MAGNETIC PROPERTIES OF TITANIUM-CONTAINING LOW-NICKEL MARAGING STEEL PRODUCED BY ELECTROSLAG REMELTING TECHNOLOGY

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Abstract

The study of the correlation between structure and physical properties is of fundamental importance in material science. All the physical and chemical properties of a material are strongly structure dependent, and the knowledge of the microstructure is of basic importance in the design and development of new material for technological application.

In this work, effect of Electroslag on cleanliness: size, count, distribution of non-metallic inclusion and consequently on the magnetic properties of Ti-containing cobalt-free low-nickel Maraging steel were studied. Microstructure and effect of chemical composition is present. Identification and quantitative of different phases were measured by X-ray diffraction. Also, quantitative of magnetic and non-magnetic phases was measured by magnetization measurements.

The experimental results indicated the strong positive effect of Electroslag Remelting, ESR on reducing the number of large NMI. The accumulative count of NMI decreases by different investigated ESR slags. ESR process redistributes and decreases the count of non-metallic inclusions. The number of NMI per mm² decreases by ESR under investigated slags.

Also, Results indicate that, the values of magnetic properties changes with changes in chemical composition, production technology, size and distribution of second phase.

Keywords: ESR- Electroslag- Maraging – X-ray- Magnetization – Coercive Force- Cleanliness - Microstructure

1. INTRODUCTION

The 18 Ni Maraging steel are high alloyed low carbon steels with an additions of various alloying elements such as Co, Mo, Ti, and Al for precipitation hardening. In Co-free Maraging steels; titanium is used as one of the primary strengthening elements to replace the expensive cobalt. Ti-strengthened Maraging steels can be hardened by a single step aging treatment. After solution treatment, the heavily dislocated martensite is hardened by the precipitation of (NiFe)₃(TiMo) particles during aging. These steels are classified as materials of ultra high strength combined with good toughness[1-4]. These quality steel grades require sophisticated production technology. The high strength to weight ratio, good weld-ability, ease of machining in the solution annealed condition, and dimensional stability during aging make Maraging steel an ideal choice for critical rocket motor casing applications in aerospace industries. The properties of Maraging steel depend to a large extent on the production and refining technology which affect homogeneity of alloying elements (microstructure) as well as the cleanliness of the produced steel. Electroslag refining is a useful remelting process by which clean steels can be produced for sophisticated applications.

The study of the correlation between structure and physical properties is of fundamental importance in material science. All the physical and chemical properties of a material are strongly structure dependent, and the knowledge of the microstructure is of basic importance in the design and development of new material for technological application.
The magnetic properties of ferromagnetic materials are sensitive to the microstructural changes induced by thermal and mechanical treatments. It has also been shown by a number of authors that magnetic properties obtained from the magnetization curve depend strongly on the stress/strain history of the material. The domain-wall movement during magnetization is greatly influenced by microstructural features.

It is known that residual stress distribution or microstructural defects such as precipitates, inclusion, second phase, grain boundaries and dislocations in materials can hinder magnetic domain wall movement and thus increase coercivity. Previous reports on the relationship between grain size and magnetic coercivity of steels are contradictory. Yamaura et al., Sakamoto et al. and Kim et al. reported that the grain size affects the magnetic coercivity largely. On the other hand, Kwun et al. and Jiles reported that it affects the magnetic coercivity little. The above-mentioned contradictory results are thought to be due to the different carbon content of the specimens investigated. In other word, grain size have an effect on the magnetic coercivity in case of ultra low carbon steel, while it doesn’t in case of high carbon steel because large amount of carbide particles play a more dominant role than grain boundaries in determining the magnetic coercivity.

Louis Néel inclusion theory predicts $H_c \approx V_v$, where $H_c$ is the coercive field and $V_v$ is the inclusion volume fraction. Louis Néel approach is based on the assumption that magneto-static energy is stored around second phase particles (inclusions and carbides) and that magneto-static energy can be decreased when domain walls intersect the particles, causing the walls to be “pinned” by the inclusions.

