Some aspects concerning the mechanism of hardening of maraging 300 steel

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Maraging steels are characterised by ultra-high strength due to the precipitate formed during ageing. The development of new maraging steels has drawn much attention from the civil and military industry, targeting specific applications. Maraging steels work well in electro-mechanical components where ultra-high strength is required, along with good dimensional stability during heat treatment. Several desirable properties of maraging steels are: ultra-high strength at room temperature; good weldability; section size is an important factor in the hardening process; simple heat treatment, which results in minimum distortion; superior fracture toughness compared to quenched and tempered steel of similar strength level; low carbon content, which precludes decarburization problems. These factors indicate that maraging steels could be used in applications such as shafts, and substitute for long, thin, carburized or nitrided parts, and components subject to impact fatigue, such as print hammers or clutches. The study has been conducted on samples which have been placed in solutions with different cooling speeds (water, air) and then subjected to the thermal treatments for precipitation until the apparition of the austenite. The paper presents briefly some aspects regarding the present stage in production of maraging steels and the effect of thermal treatment on the mechanical characteristics and on the types of intermediate metallic compounds which result in the process of hardening by precipitation for maraging steel.
Key words: Hardening by precipitation; maraging steels; thermal treatments.

1. Introduction

The recent rapid development of this type of steel is due to an assembly of highly important properties such as: high mechanical resistance, with remarkable ductility and tenacity; simple thermic treatments; good weld ability; cryogenic resistance; good deformability and processability (Decker et al., 1964; Dennis et al., 1968; Decker et al., 1962). In the case of usual hardenable steel utilized in the car construction industry, the process of hardening results in the formation of a hard and fragile martensite, which shall in turn be reannealed to obtain desired mechanical characteristics. In the case of maraging steel on the other hand, hardening results in the formation of a soft, ductile martensite, with a high content in nickel and very little carbon. The high mechanical characteristics are obtained through an ageing treatment due to the precipitation of some complex intermetallic phases (Castagne et al., 1969). An important limitation concerning the production of conventional high-resistance steel is represented by the association between the deformations and fragile cracking's. The higher the mechanical resistance, the more fragile is the type of cracking at high solicitations. Carbon is the main element which confers the high resistance but in the same time the fragile character of steel, which is why the actual tendency regarding the development of high-resistance alloys is to dramatically lower the contained carbon. On the other hand, a very low percent of carbon (< 0,03 %) needs to be associated with a martensitic, soft and massive structure, and with hardening by ageing. And this is actually how the name of „maraging" came into play. The development of maraging steel emerged from the Fe – Ni binary alloy, with a percent of Ni ranging between 18% and 25%. This results in a massive martensite if air-cooled. This martensite does not contain carbon as it is the case with usual Fe-C steel; it is not modified tetragonally, having a regulated cubic shape. It is called 0 solid solution, having the same chemical composition like the austenite it resulted from. The elements for alloying selected after Ni have been Mo ~ 5 % and Ti ~ 1 %. Applying an ageing treatment in the 450 – 500 °C intervals has led to the formation of the following precipitates: Ni_3Mo or $Ni_3(MoTi)$ Ni_3Ti or Fe_7Mo_6. Excess

