STUDY OF PRECIPITATION HARDENING DURING THE AGING AND OVERAGING IN MARAGING CLASS 300 STEEL

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Abstract. *The precipitation hardening behavior of an 18Ni-Co-Mo-Ti maraging 300 solution treated and aged in the 440°C-650°C range was investigated. The aging at 440°C, 480°C, 510°C and 560°C was modeled by an expression derived from the equation of Johnson-Mehl-Avrami (JMA). The activation energy for precipitation was determined (132 kJ/mol) and compared to published values for 18Ni-Co-Mo-Ti maraging 250 and 350 steels. The model for overaging based on the Orowan mechanism was tested in samples treated at 560°C, 600°C and 650°C but was found to be valid only for 560°C. The softening of samples aged at 600°C and 650°C is rather due to austenite precipitation than to $Ni_3(Mo,Ti)$ and Fe_2Mo coarsening. Equations of the potential tipe law were fitted for the overaging at 560°C, 600°C and 650°C.*

Keywords*: Maraging steels, Precipitation hardening, Overaging*

1. Introduction

Maraging steels are age hardenable alloys for special purposes where the combination of high strength and good toughness is required. The microstructure of the as quenched 18% maraging steel consists of low carbon and high nickel and cobalt martensite. The strengthening in low temperature aging (<450°C) is produced by ordered and coherent phases such as μ, S and X phases. The aging above 450°C produces an intense hardening due to the precipitation of $Ni_3(Mo,Ti)$ and Fe_2Mo phases (Magnée *et al*,1974; Lecomte *et al*,1985 and Tewari *et al*,2000). Aging between 500°C and the A_s temperature produces austenite precipitation by a diffusion controlled reaction (Tavares *et al*, 2002 and Peters, 1968). According to Li and Yin (1995) the austenite formation occurs at the same moment and as consequence of the partial dissolution of $Ni_3(Ti,Mo)$ and precipitation of Fe_2Mo. Depending on the martensite start temperature (M_s), the austenite formed by this way may be retained, partially or totally transformed into martensite during the cooling to room temperature. M_s decreases with the nickel content of the austenite, which is found to decrease with the aging temperature (Ahmed *et al*, 1994,1995). As a consequence, M_s increases with the aging temperature above 500°C. The amount of austenite observed at room temperature increases with the aging temperature till a peak value and then decreases as the temperature M_s decreases. The maximum amount of reverted austenite observed at room temperature in 18Ni Co-containing maraging steels is obtained by aging treatments between 620°C and 670°C (Habiby *et al*, 1994).

Recently, Wilson (1997) presented and applied models for aging and overaging of precipitation hardenable alloys. In recent work (Sha, 2000) applied these models for a maraging C-300 steel aged at 510°C. The equation used for aging is based on the Jonhson-Mehl and Avrami model (Jonhson and Mehl, 1997 ; Avrami,1968). The equation proposed for overaging is based on the Orowan mechanism. In the present work, these equations were tested for an 18Ni-Co-Mo-Ti maraging 300 steel aged in the 440°C – 650°C range.

2. Experimental Methods

A 2.5mm thick sheet of maraging 300 steel (composition shown in Table 1) was solution treated at 900°C for 40 minutes. After this the samples were aged at 440, 480, 510, 560 and 650°C for different times from 15 minutes to 24 hours. All heat treatments were conducted in vacuum-sealed quartz tubes.

Table 1. Chemical composition of the maraging steel studied (% weight).

Element	C	Ni	Co	Mo	Ti	Al	Mn	Fe
Wt.%	0.01	17.86	9.41	4.84	0.76	0.14	0.01	Bal.

Vickers hardness tests and X-ray diffraction analysis (XRD) were carried out in all conditions. All the X-ray measurements were carried out using a diffractometer PHILIPS®, model X´Pert Pro, in step scan mode with step size of 0.02° and time per step of 3s. CuKα (1.54056Å) radiation was used with 40kV and 40mA. In order to keep the beam completely on the sample for low incident angles a divergence slit of 1° was used.

3. Results

Figure 1 shows the precipitation hardening curves of the maraging 300 steel aged at 440, 480, 510 and 560°C. The aging curves at 440°C and 480°C do not present overaging till 24 hours. The maximum hardness is obtained by the aging at 480°C for 10 and 24 hours. The samples aged at 510°C achieve a maximum hardness of 629HV at 4 hours of aging, and undergo a slight overaging after this.