The contamination of Maraging steels with non metallic inclusions (NMI), homogeneity of matrix composition, zone segregation of alloying elements have great influence on their magnetic properties. For the above reasons electroslag refining, ESR is used to produce such steels from electrodes prepared by induction furnace. In this work, two series of titanium containing cobalt free Maraging steels were produced by ESR using three different slag chemicals compositions. This work aims at; study the effect of cleanness and microstructure on magnetic properties of titanium containing free cobalt low nickel Maraging steel produced by Electroslag Remelting, ESR.

2. EXPERIMENTAL WORK

2.1 Material production

During the course of this work, new grades of low nickel free cobalt Maraging steel have been developed with different titanium, molybdenum and chromium contents. Maraging steel with 12 mass % Ni as base metal were developed. Investigated steels group includes three grades of steel with titanium content varies from 0 to 0.677 mass%. New production technique is used, in this technique Maraging steel were produced as consumable electrode in open-air induction furnace followed by remelting in ESR furnace under different three chemical composition of CaF$_2$ based slag. These slags have approximately the same density and different viscosity, interfacial tension and basicities, table 1. Melting practice and production condition of such steels were reported elsewhere.

<table>
<thead>
<tr>
<th>Flux No.</th>
<th>Chemical Composition, wt. %</th>
<th>Physical Properties$^{(16)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaF$_2$</td>
<td>CaO</td>
</tr>
<tr>
<td>F1</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>F2</td>
<td>52.5</td>
<td>-</td>
</tr>
<tr>
<td>F3</td>
<td>70</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition and physical properties of synthetic slags at 1600°C
2.2 Chemical composition of investigated steel

To evaluate the efficiency of ESR process, effect of slag chemical and physical properties and the behavior of alloying elements during the refining process, samples from consumable electrode produced by air melting induction furnace, IF and ingots produced by electroslag remelting, ESR at the top and the bottom of the ingots were taken both at the center, half radius and the edge then chemically analyzed by using spectrographic analysis (SPGA).

2.3 Non-metallic Inclusions Evaluation:

As non-metallic inclusion (NMI) have strong effect on the properties and behavior of steel, shape and size distribution of NMI have their own effect on the technological properties of Maraging steel. So it is of great importance to determine shape and size distribution of NMI before and after ESR process.

For size distribution of nonmetallic inclusion, NMI (oxide, sulphide, carbide and nitride), a semi automatic Carl Zeiss particle size analyzer was used in conjunction with optical micrographs taken from polished specimen. The size evaluation is based on the equivalent circle area diameter (ECAD)

2.4 Optical micrography

Maraging steel obtained from air melted induction furnace, IF and electroslag remelting, ESR were cut into 10 mm x 10mm square specimen pieces for observation under optical microscope. Careful machining and grinding first flattens the specimen surface. The flat surface was then polished using emery paper (80–1200 grit). Final polishing of the sample surface has been carried out on a polishing cloth smeared with paste of fine particles of alumina to ensure scratch – free polished surface. In order to reveal the surface details, the polished surface of the samples are finally etched with an etchant containing 1 gm of CuCl₂ + 30 ml HCl + 50 ml HNO₃ +100 ml H₂O. Subsequently, the metallographically polished and etched samples are observed in an optical microscope with reflected light at different magnification.

2.5 Second phase austenite measurements

A quantitative determination of the volume fraction of the existing phases, especially the retained austenite, is essential for the evaluation of the Maraging steel properties. The amount of retained austenite in investigated Maraging steel was evaluated by magnetic measurements. Magnetic method was used during the course of this work because magnetization measurements have intrinsic advantages, as they are accurate and probe the bulk of the materials. The intrinsic saturation magnetization per unit mass (Bs) were performed in vibrating samples magnetomer (VSM) in VSM LDJ9600-1 magnetomer. An applied magnetic filed is used to induce a magnetization in sample. The magnetic fields was applied to max value of 5 KOe and then decreased stepwise to zero fields, i.e. from 5 to 0.25 KOe in step of 0.25 KOe, from 0.25 to 0 KOe in step of 0.05 KOe. The measurements were performed in decreasing field in order to create well-defined field history for the magnetization. The relative error of the measurements data is smaller than 0.5 %. The obtained data from magnetization were confirmed by XRD measurements for number of samples. The X-ray diffraction was carried out in BRUKER AXS - D8Advance diffractometer use KCuα radiation. The volume fraction of austenite, Va, was calculated by the following equation:

\[ V_a = \frac{1.4 I_A}{I_M + 1.4 I_A} \]  

