

Military Technical College
Kobry El-Kobba
Cairo, Egypt



12-th International Conference
on
Aerospace Sciences &
Aviation Technology

IMPROVEMENT OF MECHANICAL PROPERTIES OF MARAGING STEELS USING ESR TECHNIQUE

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ABSTRACT

Electroslag refining is a useful remelting process by which clean steels can be produced for sophisticated applications. In this investigation, maraging steels have been electroslag refined and the improvement in its ductility have been assessed using hardness, and tensile strength tests; electroslag refining has improved the ductility considerably. Results indicate that ESR obtains higher recovery of alloying elements under slag of high viscosity and low interfacial tension (slags 1 and 3). Results indicate that it should be possible to raise both strength and toughness for ESR ingot to much higher value using appropriate remelting condition and heat treatment. It is clear from experimental data that there is a steady rise in peak hardness level in the case of the three types of investigated slags for all steel under investigation. At the same time, there is a widening in the aging temperature at which peak hardness is attained in order ESR2, ESR3, ESR1. This result also clarifies that ESR steel has higher retained austenite content than IF heats, which depends mainly on its chemical compositions. In other hand, ESR process under any of the investigated fluxes leads to uniform distribution of austenite grain. The improvement in tensile properties in ESR steel has been attributed primarily to the removal of non-metallic inclusions, the reduction in sulphur content, fine and well distributed microstructure and sufficient austenite content.

KEY WORDS

Electroslag refining – new production technique - free cobalt- maraging steel – tensile properties – non metallic inclusion – retained austenite

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INTRODUCTION:

Over the past 40 years, a generic class of ultra-high strength maraging steels has been developed mainly for aircraft, aerospace and tooling applications. Maraging refers to the ageing of martensite, a martensite that is easily obtained at normal cooling rates due to the high nickel content [1]. The ultra-high strength of maraging steels is due to precipitation, usually of intermetallic compounds, during the ageing process [2–5]. Recent studies revealed that strengthening of 18 wt.% Ni (18Ni) maraging steels results from the combined presence of Ni_3Ti and Fe_2Mo [4] or Fe_7Mo_6 [5] precipitates. The formation of Ni_3Ti takes place rapidly due to the fast diffusion of Ti atoms [4,5]. In the past, Bohler Edelstahl GmbH made maraging steels via two production routes. The first followed the traditional route: melting in an electric arc furnace followed by ladle metallurgy. The electrodes were remelted in a vacuum arc furnace. The second was the double vacuum melting route meaning vacuum melting followed by vacuum remelting. Due to high cost of this technology, ESR technique have been used by steel technology department in central metallurgical research & development institute, CMRDI, to produce a new maraging steel. Maraging steel electrodes can be produced in the IF, mainly for tool steel grades. This route can process cheaper raw materials and back scrap with a composition similar to the steel to be produced. No complicated scrap preparation is necessary, but melting of steel containing Ti, Mo and Cr is a problem. The high affinity of titanium and aluminum for oxygen and nitrogen causes a significant increase in the inclusion level and an unsatisfactory electrode surface when these alloys are cast in air. The apparent advantages of low cost raw materials and the cheaper production route provided by open melting must be offset against the increased tendency to form cracks in the electrode and the VAR-ingot. Hot forming problems and reduced yield are caused by poor ingot quality. For this reason, this production route was replaced by the open air induction melting followed by ESR process.

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.

The chemical composition analysis, hardness values measurements for as forged ingots as well as heat treated samples, microstructure, austenite content, tension ductility and behavior of non metallic inclusions were determined for steel samples produced by air induction melted and ESR techniques.

The main objective of this investigation is to examine the effects of a new remelting technique on the morphology, microstructure and mechanical properties of the new low nickel free cobalt maraging steel.

EXPERIMENTAL:

During the course of this work, a new grade of low nickel cobalt free Maraging steel has been developed with different contents of titanium, molybdenum and chromium. Steel group M1, M2, M3, M4 nominated of Maraging steel with 12 wt. % Ni as base metal were developed. In this group of steel, titanium content varies from zero to 1.6 wt. percentage.