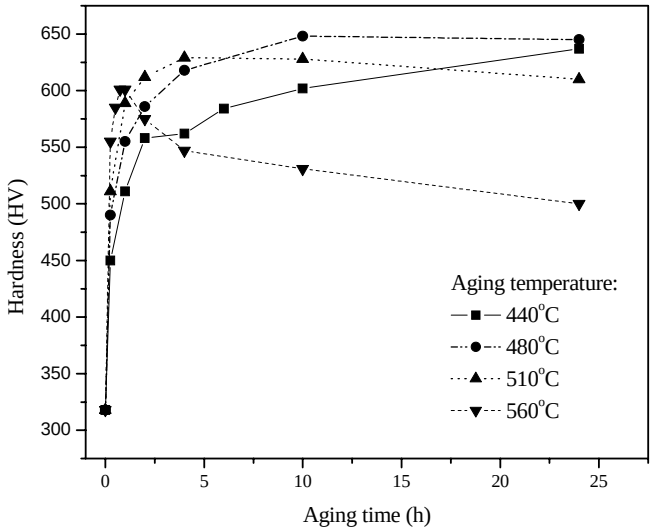

Figure 1. Hardness *versus* aging time at 440°C, 480°C, 510°C and 560°C.

Many studies have been built on Friedel´s idea, and have tested it experimentally. For the present purposes, it is adequate to accept that the increase to the yield strength is function of a fraction *f* of shearable particles of radius r:

$$\Delta\sigma_y = c_1 f^{m_1} r^{m_2} \tag{1}$$

For most dislocation-particle interactions, both m_1 and m_2 have the value 0.5. The relationship between aging time t and radius r of zone or precipitate (considered spherically) is given by Zener´s.

$$r = \alpha .(D.t)^{\frac{1}{m_3}} \tag{2}$$

Where $m_3 = 2$.

The Johnson-Mehl Avrami (JMA) equation can be used to describe the relationship between transformation fraction and time at a certain temperature. For early stages of aging the JMA equation can be expressed:

$$f = f_{eq}\{1 - exp[-(kt)^{m_4}]\} \approx f_{eq}(kt)^{m_4} \tag{3}$$

For maraging steels, the increase of the yield strenght is proportional to the hardness increase. For polycrystalline materials, after applying the Taylor factor Mt, one has:

$$\Delta\sigma_y = q.\Delta H = M_T \Delta\tau_y \quad (4)$$

Combining equations (1)-(4), we have in recent work (Guo and Sha, 2002):

$$\Delta H = (K \cdot t)^n \quad (5)$$

Where this equation (5) is the model for kinetics of early stages of aging precipitation in hardenable alloys is given by an expression derived from the Jonhson-Mehl Avrami equation (Guo and Sha, 2002):

Where K = temperature dependent rate constant
n = time exponent, slightly temperature dependent
ΔH = increase of hardening (HV)
t = aging time (h)

Table 2 shows the n and K values obtained by plotting ln(ΔH) *versus* ln(t) in the Fig. 2. Then values obtained at 440°C, 480°C and 510°C are close, but the one obtained at 560°C is smaller. This is attributed to the softening effect caused by austenite precipitation at this temperature, even before the overaging. Figure 3 shows the X-ray diffractogram of the sample aged at 560°C by 45 minutes with austenite peaks.

Table 2. n and K values at 440°C, 480°C, 510°C and 560°C.

Temperature (°C)	Time range (h)	n	K (h^{-1})	R
440	0.25 – 10	0.20 ± 0.02	1.3×10^{11}	0.97
480	0.25 – 2.0	0.20 ± 0.01	5.0×10^{11}	0.99
510	0.25 – 2.0	0.21 ± 0.02	3.9×10^{11}	0.99
560	0.25 – 0.75	0.16 ± 0.01	1.7×10^{15}	0.99