Where I_A is the average of the integrated intensity from the (111)_A and (200)_A planes and I_M is the intergraded intensity from the (110)_M planes. The correction factor 1.4 was determined experimentally by Miller (17-18).
2.6 Magnetic properties of investigated steels:
The magnetic properties (coercive force (Hc), saturation magnetization (Bs), remanence (Br) and residual magnetization (Mr) were measured at room temperature by an extraction method with a maximum applied field of 5KOe. The magnetic measurements were performed in vibrating samples magnetometer ((VSM)-LDJ9600-1).

3. RESULT & DISCUSSION
To evaluate the effect of electroslag remelting parameter on the behaviour of different alloying elements table 3. were constructed. Table 3. shows the average chemical composition of consumable electrodes produced by induction furnace and ingots electro-slag remelted under different investigated slags. It is noticeable that the yield of alloying elements in ESR under different investigated slag is high.

Table 1: Chemical composition of investigated steel

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Process</th>
<th>Chemical composition wt, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>M1</td>
<td>IF</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>ESR1</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>ESR2</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>ESR3</td>
<td>0.030</td>
</tr>
<tr>
<td>M2</td>
<td>IF</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>ESR1</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>ESR2</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>ESR3</td>
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<tr>
<td>M3</td>
<td>IF</td>
<td>0.039</td>
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<td></td>
<td>ESR1</td>
<td>0.023</td>
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<td></td>
<td>ESR2</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>ESR3</td>
<td>0.029</td>
</tr>
</tbody>
</table>

3.1 Effect of electroslag parameter on non-metallic inclusions
Figure 1 shows the effect of investigated slags on the number of NMI contaminated in steels. The accumulative count of NMI of different remelting processes, induction furnace remelting (IF) and electroslag remelting (ESR) under different slags for investigated steels are shown in Fig. 2. These figures clarify the strong positive effect of ESR on reducing the number of non-metallic inclusions especially large one. The accumulative count of NMI decreases by ESR under any of the selected three slags.
Fig. 1. Effect of ESR process on the NMI total counts

Fig. 2. Effect of ESR process under different slag on reduction of accumulative count distribution occupied by non metallic inclusion for different investigated steel

The effect of investigated slags on the distribution of NMI contaminated in steels is given in Fig. 3. The reduction % in each size of non-metallic inclusions of investigated steel after ESR comparing by initial one in consumable electrode is illustrated in Fig. 4. From these results could show that ESR process redistributes and decreases the count of non metallic inclusions. Non metallic inclusions with size larger than 50µm were completely removed using any of the three slags under investigation. 40-80% of total NMI with sizes ranges from 5 -20 µm was removed by using slag no 3 and slag no. 1, receptively. On the other hand, slag No. 2 removes completely non metallic inclusions with sizes ranges from 5-20 µm. From previous results we can concluded that slag with moderate viscosity and surface tension, slag No. 2 is powerful for removal non-metallic inclusions than other investigated slag.

Fig. 3. Effect of investigated slags on the distribution of NMI contaminated in steels

Fig. 4. Reduction % in each size of non-metallic inclusions of investigated steel after ESR comparing by initial one in consumable electrode
3.2 Effect of production technology on magnetic properties of Maraging steel:

In Fig. 5. is shown the hysteresis plots for investigated Maraging steel produced by induction furnace (IF) and different electroslag remelting heats (ESR). Test was done after heat treatment under optimum condition (solid solution 820 °C– aging at optimum temperature and time). Table 2. shows summary of magnetic properties: the coercive force (Hc), saturation induction magnetization (Bs), and romance (Br) for investigated steels. The values of these properties changes with changes in chemical composition, aging condition (temperature, time), production technology, size and distribution of second phase because of the change in non magnetic particles content (austenite – non metallic inclusion).

