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A Dilatometric Study of the Phase Transformations in 300 and 350 Maraging Steels During Continuous Heating Rates

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The influences of the chemical composition and heating rate have been studied in 300 and 350 maraging steels using dilatometry. For these tests, heating was carried out with heating rates of 1, 10 and 28 °C/s. The results have shown that the precipitation mechanism for both materials in the studied range is by lattice diffusion. Furthermore, Co and Ti contents influence strongly the precipitation. The lattice diffusion mechanism in the martensite reversion is influenced by Ni and Co contents and heating rate. For small heating rates (~1 °C/s) this mechanism prevails in the 300 maraging steel while for the 350 maraging steel has a minor importance. The mechanism of martensite reversion for 350 maraging steel in the studied range is mainly by shear mechanism. For higher heating rates (~28 ºC/s) the shear mechanism prevails in both maraging steels.

Keywords: *maraging steels, precipitation, martensite reversion, phase transformations*

1. Introduction

Maraging steels are low carbon martensitic steels that can be hardened by precipitation of intermetallic phases[1,2]. These steels are used in industrial applications that demand high strength steels, such as in aerospace and nuclear technologies[3,4]. Commercial maraging steels are iron-nickel-cobalt alloys with molybdenum, titanium and aluminum additions[2].

These steels are commonly subjected to a two stage thermal treatment aiming to achieve a high strength level: a solution annealing at 820 °C, followed by aging at 480 °C. Martensitic microstructure of maraging steels is characterized by a supersaturated matrix of alloying elements containing high density of crystalline defects, mainly dislocations. This microstructure is formed during quenching from the austenitic field[5].

On heat treating, precipitate nucleation occurs predominantly on dislocations. Furthermore, high dislocation density accelerates the growing of theses precipitates during aging because solute diffusion by pipe diffusion has a lower activation energy than by lattice diffusion[6]. Studies show that precipitate formation of Ni_3X (X=Ti, Mo) occurs during aging, and the formation of a more stable phase Fe-Mo (Fe_2Mo or Fe_7Mo_6) demands higher exposure times[1,6]. Additionally, austenite nucleation for longer aging times can result both in precipitate dissolution Ni_3X (X=Ti, Mo) and in Fe-Mo precipitate formation. This causes nickel enrichment in the matrix, stabilizing the austenite and decreasing the initial temperature of the martensite to austenite transformation or reversion[7-12]. It is noteworthy that both diffusion and shear mechanisms can occur simultaneously during this transformation[8,13]. Previous studies[13] have shown that these mechanisms can depend on the heating rates. Dilatometry has been largely used for studies of phase transformations on several types of steels[14], such as low-carbon steels[15] and maraging steels[13,16]. In this work the dilatometric technique was used to study the influence of chemical composition on precipitation and the martensite reversion phenomena, as well as to evaluate the activation energies of these phase transformations during the heating stage.

2. Method and Experimental Procedure

Samples were prepared from three maraging bars with diameters of 98, 139, 140 mm respectively for the 300, 350, 350 maraging steels, supplied in the solution annealed condition. Disks of 10 mm have been cut from these bars. Chemical composition (as per certificate) of specimens of each bar were provided, and reproduced in Table 1.

Samples having 2 mm diameter and 12 mm length were machined in the radial direction from these disks. Heating and cooling cycles were performed in the quenching Adamel-Lhomargy LK 02 dilatometer of the *CETEC-MG* Research Institution. For these tests, heating was carried out under low vacuum, approximately 10^{-1} mbar with heating rates of 1, 10 and 28 °C/s. Length increase (ΔL)

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Table 1. Chemical composition (% wt) of the studied bars.

Element	Ni	Co	Mo	Ti	Al	S*	C*	O*	N*
Maraging 300 bar A	18.69	8.99	5.01	0.80	0.086	30	10	9	1.5
Maraging 350 bar B	18.16	11.92	4.81	1.22	0.074	30	30	8	2.0
Maraging 350 bar C	17.79	11.85	4.83	1.46	0.088	25	25	9	7

*content in ppm.

and temperature (T) changes were measured during heating for each heating rate.