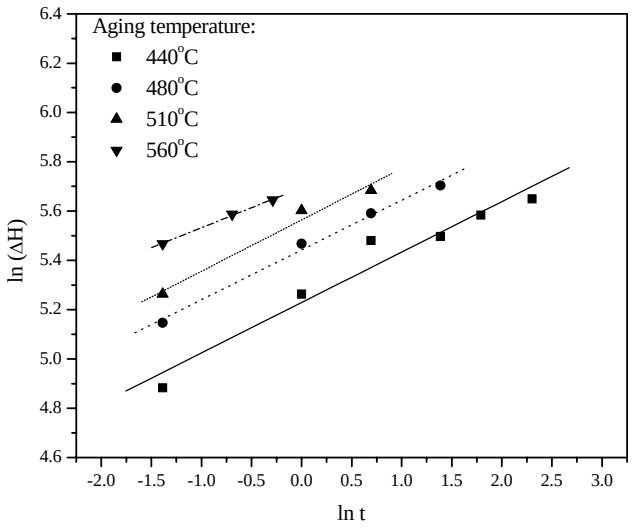

Figure 2. ln(ΔH) *versus* ln(t) for the samples aged at 440°C, 480°C, 510°C and 560°C.

The fitting for the 440°C shown in Fig. 2 presented the lowest correlation coefficient (R = 0.97). In this case, the points are better fitted by two curves (Fig. 4), where two aging stages are distinguished. The parameter n obtained for first and second stages were 0.29±0.01and 0.12±0.01, respectively. The different aging stages may be related to different types of precipitates in maraging steels.

Then and K values obtained at 510°C in this work (Table 2) are somewhat different from the ones obtained by Sha, (2000) in a maraging steel of the same type. This can be attributed to differences in the time range used to fit the curves. In this work we took points between 15 min and 2 h, while Sha, (2000) analyzed the hardening between 160s and 25min.

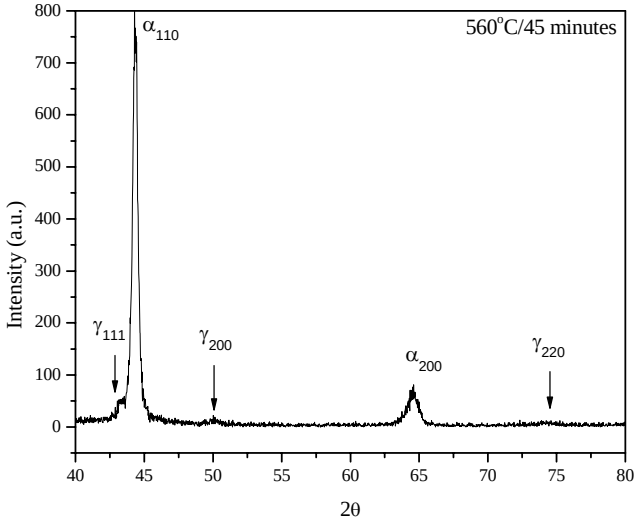

Figure 3. X-ray diffractogram of the sample aged at 560°C for 45 minutes.

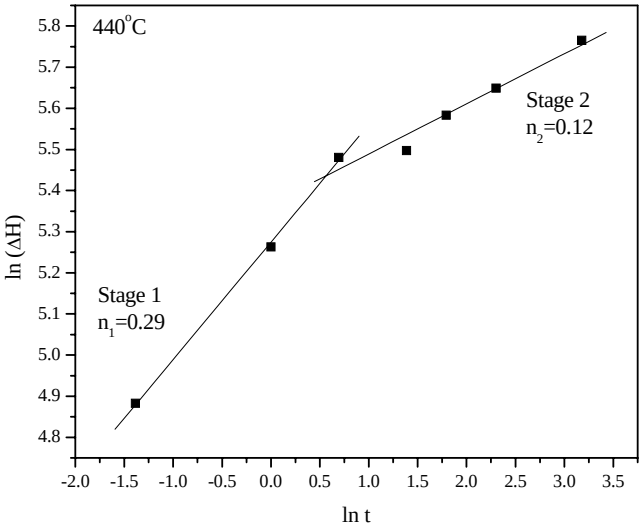

Figure 4. ln(ΔH) *versus* ln(t) for the samples aged at 440°C using two fitting lines.

The activation energy for precipitation may be obtained by plotting the logarithm of the time taken to achieve the peak hardness against 1/T. The results may be fitted by an Arhenius type equation:

$$ln(t) = \frac{Q}{RT} + constant \tag{6}$$

Where Q = activation energy for the precipitation (kJ/mol)
t = time taken to attain peak hardness at each temperature (h)
R = universal gas constant (0.008314 kJ/mol·K)
T = aging temperature (K)

An activation energy of 132 ± 10 kJ/mol was obtained from the slope of the fitted line (Fig. 5). Using the same method of this work Viswanathan *et al.* (1993) found an activation energy of 164 kJ/mol in the maraging 350 and Zhang *et al.* (1997) found 85.8 kJ/mol in the maraging 250. Table 3 shows the comparison of these data and presents the base chemical composition of each grade. The three steels present about the same nickel (18%Ni), but differ in the Co, Mo and Ti contents. The Ti/Mo ratio and the cobalt content increase from the 250 to the 350 grade. These modifications enhance the precipitation hardenability providing higher strength levels and aging peaks, but increase the activation energy for precipitation.

