NEW MARTENSITIC STAINLESS STEEL HARDENABLE BY PRECIPITATION FOR HYDROPOWER TURBINES

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Our study is focused on the obtaining of a new martensitic stainless steel having an unconventional chemical composition and designed for hydropower turbine applications. The proposed metallic material was produced in special conditions using an induction furnace with cold crucible under vacuum and argon atmosphere, ensuring an inclusion state free of impurities. The subsequent heat treatments (quenching and tempering) allowed to obtain special structures that determine interesting mechanical properties, very different comparing to classic martensitic stainless steels. Specifically, after tempering, the hardness values do not decrease as in other case of steels, but increase about 1.6 times. The structural and compositional investigations, carried-out by optical and scanning electronic microscopy associated with energy dispersive spectrometry were able to explain the structural modifications, mainly represented by precipitation phenomena of intermetallic compounds such as Ni_3Mo. The resulted data are similar to the phenomena encountered in the maraging steels class, creating a new category with duplex properties.

Keywords: martensitic stainless steel, maraging steel, heat treatment, hydropower turbine

1. Introduction

Classic materials used for obtaining hydropower rotor blades fall into the category of stainless steels. The selection between the two main classes, austenitic

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and martensitic, remains a problem connected to the necessity in order to ensure a sufficient hardness to withstand the impact of the energetic fluid and good resistance corrosion. Martensitic steels (Cr<16%, Ni=2-6%, C=0.1-0.5%) are most recommended but the corrosion resistance is not at the upper parameters [1, 2]. At the same time, the complex fatigue requirements encountered to hydropower turbine impose a higher hardness by forming precipitates inside the grain structure, increasing the welding capability through nickel addition and reducing the carbon content.

Austenitic steels (Cr = 16-28%, Ni=8-30%, C<0.1%) show advantages on good to excellent corrosion resistance, good weldability and plasticity, good creep resistance but weak mechanical properties. The possibilities to increase the resistant properties impose a partial replacement of Ni with Mn and N, but with poor results on corrosion behavior. Duplex steels (ferrito-austenitic) present advantages in terms of high traction and fatigue resistance, good weldability, good corrosion resistance under load, acceptable corrosion resistance and lower cost than the austenitic class due to lower Ni content (1.4-7%) [3, 4]. The potential for improvement is to increase the corrosion resistance by adding Mo (0.3-4%), or increasing the tensile strength by adding nitrogen. Additional alloying elements can provide extra hardening in the entire volume (Mo, N) or surface only (N) or may contribute to the passivation-repassivation phenomenon during cavitation attacks (Mo) [5, 6].

Starting from these considerations, the paper presents some results of our researches carried out in order to conceive a new stainless steel for hydropower turbine, produced in special conditions. This innovative technology could eliminate all disadvantages induced by a defective casting structure.

2. Experimental Research

The chemical composition was established in order to obtain a resistant martensitic stainless steel, which responds to complex requests of the hydropower turbines. The steel was made in an induction furnace with a cold copper crucible with an inner diameter of 35 mm and a capacity of min. 8 cm^3 and max. 15 cm^3 equipped with a casting plug, Fig. 1. The working parameters of the furnace are: nominal power 25 kW, frequency HF 100 - 400 kHz, apparent power 40 kVA, phase current 40 A, power factor 0.92, minimum water flow 12 l / min, maximum inlet pressure: 7.5 bar, water inlet: max. 24°C. The maximum working temperature of the furnace is 2800°C and the vacuum system consists of a primary vacuum pumping station including a pump of at least 1.7 m^3/h with a vacuum limit of 10^{-4} mbar and a vacuum pump pumping station for secondary vacuum of 1×10^{-8} mbar. The steel ingot is shown in Fig. 2.

Fig.1. Induction furnace with cold crucible, vacuum and argon atmosphere

Fig.2. Shape of the stainless steel ingot produced in the induction furnace with cold crucible

The chemical composition of samples, determined by emission optical spectrometry and carried out using LECO (Model: GDS 500 A machine), is presented in Table 1.