3. Results and Discussion

Figure 1 shows a typical dilatometric curve for a complete heating and cooling cycle (rate 1 °C/s), inflections indicating the phase transformation temperatures.

During the heating and cooling thermal cycling, three phase transformations in the maraging steels may be observed: precipitation, martensite reversion and martensitic transformation. In this work, tests have been performed only for the phase transformations occurring during continuous heating, analyzing precipitation and martensite reversion.

It is well known that for the dilatometric technique that the maximum transformation rate can be used to evaluate the activation energy[17,18]. These activation energies were determined through the linear thermal expansion coefficient α_L[17,18]. This coefficient is obtained by the slope of dilatometric curve.

$$\alpha_L = d(\Delta L/L_0)/dT \qquad (1)$$

Figures 2, 3 and 4 present the variation of the linear expansion coefficient as a function of temperature.

According to Habiby et al.[19] and Kapoor et al.[21], the solute in the matrix during heating leads to precipitation in the maraging steels causing a lattice contraction and changes of specimen macroscopic dimensions. Figures 2, 3 and 4 show the temperatures where the maximum rate of phase transformation for precipitation and martensite reversion occurred. It must be pointed out, in Figure 2, 3 and 4, that for higher heating rates the time available for precipitation decreases leading to a smaller specimen contraction. This is due to the smaller quantity of precipitates formed during heating for higher heating rates[21].

For samples of bar A (maraging 300) a smaller contraction during precipitation could be observed when compared to samples of bar B and C (maraging 350). This is linked to bar A has a smaller quantity of Ti and Co is in solid solution in the martensite, hence forming a smaller amount of precipitates[5,20].

Kapoor et al.[13] have shown that the reversion mechanisms occur by shear or by diffusion and that these depend on the heating rates. The present research also showed that this reversion occur in two steps. For slower heating rates, there is a predominance of diffusion in the first step, while in a second step shear predominates[13]. On the other hand, for higher heating rates, reversion occurs as a unique step with predominance of the shear mechanism[13]. Furthermore, Peters has shown that nickel accelerates the formation of austenite, while cobalt slows it down[9]. Again Figures 2, 3

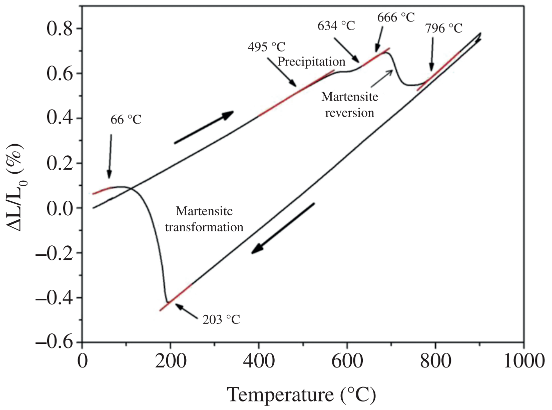


Figure 1. Dilatometric curve of heating and cooling for bar B, heating rate =1 °C/s.

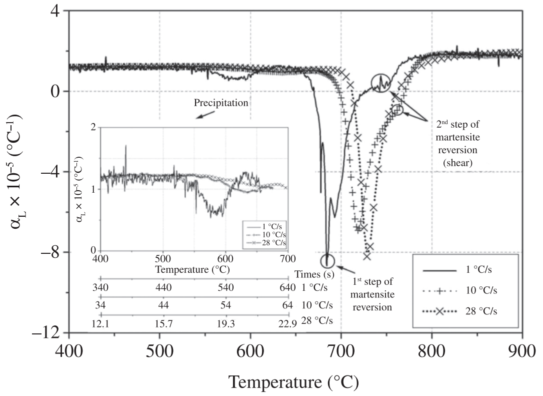


Figure 2. Linear expansion coefficient between 400 and 900 °C (for bar A) for different heating rates