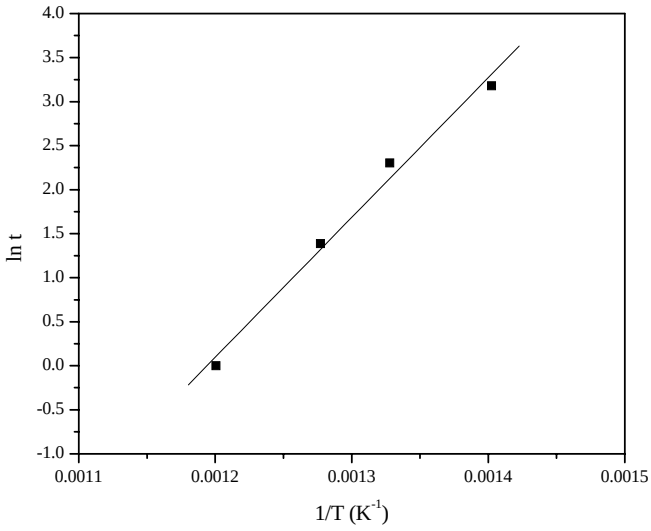

Figure 5. ln(ΔH) *versus* ln(t) for the samples aged at 440°C, 480°C, 510°C and 560°C.

Table 3. Activation energies for precipitation.

Steel	Base chemical composition (wt.%)	Q (kJ/mol)	Reference
Maraging 250	18Ni-8.5Co-5.0Mo-0.4Ti-.1Al	85.8	Zhang *et al.* (1997)
Maraging 300	17.9Ni-9.4Co-4.8Mo-0.8Ti-0.1Al	132	this work
Maraging 350	18.4Ni-12.3Co-4.0Mo-1.6Ti-0.1Al	164.0	Viswanathan *et al.* (1993)

Recently, Wilson (1997) and later Sha, (2000) have also proposed a model for overaging based on the Orowan mechanism:

$$\left(\frac{1}{\Delta H}\right)^3 = M(t - t_o) + \left(\frac{1}{\Delta H_o}\right)^3 \qquad (7)$$

Where ΔH = difference between the hardening of the overaged sample and the solution treated one (HV);
M = temperature dependent rate constant
t_o = time at peak hardness (h)
ΔH_o = increase in hardness at commencement of coarsening time t_0 (HV)

Figure 6 shows the precipitation hardening curves of the maraging 300 steel aged at 560, 600 and 650°C and Fig. 7 shows the fittings $(\Delta H)^{-3}$ *versus* aging time at 560°C and 600°C used to obtain the parameters M and ΔH_o presented in Table 4. The correlation coefficients (R) of the linear fittings are also shown. The comparison between the ΔH_o obtained by the fitting with the experimental value also gives an idea of the validity of the model. The work of Sha, (2000) shows the application of Eq. (7) on the overaging of a Cr-containing maraging steel at 520°C. At this temperature he obtained a good correlation coefficient (R^2 = 0.98) with the modeled ΔH_o (140HV) very close to the experimental value (141HV). In the present work, the model applied at 560°C presents satisfactory results, with R = 0.99 (R^2 = 0.98) and ΔH_o (253HV) close to the experimental value (257HV). The modeling at 600°C and 650°C does not give good results. At 600°C the correlation coefficient is very low (R = 0.91) and the determined ΔH_o value (184 HV) is very different from the experimental value (207HV). The fitting at 650°C (not shown) gives an R = 0.97 and a negative ΔH_o, which has no physical meaning.