titanium neutralizes carbon by forming carbon carbide. This alloying had a supplementary effect: lowering the point of martensitic MS and MF transformation. The following element introduced in maraging steel was Co. Its effect is significant for the formation of a high-resistance and high-tenacity alloy by lowering the solubility of Mo in Fe (solid solution), consequently leading to the formation of more precipitates, which in turn results in the increase of the martensitic MS and MF transformation temperatures. Other potential alloying elements are Al, Nb, Zr, Be, W, V, Cu, Ta. These are substitution elements which produce the hardening. The normal thermic treatment cycle for maraging Co-Mo-Ni steel, laminated or forged, consists of a solubilization reannealing at 820 °C with air-cooling followed by an ageing treatment for the martensite (maraging) at 480 °C or 450 °C with air-cooling. At the temperature of 820 °C the phase transformation takes place (α⇨γ), as well as the recrystallization of the austenite and the dissolution of the precipitates. After the cooling at 820 °C, regardless of the speed, the γ⇨α transformation takes place (austenite-martensite). The hardening of maraging steel is obtained by the thermic ageing treatment, a period in which the formation of the intermetallic precipitates in the martensitic mass takes place. (Bourgeot et al., 1973; W, Sha et al., 1993; Thomas et al., 1969, Yi-He et al., 2005). This excellent complex of mechanical and technological features is due to hardening by precipitation of a series of intermetallic compounds in the special martensitic mass (lath martensite).There are two types of mechanisms responsible for the hardening of the precipitates, which are implied in the movement of the dislocations: - a looping mechanism (Vasudervan et al., 1990), (Sinha et al., 1998); -a shearing mechanism (Viswanathan et al., 1993), (Floreen et al., 1962) and the reannealed austenite.

2. Experimental works
2.1 Choosing the system of experimental materials
The stated purpose of the paper is to expand the field of use of maraging steels to the area of high temperatures, starting from a classic maraging 300 steel (breaking strength 300 ksi) with the following average composition in percent: C <0.02%, Ni-18 %, Co-9%, Mo-4.8%, Ti-0.6%, Al-0.1%. The study of complex and specific structural transformations for maraging steels (precipitation hardening steels), the analysis of the types of precipitation that appear depending on the temperature, allow us to make the following pertinent statements. The structure of precipitation hardening steels is of three types: Austenitic; Semi-austenitic; Martensitic. As an example, we quote the following chemical composition established for the three types of steels precipitate. From the point of view of chemical composition, there is a great diversity of maraging steels, namely: steels maraging with Cr – Cr, Mo, Co; maraging steels without Co – Ni, Mo, Ti, Al; steels maraging with Co – Ni, Co, Mo, Ti, Al. Hardening by precipitation can take place depending on the proportion of the alloying element in both the austenitic matrix and the martensitic matrix. Precipitation treatments preceded by solution treatments performed on the background of a martensitic structure are the most efficient in terms of the complex of physical-mechanical and structural characteristics, as well as in terms of simplicity of technology to achieve them (classic equipment heating, no protective atmosphere, cooling medium, air). How can we expand the scope of maraging steels containing Ni, Co, Mo, Ti, Al? Is there a close correlation between the temperature of martensitic → austenite structural transformation and the initial dissolution temperature of intermetallic precipitates in steel during aging treatment, so that the stability of the intermediate compounds increases with increasing temperature of martensite-austenite transformation? We can by increasing the concentration of the elements Ti, Si, Al and introducing alloying of Nb and Zr in the case of prolonged use of the alloy in the austenitic (750 °C) occur precipitates or agglomeration consistent alloying elements to strengthen the material and to increase the resistance of the hot use. The experimental methodology will focus on the following aspects: Increasing the martensite-austenite transformation temperature from approx. 500 °C to 700-750 °C by decreasing the Ni content; Increasing the concentration of alloying elements with hardening effect, namely Ti, Al, Si; Adding new hardening alloying elements, Zr and Nb. The chemical composition of the experimental batches will be balanced so as to prevent the occurrence of high concentrations of ferrite δ. The laboratory phase experiments focused on studying the effect of increasing the temperature of martensite → austenite transformation and the additional alloying with the elements Al, Zr, Nb, Si, Ti on the hot physical-mechanical characteristics (up to 550 °C). The chemical compositions desired to be made are shown in Table 1:

Table 1: Nominal chemical compositions desired in the experiments

Elements	Standard 300 maraging steel	Transformed maraging steel	Al-Si-Ti alloy maraging steel	Si-Zr-Nb alloy maraging steel
Ni	18,50 %	12,50 %	12,50 %	12,50 %
Co	9,00 %	9,00 %	10,50 %	10,50 %
Mo	4,80 %	4,80 %	4,80 %	4,80 %
Ti	0,60 %	0,60 %	1,50 %	0,60 %
Al	0,10 %	0,10 %	2,50 %	0,10 %
Si	max. 0,10 %	max. 0,10 %	0,80 %	1,20 %
Mn	max. 0,10 %	max. 0,10 %	max. 0,10 %	max. 0,10 %

C	max. 0,03 %	max. 0,03 %	max. 0,03 %	max. 0,03 %
S	max. 0,01 %	max. 0,01 %	max. 0,01 %	max. 0,01 %
P	max. 0,01 %	max. 0,01 %	max. 0,01 %	max. 0,01 %
Zr	-	-	-	1,00 %
Nb	-	-	-	2,50 %

The chemical compositions of the steels used in the experimental and characterization research are shown in Tables 2, 3 and 4. The chemical analyses were determined by RX-WDXRF on an Axios Advanced apparatus.

Table 2: Elementary chemical composition of batches used in experiments

Element [%]	Al	Ti	C	Mn	Ni	Si	Co	Mo	Nb	Zr
S1T1	0,254	0,0030	0,015	1,310	11,43	1,460	10,17	5,710	0,0130	<0,0006
S1T2	3,530	0,0027	0,028	0,742	11,05	0,589	10,03	5,500	0,0124	<0,0006
S1T3	2,650	0,8000	0,023	0,657	10,33	3,060	12,26	5,090	0,0194	0,0017
S2T1	0,250	0,4620	0,008	1,150	13,04	1,090	10,95	5,439	0,3420	0,0530
S2T2	0,178	0,2970	0,005	1,090	12,39	1,760	10,87	5,350	0,7960	0,1630
S2T3	0,105	0,0220	0,004	1,000	12,03	3,160	10,57	5,446	2,9700	>0,2500

Table 3: Chemical analysis of the studied steels

No.	Element	M01	Z-S_1T_1	Z-S_1T_2	Z-S_1T_3	Z-S_2T_1
1	Ni	17,820	11,5600	11,680	10,530	13,460
2	Co	8,930	10,6200	10,300	12,500	11,350
3	Mo	4,480	5,6200	5,570	4,970	5,349
4	Ti	0,690	0,0045	0,045	0,798	0,460
5	Al	0,060	0,2680	3,620	2,780	0,253
6	Si	0,090	1,4800	0,560	3,050	1,040
7	Mn	0,080	0,5330	0,395	0,295	0,605
8	C	0,028	0,0220	0,028	0,023	0,006
9	S	0,009	0,0100	0,008	0,007	0,008
10	P	0,015	0,0160	0,013	0,012	0,016
11	Zr	-	0,0050	0,020	0,050	0,160
12	Nb	-	0,0120	0,012	0,194	0,350

Table 4: Chemical analysis of maraging steels used to determine hot characteristics

Elements	Standard 300 maraging steel	Transformed maraging steel	Al-Si-Ti alloy maraging steel	Si-Zr-Nb alloy maraging steel
Ni	17,820	12,700	12,820	12,780
Co	8,930	8,720	10,250	10,320
Mo	4,480	4,620	4,740	4,680
Ti	0,690	0,480	1,420	0,540
Al	0,060	0,080	2,360	0,070
Si	0,090	0,043	0,060	1,160
Mn	0,080	0,050	0,070	0,066
C	0,028	0,024	0,022	0,029
S	0,009	0,006	0,008	0,007
P	0,015	0,005	0,007	0,009