Table 1

Chemical composition, %

Cr	Ni	Mo	Si	Cu	Mn	Ti	Al
9.92	9.61	5.07	0.295	0.147	0.351	0.923	0.049
Nb	C	V	Co	P	S	Fe	
0.0889	0.0223	0.0022	0.0356	0.0204	0.0204	73.8	

Considering the resulting composition, the steel structure was identified by positioning in Schaeffler's structural diagram, as it is seen in the Fig. 3.
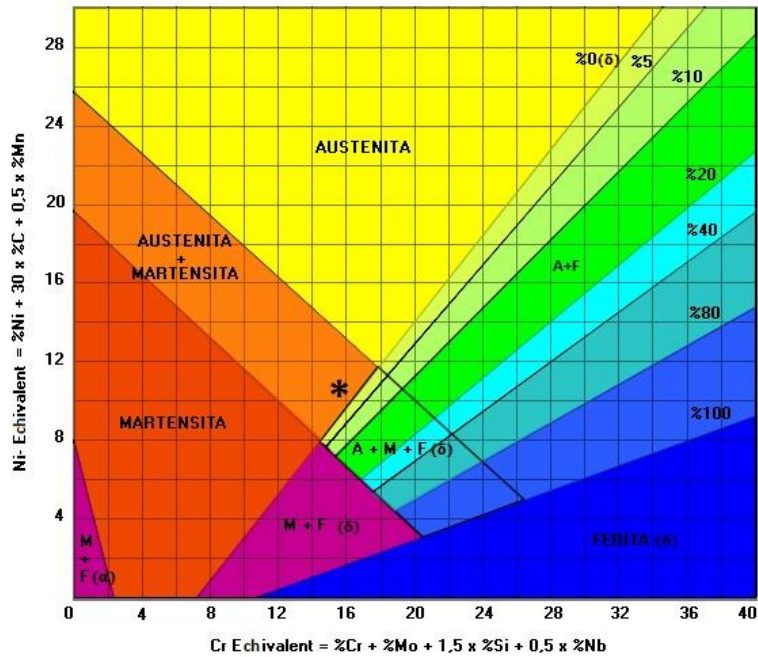
Fig.3. Positioning in the Schaeffler diagramof the obtained steel

According to Fig. 3, the proposed stainless steel structure is austenito-martensitic. Subsequently the samples were submitted to heat treatment, in order to observe the structural modifications and its effects on mechanical properties. Concretely, the heat treatment was composed by a martensitic quenching and tempering. The work parameters were the following: for quenching T=1000^{0}C/holding time=30min/water cooling and for tempering T=480^{0}C/holding time 3h/air cooling.

3. Experimental results and discussion

The first step of the investigation was represented by the hardness test, applied at different stages of material processing. This test was performed using INNOVATEST Model: FALCON 500 micro hardness equipment. The hardness measurements were made in 5 different points and after that, the average value was calculated. The results are presented in table 2.

Table 2

Material hardness variation

Hardness (HV)	As cast state	Quenched state	Tempered state
	308	315	512

Following the fundamental principle of Materials Science which highlights the major involvement of the structure on the properties, the second step in the research was represented by the structure investigation, especially modified by the heat treatment. Thus, the structures highlighted through optical microscopy using a metallographic microscope (OLYMPUS Model: BX 51 M) and a scanning electronic microscopy associated with energy dispersive spectrometry using a FEI Quanta FEG 450 SEM. The samples, prepared for metallographic analysis, were subsequently attacked with Marble's reagent for 15-20 seconds.

In Fig. 4 and Fig. 5 the results of structure and compositional studies are presented.