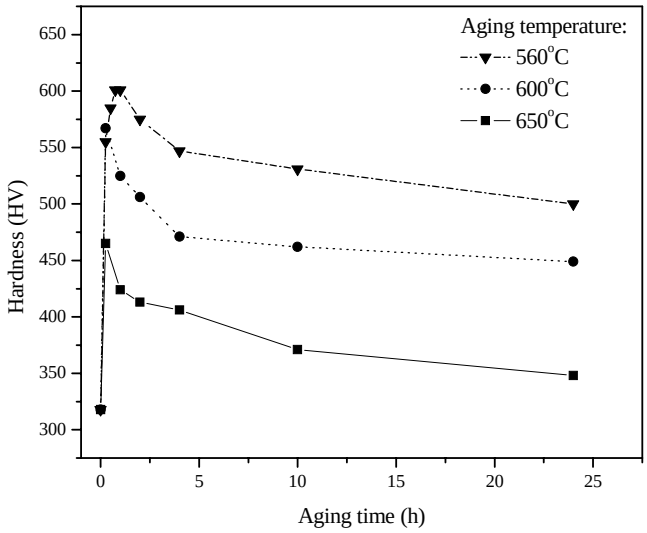

Figure 6. Hardness *versus* aging time at 560°C, 600°C and 650°C.

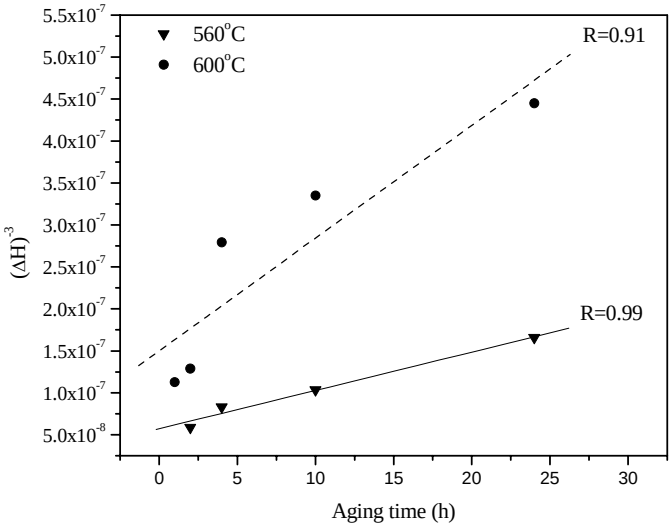

Figure 7. Plots of $(\Delta H)^{-3}$ *versus* aging time at 560°C and 600°C for modeling of the overaging kinetics.

Table 4. M and ΔH_o values at 560°C and 600°C.

Temperature (°C)	M	ΔH_o (model)	ΔH_o (experimental)	R
560	4.57E-09	253	257	0.99
600	1.30E-08	184	207	0.91

The overaging of the maraging steel aged in temperatures higher than 500°C is enhanced by the austenite formation. Figure 8 show the X-ray diffractogram of the sample aged at 510°C for 24 hours with austenite peaks. However, despite this, satisfactory fittings are obtained at 520°C (Sha, 2000) and 560°C (in this work). Figure 9 shows that the amounts of austenite formed at 600°C and 650°C are much higher than at 560°C and 510°C, which seems to be the reason why Eq. (7) does not describe well the overaging at 600°C and 650°C.

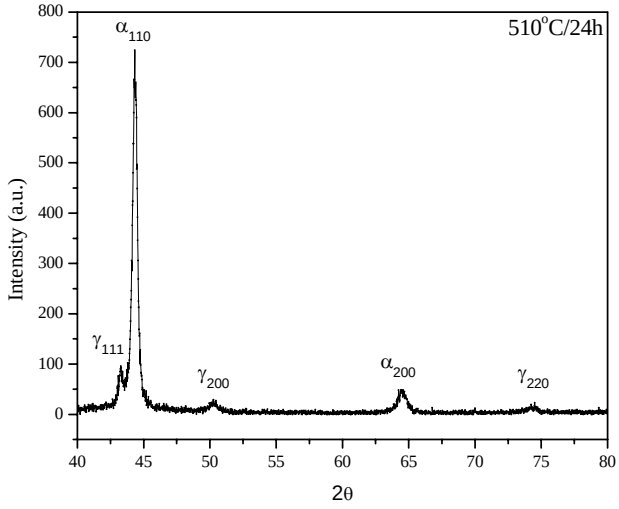

Figure 8. X-ray diffractogram of the sample aged at 510°C for 24 hours.