Zr	-	-	-	0,870
Nb	-	-	-	2,340

Note: Batches vacuum arc remelting and vacuum through Ø 100 mm

2.2 Study of steel refining precipitation hardening maraging type modified by treatment pot

The purpose of the experiments and the experimental tests carried out consisted in the elucidation of the following aspect: it is possible that the treatment ladle calcium, magnesium and mischmetal successfully to replace the vacuum treatment? In order to obtain the answer to the previous question, modified maraging alloy batches were developed in an air induction furnace. The chemical composition was according to Table 2 - S_1T_1. Two of the batches were quenched in the classical manner with Al, and another two were treated in the ferrotitanium furnace (0.05%) and in the calcium pot, Mischmetal and Mg. After quenching the liquid, the batches were poured into ø 80 mm ingot moulds. From the ingots classically cast with Al and from those treated with calcium refiner Mischmetal + magnesium + titanium, electrodes were formed which were melted in vacuum by the process of melting in arc and vacuum.

Table 5: Development of modified maraging steel batches (12% Ni)

Elements	Standard 300 maraging steel	Treatment in a pot with Mischmetal + Mg + Ti + Ca	Treatment in vacum
SA 1	X	-	X
SA 2	-	X	X
SA 3	X	-	-
SA 4	-	X	-

Note: After melting in vacuum the ingot has a diameter of Ø 100 mm

From the cast ingots obtained by the three methods, we took-off test tubes for gas analysis and EDAX analysis. The samples were taken-off from the area of ingot crop ends, the most unfavourable area from the viewpoint of microstructure purity.

Aluminium abated sample elaborated in air – SA3 marking
The sample microstructure is shown in the electron-scan microscopy images, secondary electron images (SEI) from figure 1,2 Fe-Ni solid solution grains and inclusions arranged in inter and intragranular manner. The sample exhibits inclusions of the type: aluminium oxides and manganese sulphides MnS.
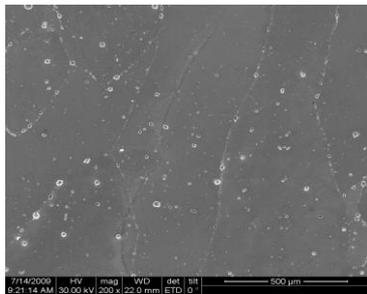
Figure 1: Microstructural Aspect of sample SA3.
General view x200
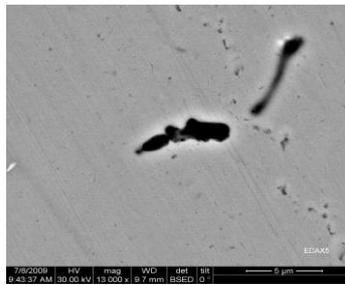
Figure 2: Microstructural aspect – sample SA3. Manganese sulphide and aluminium oxide x13000
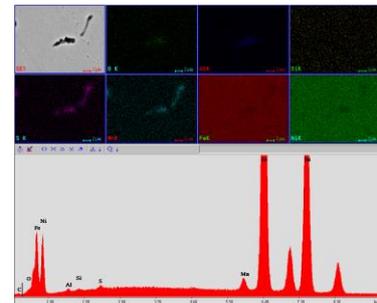
Figure 3: Secondary electron image and associated images of surface distribution of the relative intensity of the characteristic X radiation MnKα, SKα, FeKα