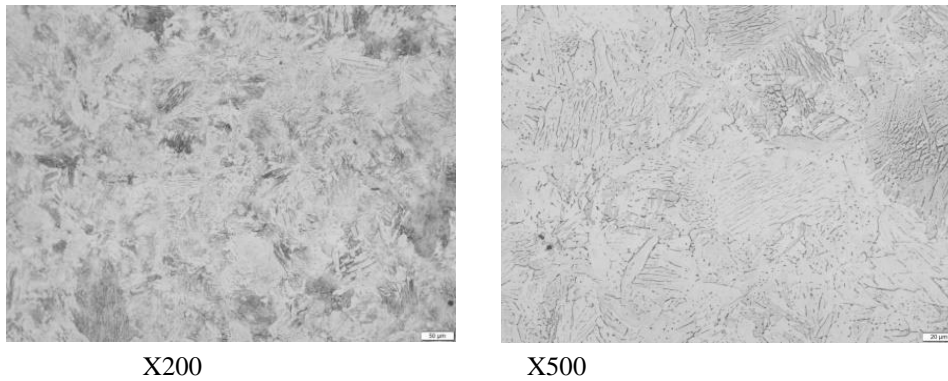X200   X500

Fig.4. Optical microscopy of casting structure Marble's reagent

The casting structure emphasizes a predominant martensitic distribution with light small areas where austenitic phase is present. The martensitic morphology is rather coarse, the needle size average being about 20- 80µm.
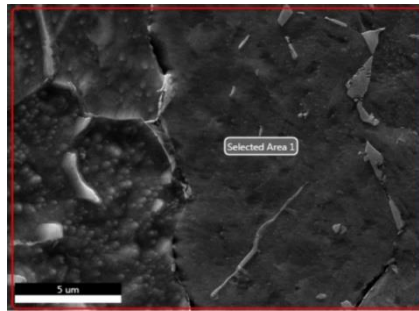

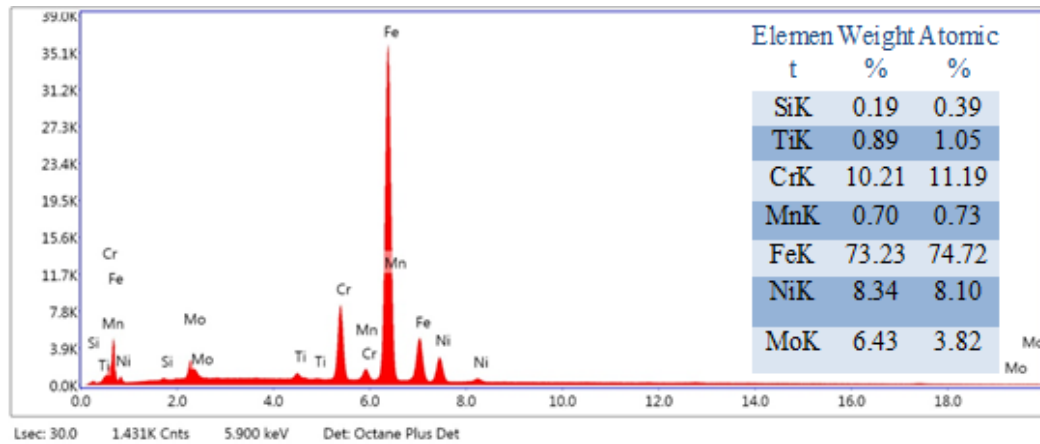Fig.5. SEM microscopy of casting structure

Fig.6. EDS spectra and local chemical composition on selected area

The SEM micrograph, shown in Fig. 5, brings more detailed information of casting structure. It's clearly defined the austenite network (light) limiting the martensitic phase. Moreover, the martensite has the appearance of lath distribution („lath martensite") typical for low carbon content steel. The EDS analysis (spectrum and local chemical analysis on selected area) provides important information on local composition. Comparing to macroscopic chemical composition of the steel, it can be observed that the two sets of values are almost in coincidence, suggesting a high homogeneity, which is a favorable signal for our applied modern process of steel fabrication.

The structural modifications after martensitic quenching are shown in Fig. 7 and Fig. 8.

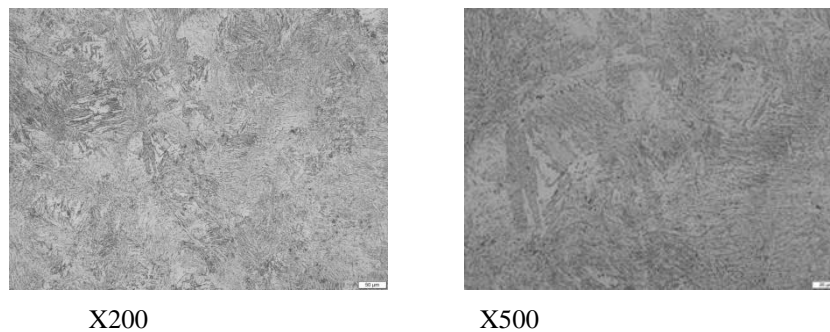X200   X500
Fig. 7. Optical microscopy of quenched structure, Marbre's reagent

The quenched structure is distinguished by a higher degree of finesse, the needle size average being about 20-45 µm. In the same time, the austenite network is restrained with favorable implications on mechanical resistance [7, 8].