With the objective of this study, electroslag remelting (ESR) of a new grade of low nickel free cobalt Maraging steels under calcium fluoride (CaF_2) based slag has been investigated. Complete chemical composition analysis of the charging material was carried out then induction furnace with capacity 100 kg was used to melt down this charging material. The molten metal was casted in cylindrical ingots with diameter 100mm and height 180mm. These cylindrical ingots were forged and used as consumable electrodes in ESR machine. Consumable electrodes were electroslag refined under pre-fused CaF_2 based flux with different addition of Al_2O_3 , CaO , and TiO_2 table 1. These synthetic slags were produced by pre-fusion of the following raw materials in submerged arc furnace: flourspare, limestone, and alumina. Chemical composition of three raw slag materials was determined by XRF and summarized in table 2. These slags have approximately the same density and different viscosity, interfacial tension and basicities.

The produced ingot from ESR is taken off from the mold after cooling about three hours. At this time, the slag skin and the slag cap were sampled after weighing and the surface appearance of the ingot was observed. ESR ingots were forged by using the same routine of forging the consumable electrode as shown in Fig. 1. Both IF and ESR samples from the top and the bottom of the ingots were taken then chemically analyzed by using spectrographic analysis (SPGA). Samples from consumable electrodes and ESR ingots were cut off and prepared for microscopic examination. In order to reveal the surface details, the polished surface of the samples are finally etched with an etchant containing 1 gm of CuCl_2 + 30 ml HCl + 50 ml HNO_3 + 100 ml H_2O [6].

NMI samples from the different ingots produced from induction furnace and electroslag refining isolated by using electrochemical cell as described elsewhere [7].

Strengthening of maraging steels is achieved by soaking at definite temperature for definite time. Their high strength is attained by combining two strength mechanisms: Martensitic transformation and Martensitic aging. To optimizing the heat treatment process (aging time and temperature) specimen from each forged steel before and after ESR were subjected to solution treatment at 820 ± 5 °C for 60 min then air cooled (AC). The effect of variation of aging temperature (400, 425, 450, 475, 500, 525, and 550) and time (60, 120 and 240 min) on hardness were established for all steels after solution annealing treatment. Tensile strength was determined for different steels after optimum heat treatment conditions.

RESULT & DISCUSSION :

1. Production technology:

It is noticeable that yield and recoveries of alloying elements in ESR are high. Table 3. shows the chemical composition of consumable electrodes produced by induction furnace and ingots remelted under different investigated slags. Samples were cut then ground and polished to evaluate chemical composition, and hence the recovery of alloying elements. The recovery of alloying elements in all ingots produced by electroslag remelting (ESR) process using any of the three based calcium fluoride slags are given in tables 4. Recovery can be defined as metal out wt % divided by metal in wt %.

The small deviation in chemical composition in produced ingot than consumable electrode may be attributed to transfer of oxygen from atmosphere into metal through slag enhancing oxidation process. Thus, most alloying elements (except carbon) are slightly lower in ingot than consumable electrode. On the contrary, to the other alloying elements, carbon content in the ingot is slightly higher than consumable electrode. This behavior may be attributed to the effect of carbon content in slag at the start of operation. This slag was pre-fused in an arc furnace. Carbon is picked up by slags to some extent.

2. Hardness :

The general influence of ESR technique and alloying element on hardness of low nickel free cobalt maraging steel is illustrated in Fig. 2. Fig. (2) illustrates the aging curves for different maraging steels under investigation at different aging temperatures and at different time. The hardness of investigated steels produced in IF (induction furnace) and ESR increases as aging temperature increases, a widened peak hardness is obtained (as illustrated in Fig. 2. Further increase in aging temperature above peak aging temperature is accompanied by decreasing in hardness through overaging. From this figure, it is clear that there is a steady rise in peak hardness level in the case of the three types of investigated slags for all steel under investigation. At the same time, there is a widening in the aging temperature at which peak hardness is attained in order ESR2, ESR3, ESR1 as shown in Fig. 2. Furthermore, it is clear from Fig. 2, that the effect of ESR technology on aging temperature could be obtained by comparing the results obtained in case of rude steels (air melted induction furnace) with remelted by ESR. The change of aging temperature and gain of hardness obtained by ESR technique may be attributed to increasing the percentage of intermetallic compound, decreasing percentage of retained austenite and decreasing of grain size. The presence of these precipitates increases the strength and the hardness of the steel. From this figure it could be concluded also that the remelting of the consumable electrodes under the CaF₂ based slag generally enhances the hardness profile upon aging.