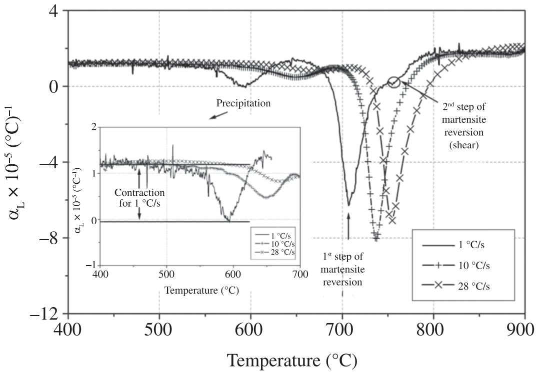


Figure 3. Linear expansion coefficient between 400 and 900 °C (for bar B) for different heating rates.

and 4 show that for bar C shear prevails while for bars A and B the two steps may be observed (see arrows for the 2nd step of martensite reversion). Further, it may be observed that this splitting (into the two steps) occurs for 1 °C/s and 10 °C/s for bar A and at 1 °C/s for bar B. This is linked to higher Ni and smaller Co contents of bar A (300 maraging), increasing the influence of diffusion on the reversion reaction for smaller heating rates, if compared to the bars B and C (350 maraging).

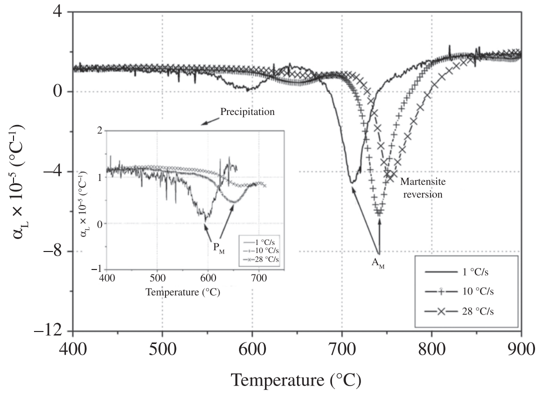
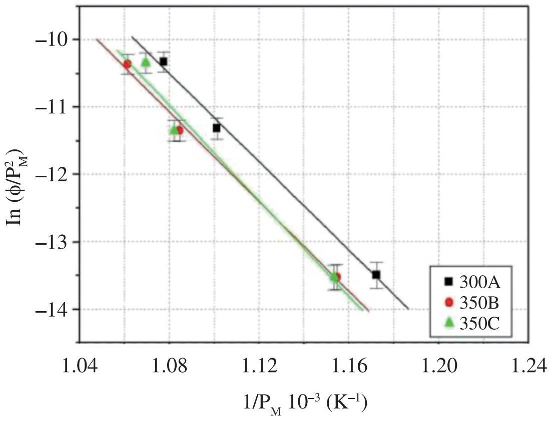
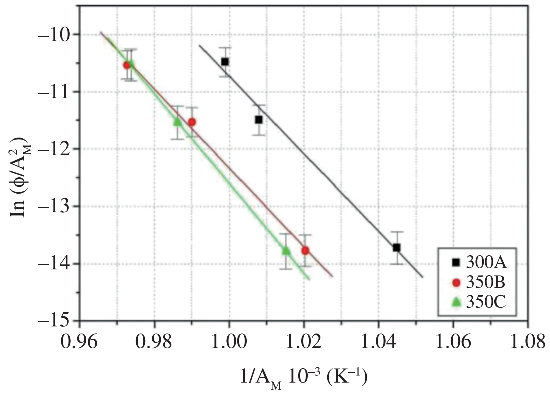


Figure 4. Linear expansion coefficient between 400 and 900 °C (for bar C) for different heating rates.



(a) Precipitation



(b) Martensite reversion

Figure 5. Method for the evaluation of the E values: (a) precipitation and (b) martensite reversion (P_M is the temperature for which there is a maximum precipitation rate and A_M is the temperature for which there is a maximum martensite reversion rate, see Figure 4).