![Hysteresis plots](image)

**Fig. 5.** Plots of hysteresis loop for investigated Maraging steel

![Effect of wt non-metallic inclusion](image)

**Fig. 6.** Effect of wt non-metallic inclusion for investigated steels

**Table 3:** Summary of magnetic properties of investigated Maraging steel

<table>
<thead>
<tr>
<th>Steel no.</th>
<th>process</th>
<th>Hc</th>
<th>Hk</th>
<th>Br</th>
<th>Bs</th>
<th>Mass, g</th>
<th>Bm</th>
<th>Magnetic method</th>
<th>X-ray method</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total gamma</td>
<td>Martensite</td>
</tr>
<tr>
<td>M1</td>
<td>IF</td>
<td>33.73</td>
<td>3455.00</td>
<td>1.27</td>
<td>168.30</td>
<td>2.32</td>
<td>199.22</td>
<td>10.50</td>
<td>89.50</td>
</tr>
<tr>
<td>ESR1</td>
<td>34.62</td>
<td>2929.00</td>
<td>1.81</td>
<td>151.70</td>
<td>3.33</td>
<td>190.71</td>
<td>20.46</td>
<td>79.54</td>
<td>19.7</td>
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<tr>
<td>ESR2</td>
<td>25.94</td>
<td>3142.00</td>
<td>1.55</td>
<td>180.40</td>
<td>3.87</td>
<td>189.82</td>
<td>4.96</td>
<td>95.04</td>
<td>4.4</td>
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<tr>
<td>ESR3</td>
<td>27.36</td>
<td>3358.00</td>
<td>1.41</td>
<td>170.20</td>
<td>2.52</td>
<td>187.40</td>
<td>9.18</td>
<td>90.82</td>
<td>8.0</td>
</tr>
<tr>
<td>M2</td>
<td>IF</td>
<td>26.13</td>
<td>3134.00</td>
<td>1.60</td>
<td>150.80</td>
<td>4.51</td>
<td>200.56</td>
<td>19.82</td>
<td>80.18</td>
</tr>
<tr>
<td>ESR1</td>
<td>27.10</td>
<td>3596.00</td>
<td>1.21</td>
<td>162.40</td>
<td>2.19</td>
<td>188.93</td>
<td>14.04</td>
<td>85.96</td>
<td>13.7</td>
</tr>
<tr>
<td>ESR2</td>
<td>28.46</td>
<td>3092.00</td>
<td>1.68</td>
<td>172.90</td>
<td>4.00</td>
<td>188.10</td>
<td>8.08</td>
<td>91.92</td>
<td>7.6</td>
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<tr>
<td>ESR3</td>
<td>18.10</td>
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<td>186.10</td>
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<td>188.77</td>
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<td>98.58</td>
<td>0.7</td>
</tr>
<tr>
<td>M3</td>
<td>IF</td>
<td>20.63</td>
<td>3300.00</td>
<td>1.06</td>
<td>167.40</td>
<td>3.51</td>
<td>187.55</td>
<td>10.74</td>
<td>89.26</td>
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<tr>
<td>ESR1</td>
<td>19.27</td>
<td>3119.00</td>
<td>1.00</td>
<td>173.80</td>
<td>3.13</td>
<td>187.64</td>
<td>7.37</td>
<td>92.63</td>
<td>7.1</td>
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<tr>
<td>ESR2</td>
<td>21.51</td>
<td>3195.00</td>
<td>1.23</td>
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<tr>
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<td>3.28</td>
<td>189.93</td>
<td>2.39</td>
<td>97.61</td>
<td>1.9</td>
</tr>
</tbody>
</table>
3.3 Effect of non metallic inclusions on magnetic properties of Maraging steel:

It well known that, Inclusion may take many forms. They may be oxide, sulphide, carbide and nitride particles and the like existing as impurities in the steel matrix. They may be simply holes or crack. From magnetic point of view an inclusion in the domain region which this different spontaneous magnetization from surrounding material, or none at all. We will regard an inclusion simply as a non magnetic region.