Ladle treated sample with Ti, Mischmetal, Mg, elaborated in air – SA4 marking
The sample microstructure is shown in the electron-scan microscopy images, secondary electron images (SEI) from figure 4, 5, Fe-Ni solid solution grains and inclusions of the type titanium nitrides.
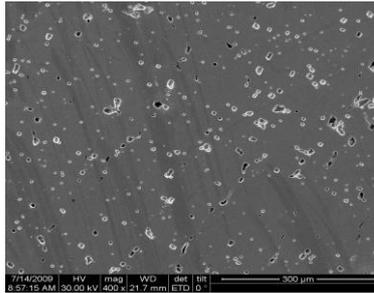
Figure 4: Microstructural aspect of sample SA4.
General view x400
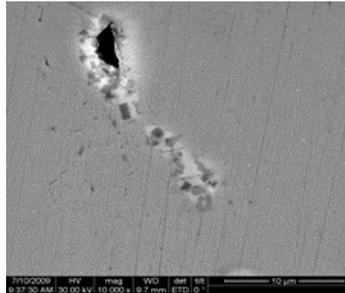
Figure 5: Titanium nitrides visible in sample SA4
x10000
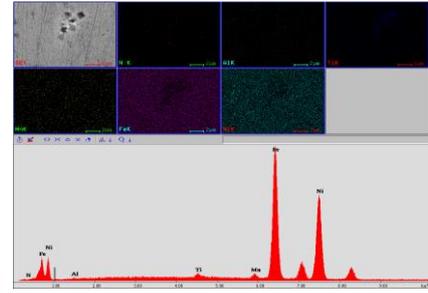
Figure 6: Secondary electron image and associated images of surface distribution of relative intensity of the characteristic X radiation NKα, AlKα, SKα, TiKα, MnKα, FeKα, NiKα on the microzone from figure 4
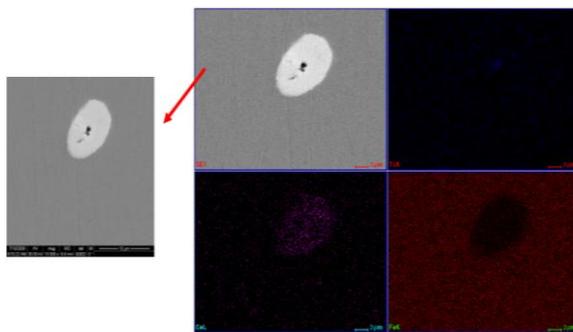
Figure 7: Cerium and lanthanum segregation
x10000
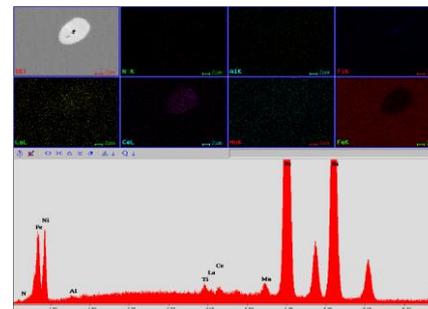
Figure 8: Secondary electron image and associated images of surface distribution of the relative intensity of the characteristic X radiation MnKα, SKα, FeKα CKα, O2Kα, AlKα, SiKα and NiKα on the microzone from figure 4. One may notice a cerium and lanthanum segregation and titanium nitride in the middle.

Aluminum abased sample, elaborated in air and remelted in vacuum (VAR)–SA1 marking
The sample microstructure is shown in the electron-scan microscopy images, images of backscattered electrons from figure 9, 10 images that highlight the presence of oxides in the iron-nickel solid solution. The particles that appear in dark contrast are inclusions present in the FeNi solid solution.
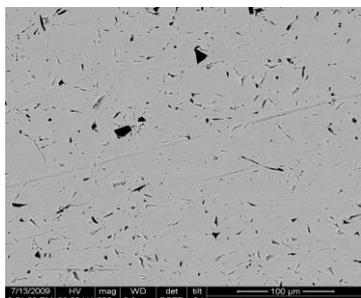
Figure 9: Images of backscattered electrons showing the general aspect of inclusion microstructure and morphology
x800
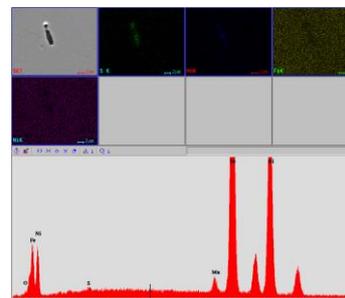
Figure 10: - Microstructural aspect of sample SA1 where one can see the presence of manganese sulphide
x10000
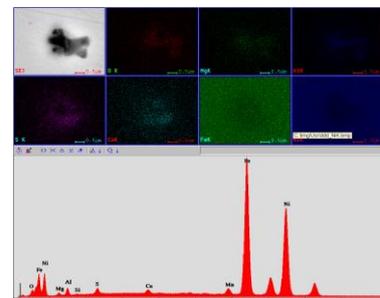
Figure 11: Detail highlighting the presence of aluminium and magnesium oxides and also a high concentration of sulphur and calcium in the analysed microzone sulphide
x10000