Viswanathan et al.[16] have shown that activation energies of these transformations, which were evaluated through the Kissinger method[17], can be written in a simplified form by:

$$ln(\Phi/T_M^2) = - E/RT_M + C \qquad (2)$$

Where, Φ is the heating rate (°C/s), E is activation energy (kJ/mol), R the gas constant (J/mol.K), T_M is the temperature (K) for which there is a maximum phase transformation rate and C is an arbitrary constant. This equation is applicable only for a maximum transformation rate (measured by the maximum sample contraction rate)[17].

Figure 5 shows the linear regression obtained for the evaluation of the activation energies using the Kissinger method and Table 2 presents the activation energies (E) obtained through the slope of this linear regression. In that Table the obtained values of E are compared with the results from other authors[16,21,22].

Vasudevan et al. reported that initial precipitation occurs on dislocations, followed by a growing step of the precipitates by pipe diffusion[6]. Table 2 also shows that there is some discrepancy in the obtained activation energy values of this research from those reported by Viswanathan et al.[16]. The values diverge possibly due to different range of heating rates (Φ), because Viswanathan used heating rates in the range of 10 to 40 °C/min (0.17 to 0.67 °C/s). Furthermore, they suggested that for smaller heating rates (see Table 2), the redistribution of solute reaches a sufficient level in order to allow precipitation on dislocations by pipe diffusion (due to lower activation energies). Guo et al.[22] and Kapoor and Batra[21] have been observed that for higher heating rates, solute diffusion would be occurring by lattice diffusion (due to higher activation energies). In addition, from Table 2 it may be observed that the estimated activation energies for lattice diffusion are very close to those of the activation energies for lattice diffusion of the Ti (272 kJ/mol) and Mo (238 kJ/mol) in ferrite (similar to martensite)[16,22].

Table 2 also indicates that there is discrepancy in the values of martensite reversion activation energy as a function of the heating rate. For smaller heating rates, the lattice diffusion mechanism is predominant because the activation energies (224 and 342 kJ/mol) are close to those of nickel (246 kJ/mol) and molybdenum (238 kJ/mol) (for which the mechanism is diffusion in ferrite)[16,22]. For higher heating rates Kapoor and Batra[19] suggest that for $\Phi < 2$ C°/s the value of E is 423 kJ/mol and for $\Phi > 2$ C°/s the value of E is 828 kJ/mol. This observation has shown that activation energy is larger due to the shear mechanism that occurs in a more expressive way.

This work analyzed similar materials and pointed out that the shearing mechanism occurs also with larger intensity for higher heating rates (by comparing E in the range of 562 and 646 kJ/mol).

Table 2. Comparison of the activation energies for precipitation and martensite reversion for different maraging steels.

Reference	Precipitation (kJ/mol)	Martensite reversion (kJ/mol)	Heating rate
Bar A (maraging 300)	272 ± 18	562 ± 69	1 to 28 °C/s
Bar B (maraging 350)	276 ± 19	569 ± 36	1 to 28 °C/s
Bar C (maraging 350)	294 ± 51	646 ± 8	1 to 28 °C/s
Guo et al. (maraging 250)[22]	205	342	5 to 50 °C/min
Viswanathan et al. (maraging 300)[16]	145 ± 4	224 ± 4	10 to 40 °/min
Kapoor and Batra (maraging 350)[21]	265	423; $\Phi < 2$ C °/s 828; $\Phi > 2$ C °/s	0.2 to 200 °C/s

4. Conclusions

From the above observations it may be concluded that:

- The precipitation mechanism for both materials in the studied range is by lattice diffusion Furthermore, Co and Ti contents influence strongly this transformation;
- The lattice diffusion mechanism in the martensite reversion is influenced by Ni and Co contents and heating rate. For small heating rates (~1 °C/s) this mechanism prevails in the 300 maraging steel while for the 350 maraging steel has a minor importance;
- The mechanism of martensite reversion for 350 maraging steel in the studied range is mainly by shear mechanism. For higher heating rates (~28 °C/s) the shear mechanism prevails in both maraging steels.

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