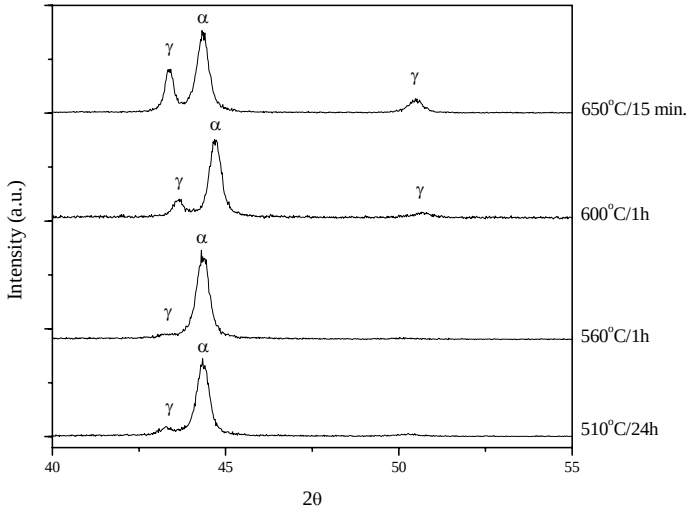

Figure 9. Comparison between the X-ray diffractograms of the samples aged at 510°C for 24 hours, 560°C for 1 hour, 600°C for 1 hour and 650°C for 15 minutes.

On the other hand, the overaging of the maraging 300 steel at 560°C, 600°C and 650°C can be mathematically described by an equation of the type (Fig. 10):

$$H(t) = H_1 \cdot t^p \tag{8}$$

Where: H = hardness value (HV)
t = aging time (h)
H_1 = hardness value at t = 1h
p = negative exponent of time

Figure 10 shows the curves fitted for 560°C, 600°C and 650°C. Table 5 shows the parameters of the equations (H_1 and p) and the correlation coefficients obtained. The H_1 obtained by the model and the experimental values (also shown in Table 5) are very close, which validates the model.

Table 5. H_1 and p values at 560°C, 600°C, 650°C.

Temperature (°C)	p	H_1 (model)	H_1 (experimental)	R
560	-0.053	594.3	601	0.99
600	-0.054	523.3	525	0.98
650	-0.061	428.8	424	0.99

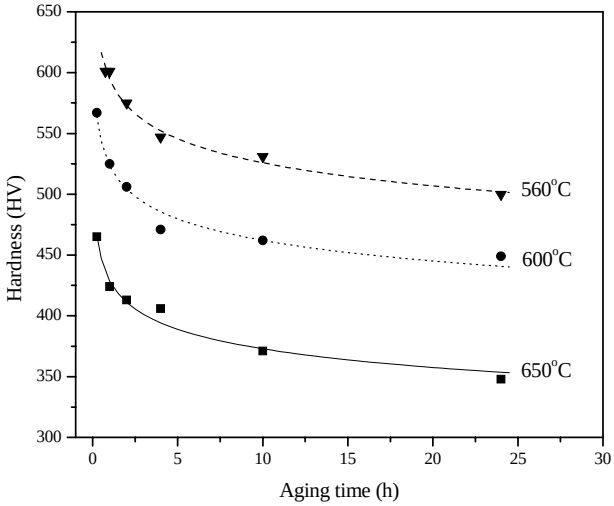

Figure 10. Fittings of the hardness *versus* aging time curves at 560°C, 600°C and 650°C in the overaged portion.

4. Conclusions

The age hardening of the maraging 300 steel between 440°C and 560°C can be modeled by the equation $\Delta H = (kt)^n$ with good correlation coefficients (R). The n values found at 440°C, 480°C and 510°C were 0.20, 0.20 and 0.21, respectively. The n value falls to 0.16 at the aging temperature of 560°C, which is attributed to the influence of austenite formation during the aging at this temperature. The aging at 440°C could also be modeled by two curves, representing different stages of precipitation.

An activation energy for precipitation hardening of 132 ± 10 kJ/mol was calculated by the Arhenius equation. This value is between the ones obtained in maraging 250 and maraging 350 steels.

The model proposed by Wilson, (1997) for overaging was tested for the samples aged at 560°C, 600°C and 650°C but was only valid at 560ºC. The overaging at 650°C, 600°C is rather due to the softening effect of the intense austenite formation, and for this reason, is not described by the equation proposed by Wilson [10]. On the other hand, the overaging at 560°C, 600°C and 650°C was well described by an equation $H = H_1 \cdot t^p$, where H_1 is the hardness value for t = 1h and p is a negative exponent.

3. Acknowledgements

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