3. Microstructure:

Fig. 3. shows the microstructure of different heats of maraging steel under investigation produced by induction furnace and electroslag re-melting after optimum aging conditions. Structure of steel produced by both IF and ESR comprises of martensite + retained austenite+ fine intermetallic compound. By comparing between microstructure of investigated steels we found that, the structure of ESR are very finer, well distributed and free from segregation or band structure than IF steels.

Typical light micrographs of the material produced by IF and aged under optimum condition are shown in first row in Fig. 3. The microstructure, in general appeared lamellar in morphology. The prior-austenite grain boundaries could not be resolved easily. The bright patchy regions, shown by arrows in the micrograph, correspond to regions having considerable volume fraction of reverted austenite. The presence of inter lath austenite, though not fully resolved, is also indicated in the microstructure.

The light micrographs of the material produced by ESR in the peak-aged conditions are shown in Fig. 3. The microstructure in the peak-aged condition essentially consisted of packets of martensite, within prior-austenite grains. The austenite grains, which had transformed into packets of martensite, could still be recognized due to the preferential etching along their boundaries and also due to the fact that the martensite packets within an austenite grain did not extend beyond the respective prior-austenite grain boundary. The martensite substructure could not be observed because of the narrowness of the martensite laths. During aging of the steels under investigation the well-known precipitation reactions occur leading to hardening. It is generally believed that initial precipitation in cobalt free molybdenum containing maraging steel at 480°C occurs as Ni_3Mo , which on prolonged aging is replaced by either Fe_2Mo or the σ phase [8]. Since the alloy additionally contains titanium as a supplemental hardener, the precipitation of Ni_3Ti has also been reported; alternatively, it has been suggested that part of the titanium may be present in the molybdenum precipitate, i.e. as $\text{Ni}_3(\text{Mo}, \text{Ti})$ [9].

The substructure of lath martensite consists predominantly of a high density of tangles dislocations within laths[10].

4. Effect of ESR process on austenite reversion

The percentage of retained austenite influences significantly the mechanical properties of maraging steels; limiting its usefulness as a high strength material (i.e. dual phase). Further deterioration in the mechanical properties of maraging steels is obtained by micro-segregation of retained austenite in localized area i.e. the solute segregation to the existing dislocations that causes dislocation locking.

The amount of retained austenite formed after solution treatment and after aged at optimum condition for consumable electrode produced by IF and ingots produced from different heats of ESR were studied using X-ray diffraction and magnetic balance methods. For IF steel, after solid solution annealing treatment at 820 °C for 1 h (air cooled), with no refrigeration treatment, about $1 \pm 0.5\%$ retained austenite

was detected X-ray diffraction results confirmed that there is a complete martensite transformation after solution-treatment for investigated steels, Fig. 4. Magnetic method is also used during the course of this work. Magnetic method gives higher accuracy for determined retained austenite. Confirmed the results obtained by x-ray method as shown in table 5. For different steels under investigation austenite contents were detected by both methods as shown in table 6.

It is clear from table 6 and Fig. 5. that, the amount of retained austenite in IF steels melted is depend mainly on chemical composition of investigated steels. Increasing the amount of alloying elements i.e. Mo, Cr, and Ti is accompanied by increasing the tendency to form retained austenite. Furthermore, the negligible effect of ESR process on the amount of retained austenite is shown in Fig. 6. This figure clarifies that the amount of retained austenite depends mainly on its initial amount depends mainly on its chemical compositions. In other hand, ESR process under any of the investigated fluxes leads to uniform distribution of austenite grain as shown in Fig. 3. It is expected that this redistribution of austenite grains may improve the mechanical properties.