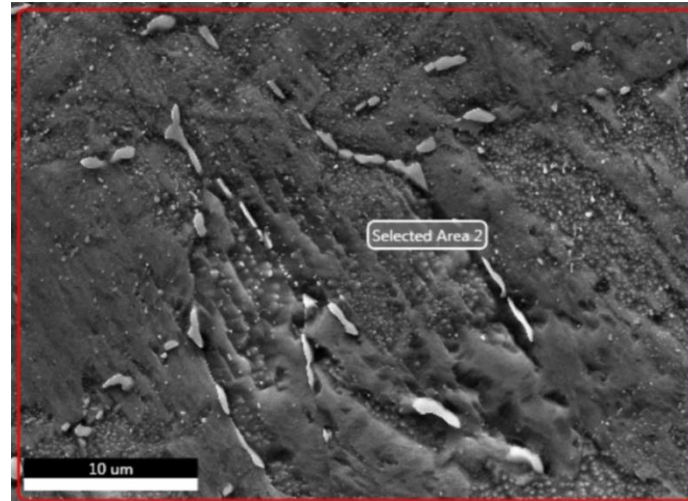More specific, the casted steel hardness is about 308 HV, while quenched steel hardness is about 315 HV.

Fig.8. SEM microscopy of quenched structure

The SEM image brings more categorical assertions regarding the network of austenite, being clear to observe that it is reduced in a relevant mode. At the same time, the acicular martensitic structure with the "lath" distribution is more refined, predicting a better mechanical behavior.

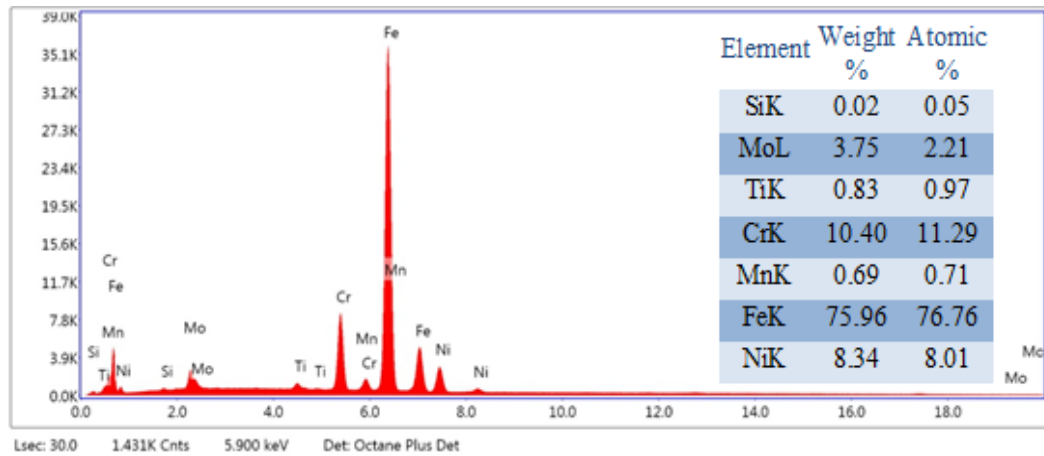| Element	Weight %	Atomic %
SiK	0.02	0.05
MoL	3.75	2.21
TiK	0.83	0.97
CrK	10.40	11.29
MnK	0.69	0.71
FeK	75.96	76.76
NiK	8.34	8.01

Fig.9. EDS spectra and local chemical composition on selected area

The EDS analysis emphasizes the same aspect revealed by the casting structure that the steel maintains the same homogeneity after quenching.

The structural details after tempering are clustered in Fig. 10 and Fig. 11.

