of formation of A₃B type precipitates. These precipitates are of hexagonal closepacked (HCP) structure and are favoured because of the good lattice fit with the b.c.c. martensite [12]. Increase in hardness values from 400 °C (Fig. 4) provides further evidence of the formation of hardening precipitates.

The lattice parameter of martensite shows a small contraction dip at 530 °C (Fig. 1) which is probably due to the onset of austenite formation. X-ray analysis for phase determination reveals the presence of austenite phase at 530 °C, however, due to very small quantity (less than 2%), a quantitative measurement could not be carried out. Martensite lattice parameter continues to decrease with gradual increase in the volume % austenite until a minimum is reached at 650 °C which corresponds to the maximum austenite which is stable at room temperature. The reduction of lattice parameter can be seen due to considerable depletion of alloying elements from the martensite phase as a result of precipitate and austenite formation [17]. The lattice parameter of martensite exhibits an increase with decrease in vol % austenite when aged between 650 to 710 °C (Fig. 1). This increase can be attributed to the dissolution of austenite [1] resulting in the enrichment of alloying elements in the martensite phase. The lattice parameter values of martensite tapers off around 710 °C where vol % austenite is also observed subsiding (Fig. 1).

High temperature *in situ* X-ray measurements give confirmatory evidence that the onset of austenite formation in this steel occurs at 525 °C [18]. High temperature *in situ* dilatometric study (Fig. 2) conducted in this investigation exhibits a contraction of the sample at 530 °C which is clearly due to the onset of austenite formation, in contrast to the published work [19], in which dilatometric contraction around 530 °C was regarded as characteristic of the change in the type of precipitates rather than the onset of austenite formation.

A small dilation hump which is observed in Fig. 2 between 580–640 °C has also been reported by previous investigators [19, 20] but the reason for such dilation occurring in this temperature range is not clear. *In-situ* high temperature X-ray measurements show that austenite phase increases gradually with temperature reaching 100% value at 760 °C [18]. The formation of austenite phase which is a close packed structure shows pronounced contraction when martensite to austenite phase transformation takes place [20]. The reason for this dilation hump observed between 580–640 °C (Fig. 2) may be speculated due to a change of precipitate type which is discussed as follows.

The precipitates that are formed in these steels during the early stages of ageing treatment are A₃B type of intermetallics which transform to A₂B type of precipitates at higher ageing temperatures. Ni₃Ti has been identified at early stages of precipitation, the orientation relationship between martensite and Ni₃Ti is observed to be [12]

$$(011)m \parallel (0001)\eta$$

$$[1\bar{1}1]m \parallel [11\bar{2}0]\eta$$

These precipitates are favoured because of their good lattice fit with the martensite matrix [12]. Based on the lattice parameter of these two structures, the lattice mismatch between the close-packed direction is obtained as 2.22% [12]. Fe₂Mo which is formed at much higher temperature [21] has lattice parameters $a = 0.474$ nm and $C = 0.773$ nm [3]. The lattice mismatch between the close-packed direction of martensite and Fe₂Mo is calculated to be 4.9% [22] which is two times higher in magnitude as compared to the lattice mismatch between martensite and Ni₃Ti precipitate. It therefore can be speculated that the small dilation hump observed between 580 and 640 °C (Fig. 2) may be due to the change from A₃B to A₂B type of precipitates. The resumption of increase in length after 770 °C is attributed to the austenite finish temperature which is in agreement with the published work [20].

Changes in electrical resistivity plotted as a function of ageing temperatures (Fig. 2) substantiate the inferences drawn about the precipitation kinetics by lattice parameter changes (Fig. 1) and hardness measurements (Fig. 4). The slight initial decrease in the electrical resistivity values in stage I up to 400 °C may be associated with the accumulation of solute atoms which is also reflected in the slight increase in hardness up to 400 °C (Fig. 4). The sharp decrease in the resistivity in stage II may be attributed to the formation, and subsequent coarsening of hardening precipitates which corresponds well with the onset of decrease in the lattice parameter of martensite phase from 400 °C (Fig. 1) due to depletion of alloying elements in the martensite matrix as a result of precipitate formation. A gradual increase in the electrical resistivity value from 570 °C corresponds to the increasing amount of austenite that is retained at room temperature after cooling from 570 °C. Although a small quantity of austenite (shown in the dotted line in

Fig. 1) is observed at room temperature when aged between 530–570 °C, the electrical resistivity does not increase in this region (Fig. 2) which may be attributed to the dominating effect due to the coarsening of hardening precipitates. That the electrical resistivity observed in this study, increases with the increase in austenite volume percent, suggests that electrical and magnetic properties of maraging steels are profoundly affected by austenite in the structure, is in confirmation with the published works [10, 16, 17, 23].

5. Conclusions

1. The lattice parameters of martensite phase in 18 wt % Ni maraging steel grade 350 have been observed to vary as a function of ageing temperatures. A decrease in the lattice parameter of the martensite phase is observed when aged between 400–650 °C which is attributed to the depletion of alloying elements in the martensite phase. While the increase in the lattice parameter when aged between 650–710 °C is due to enrichment of alloying elements in the martensite phase as a result of dissolution of austenite.
2. Electrical resistivity, hardness measurements, and *in-situ* high temperature dilatometry experiments carried out in this study support the inferences drawn about the various precipitation reactions justifying observed changes in the martensite lattice parameter.

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*Received 6 March
and accepted 16 August 1995*