The effect of non-metallic inclusion, NMI on both samples (IF, ESR) were analyzed by evaluating the changes in its magnetic properties. The variation in product of the coercivity (Hc) and romance (Br) (Br*Hc) with weight percent of NMI are shown in Fig. 6. This figure shows that the magnitude of product of coercivity (Hc) and romance (Br) for both induction furnace (IF) and electroslag remelting (ESR) steels increase with increasing NMI wt, %. The result can be attributing to; non-metallic inclusion in materials can hinder magnetic domain wall movement and thus increase coercivity.

Variation on (Br*Hc) is not depending only on wt of non-magnetic particle but also on its chemical composition. Based on different studies exceptions are that the Maraging steels will normally contain Ti (C,N) which are large and angular, these particles can contain molybdenum as will as titanium. In additional it appears that smaller, globular TiC or (Ti, Mo)C particles can also be present, especially in the steels containing higher titanium and / or carbon levels. On the other hand, the presence of molybdenum with chromium can influence the formation of carbides when added together with molybdenum. With a certain ratio between chromium and molybdenum, complex carbides of the formula M₆C, which contain chromium, molybdenum and iron, can form instead of interstitial phase MoC. Other particles may be observed, those precipitated during aging of the steel. These include the precipitates normally associated with age hardening such as Ni₃Mo and Ni₃Ti. However, diversity of other phases has been reported to form during aging of even the more or less conventional Maraging steels. These include Fe₂Ti, FeMo, Fe₂Mo and Fe-Ti. Depending on the nature and size of the particles precipitated on aging they could become active in the magnetization process.

To study the effect of count and area occupied by non-metallic inclusion on product of Br and Hc Fig. 7. was constructed. All investigated steels show that increase of Br*Hc value with increasing NMI count and area. This variation of coercivity can be attributed to the domain- wall movement during magnetization is greatly influenced by count and area of non metallic inclusions. The coercivity of specimens with non-metallic inclusion on martensite matrix seems to arise from the pining of domain walls to NMI particles. The previous result was confirmed by many investigators. White arrows in Fig. 8. shows the non-metallic inclusion presence in investigated steel.

3.4 Austenite + total non magnetic particles

From previous section, the product of Br*Hc is function of non magnetic particle presence on the matrix. Fig. 9 shows the relationship of product of Br*Hc with total (austenite – non metallic inclusion) non magnetic particles and net austenite respectively. The measured magnetization induction decreased linearly as total and net non-magnetic particles increased, table 2. This reduction can be attributed to consider that austenite is non magnetic particles (paramagnetic). The results confirm work which was done by Louis Néel.
The measured coercivity increased by increase austenite and total non magnetic particles weight percent. This increasing can be attributed to consider austenite as a second phase (voids). When domain wall intersect austenite phase the magnetostatic energy associated with the austenite is reduced. Hence, the magnetic domain walls become attached to austenite within magnetic materials, because this minimizes the magnetostatic energy locally. To move the domain walls away from the voids (austenite) a certain force is required which must be supplied by the magnetic field. The larger this required force the greater coercivity of the material. Also, as we know austenite was precipitate as thin film in martensite; black arrow in Fig. 8 which increases grain boundaries so hinder domain wall movement and thus increase coercivity. These results were confirmed by many investigators [20-21].

4. CONCLUSIONS
1. Strong positive effect of ESR on reducing the number of non metallic inclusions especially large one
2. Non metallic inclusions with size larger than 50µm were completely removed using any of the three slags under investigation.
3. 40-80% of total NMI with sizes ranges from 5 -20 \(\mu m\) was removed by using slag no 3 and slag no. 1, receptively.
4. Slag No. 2 removes completely non metallic inclusions with sizes ranges from 5-20 \(\mu m\).
5. Non-metallic inclusion in materials can hinder magnetic domain wall movement and thus increase coercivity
6. The nature and size of the particles precipitated on aging they could become active in the magnetization process.
7. The domain- wall movement during magnetization is greatly influenced by count and area of non metallic inclusions. The coercivity of specimens on Maraging matrix seems to arise from the pining of domain walls to austenite and NMI particles.

**REFERENCE**