Ladle treated sample with Ti, Mischmetal, Mg, elaborated in Air and remelted in vacuum (VAR) – SA2 marking
The sample microstructure is shown in the electron-scan microscopy images and secondary electron images (SEI) from figure12 a, b and c.

a) General view x200   b) Micropinhole assembly x400   c) Micropinhole areas x800
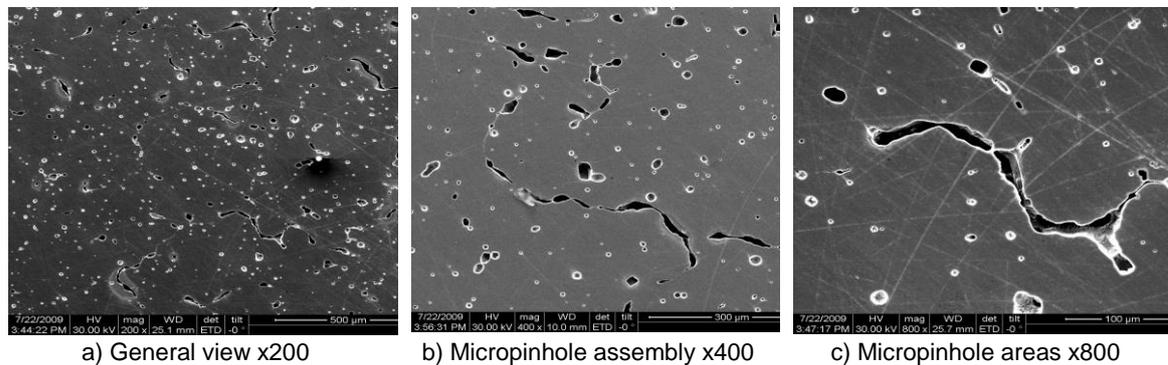
Figure 12: Microstructural aspect of sample SA2

3. Conclusions

The vacuum arc remelting treatment triggered a reduction of inclusions in terms of density and sizes. However, we may notice a small difference of distribution and sizes in case of Fe-Ni alloy allied with mischmetal and Mg. From the analysis of the gases (given in table 6), we may notice that:

Table 6: Development of modified maraging steel batches (12% Ni)

Sample marking	O2	N2	C	S
SA 1	0,0087	0,0043	0,0182	0,0104
SA 2	0,0080	0,0020	0,0177	0,0062
SA 3	0,0105	0,0045	0,0106	0,0115
SA 4	0,0092	0,0056	0,0085	0,0079

Vacuuming in case of Al abased charge (see SA3 and SA1) eliminates 20 ppm from material. In case of treatment with structural and deoxidizing refiners (Ti and Mg), vacuuming eliminates only 12 ppm from liquid.
The values obtained for the gas content when using refiners (mischmetal) during the ladle treatment are at the same level (0.0092 % - 0.0080 %) with the ones obtained by vacuuming. At the same time, excellent results were obtained in terms of decrease and morphology of inclusions (Al_2O_3, TiN).
Caesium from mischmetal manages to react with oxides and nitrides decreasing their size and creating a spatial zone around them (see figure 15 and figure 16).
The microstructure of the studied steel after conducting the thermal treatments (placing in solution and ageing) consists of lath martensite with a high density of dislocations.
Based on this martensitic structure, which lacks tetragonal structuring, with ageing, depending on temperature and maintaining duration, the precipitation of the intermetallic phases takes place, and consequently the hardening according to an Orowan mechanism.

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