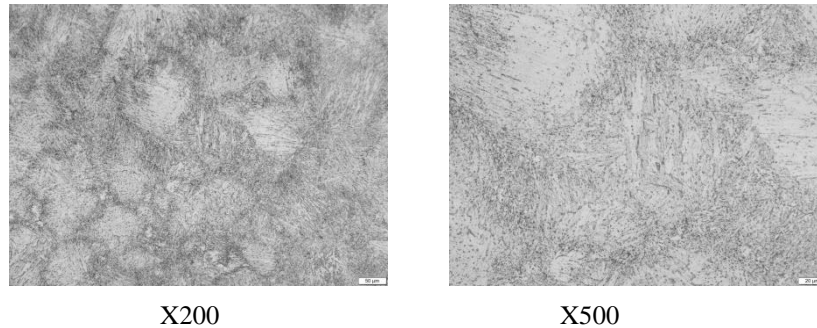|	
X200	X500

Fig. 10. Optical microscopy of quenched structure, Marble's reagent

As it is seen in the optical micrographs, the tempered structure is totally different comparing to other structures. Along the martensite needles a fine dispersion of precipitated particles is present, but with a more advanced tendency at grain boundary, otherwise marked by the austenitic traces. The tempered structure hardness is about 512 HV, almost 1.6 times higher than the quenched structure. This effect suggests that all involved transformations are closer to specific phenomena of aging process and not of tempering, being involved the precipitation (dispersion) hardening mechanism. These results are similar with outcomes from other scientific papers referring to maraging steels [9, 10, 11].
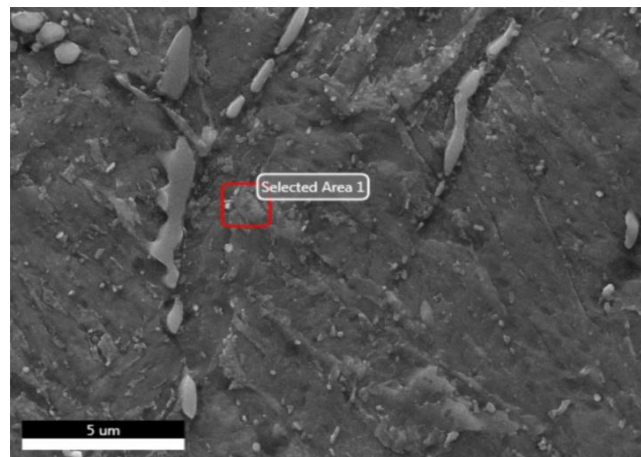

Fig.11. SEM microscopy of tempered structure

The tempered structure studied by SEM technique shows notable differences comparing to quenched structure. The most important details are underlined by the fine rounded particles resulting by a precipitation phenomenon, which are disposed onto acicular martensitic needles.
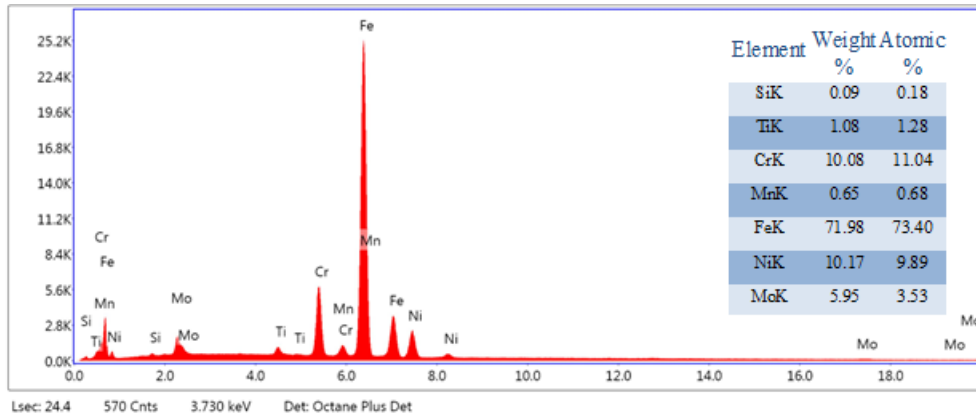
Fig.12. EDS spectra and local chemical composition on selected area A1

Its specific form suggests that they are in a transitory stage, when connection with matrix (martensitic needle) is semi-coherent. Another detail of the structure is revealed by the presence of austenitic traces, but without any special importance regarding to hardening mechanism. [12]

The EDS spectra, especially local chemical analysis, bring valuable information. As can be seen, in the area where these precipitates are presented, the composition deviates from the value which was analyzed before tempering. More concretely, the content of nickel, molybdenum and even titanium grow to the detriment of iron, suggesting that the precipitates are some intermetallic compounds. Calculating the atomic ratio of the synthesized alloy, e.g. 9.89/3.53, results the value of 2.80 which is very close to 3, a critical value. Analyzing these aspects, we consider that the intermetallic compounds involved in precipitation hardening mechanism are type Ni_3X, where X in our case is Mo (Ni_3Mo).

3. Conclusions

The paper proposes a non-conventional martensitic stainless steel, having low carbon content (approx.0.02%), 10%Cr, 10%Ni and 0.9%Ti, designed for hydropower turbine. Accordingly, to Schaeffler's diagram, the steel has biphasic austenito-martensitic structure. The new fabrication technique, involving an induction furnace with a cold crucible in vacuum and argon atmosphere, allows obtaining a correct structure after casting, without inclusions or discontinuities. Subsequently, a quenching and tempering were applied in order to confer the final properties. The micro-structural investigation gives detailed information regarding the solid-state transformations involved in properties modifying. So, the quenched structure is different by a higher degree of finesse concerning the martensitic structure, while the austenite network is clearly diminished. This information offers a positive prediction relating to mechanical resistance. The tempered structure is totally different comparing to other studied structures. Along the

martensite needles a fine dispersion of precipitated particles is present, but with a more advanced tendency at grain boundary, otherwise marked by the retained austenitic traces. The hardness of the tempered sample is about 512 HV, almost 1.6 times higher like the tempered structure. This effect suggests that the transformation mechanism is rather close to specific phenomena of the aging process and not of the tempering. The intermetallic compounds involved in precipitation are such as Ni_3Mo. The obtained data has a lot of similarities with the phenomena which are encountered in the maraging steels class, and this is creating a new category with duplex properties.

R E F E R E N C E S

[1] *Sohaciu. M, Ciuca. S., Savastru. D., Coman. G., Predescu. A., Berbecaru. A., Cotrut. C., Matei. E., Gherghescu.I. A., Predescu. C.,* Influence of turbine blades fabrication conditions on their lifetime, Optoelectronics and Advanced Materials-Rapid Communications, **Vol.**: 10, Issue: 3-4, Pages: 257-261, MAR-APR 2016;

[2] *E. Matei, C. Predescu, A. Berbecaru, A. M. Predescu, R. Trusca,* Leaching tests for synthesized magnetite nanoparticles used as adsorbent for metal ions from liquid solutions, Digest Journal of Nanomaterials and Biostructures, **vol. 6**,no. 9, 2011, pp. 1701 – 1708

[3] *G. Lucacci*, 7 – Steels and alloys for turbine blades in ultra-supercritical power plants, Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plant, 2017, 175–196;

[4] *C. Phaneendra Kiran*, *Shibu Clement*, Surface quality investigation of turbine blade steels for turning process, Measurement, **Vol.** 46, Issue 6, July 2013, pag. 1875-1895;

[5] *T. Tanuma*, 13 – Development of last-stage long blades for steam turbines, Advances in Steam Turbines for Modern Power Plants, 2017, pag. 279–305;

[6]*E. Matei, A. M. Predescu, E. Vasile, C. Predescu*, Investigations on nano-iron oxides properties used for different industrial applications,OAMRC , **vol. 5**,no. 3, 2011, pp. 296 – 301

[7] *C. Predescu, N. Ghiban, M. Sohaciu, D. Savastru, E. Matei, A. Predescu, A. Berbecaru, G. Coman,* Researches concerning the influence of the heating on quality of forged parts from micro alloyed with boron steel, OAMRC, **vol. 8** no. 1-2, 2014, pp. 149-152

[8] *Gherghescu I.A, Jicmon G.L., Cotrut C., Brânzei M., Berbecaru A.C., Predescu A. M., Ciucă S.*, Influence of aging parameters on the corrosion resistance of a biocompatible Ni50.6Ti49.4 Shape memory Alloy, Revista de Chimie, **vol. 67**, no. 9, 2016, pp. 1734-1738

[9] *G.N. Flint, J.W. Oldfield, D.P. Dautovich, F.T. Mahi*, Corrosion of Iron–Nickel Alloys and Maraging Steel", in Reference Module in Materials Science and Materials Engineering, 2017;

[10] *G.C.S. Nunes, P.W.C. Sarvezuk, V. Biondo, M.C. Blanco, M.V.S. Nunes, A.M.H.de Andrade, A.Paesano Jr.*, Structural and magnetic characterization of martensitic Maraging-350 steel, Journal of Alloys and Compounds, **Vol.** 646, 15 October 2015, Pages 321-325;

[11] *Rajkumar. V., Arivazhagan. N., Devendranath Ramkumar K.*, Studies on welding of maraging steels, Procedia Engineering, 75 (2014) 83 – 87, 7th International conference on materials for advanced technology.

[12] *Gray, V.; Galvin, D.; Sun, L.; Gilbert, E. P.; Martin, T.; Hill, P.; Rawson, M.; Perkins, K.*, Precipitation in a novel maraging steel F1E: A study of austenitization and aging using small angle neutron scattering, Materials Characterization, 129 (2017) 270-281.