5. Tensile properties:

The effect of ESR process on the mechanical properties of investigated steels is summarized in table 7. This table 7. represents the average result at room temperature. The aging process was carried out for all steels at the optimum conditions i.e. temp and time.

Examination of these results reveals generally the strong positive influence on the mechanical properties i.e, UTS, YTS, and reduction of area. Figure 6 and 7 illustrate the influence of ESR fluxes on the yield strength and elongation comparing with that of steel melted in induction furnace. It was noticed that ESR process has a rather smaller effect on the yield strength of steel with lowest content of Ti. For this group maximum increment in the yield strength gained by steel with 0.015 % Ti as shown in Fig. 8. As mention above the actual factors which control the mechanical properties of these steels are :

- solid solution strengthening
- precipitation strengthening
- retained austenite in martensite matrix

By studying table 3., the effect of Mo and Cr on the mechanical properties of investigated steels was clarified. The contribution of Mo and Cr and Mo in ultimate tensile strength indicates that the positive effect of Cr and Mo may be attributed to solid solution strengthening mechanism of each element. However, the strength increment of some investigated steels is accompanied by deterioration of steel ductility i.e. Elongation. This deterioration could not be attributed to the aggregate of austenite grains only but also to initial chemical composition steels and its contamination of NMI. The negative effect of NMI, Ti and Mo content on steel ductility is compensating by the positive effect of both Cr and austenite content. Fig.

9 and 10. used to evaluate the effect of Ti or Mo on the UTS and YTS of investigated steels. Due to high affinity of titanium towards both of nitrogen and carbon, titanium nitride and carbide precipitate at high temperatures. In nitrogen and carbon, a portion of titanium is left in solid solution. Due to the relatively higher solubility of titanium carbide in austenite comparing with titanium nitride, an appreciable amount of titanium carbide is dissolved in austenite at reheating temperature (1200 °C) prior to forging process. a portion of titanium in solution is expected to precipitation as fine precipitated of titanium carbide during and after forging causing precipitation strengthening.

In solution treatment process, titanium nitride and carbide inhibit the austenite grain coarsening during austenitizing at 820 °C leading to final microstructure. Fig. 3. illustrates the effect of increasing Ti content on steel structure produced in IF. These figure shows that the structure of induction heats are lath martensite + austenite and NMI. On the other hand microstructure of ESR ingots was very fine and well distributed and austenite grain are impeding between lath martensite Fig. 3.

Furthermore, a portion of titanium in solution is precipitated during solution treatment as Ni₃Ti, which has been confirmed by Dilatometry studies, causing intermetallic precipitation strengthening [6].

In high titanium steels, titanium in excess of stoichiometric with nitrogen and carbon and did not precipitate as intermetallic compound could be in solution causing solid solution strengthening.

Consequently, the strengthening effect of titanium solution treated maraging steel is combined effects of solid solution, microstructure refinement, non-metallic precipitation and intermetallic precipitation strengthening.

6. Effect of retained austenite :

Fig. 11 and 12. were constructed to illustrate the effect of retained austenite on the mechanical strength of investigated steels. Due to high alloying element content retained austenite were formed during solidification because M_s and M_f of this steel decreased to be around Zero temperature[6]. This means high tendency of austenite transformation during solidification and heating during aging. Retained austenite inter-lathe film can increase the strength by transforming to martensite during tensile test similar to behavior of trip steel. It could be conclude that for these steel, retained austenite has appositve effect on all tensile ductility properties.

CONCLUSION:

1. Recovery and homogeneity of alloying elements

- Recovery of all alloying elements in ESR is very high
- Higher recovery of alloying elements is obtained by ESR under slag of high viscosity and low interfacial tension (slags 1 and 3).
- The new production technique "air induction melting followed by ESR" is suitable technique for production this kind of steel.

2. Peak hardness :

- there is a steady rise in peak hardness level in the case of the three types of investigated slags for all steel under investigation. At the same time, there is a widening in the aging temperature at which peak hardness is attained in order ESR2, ESR3, ESR1

3. Microstructure :

- The structure of induction heats are lath martensite + austenite and NMI. On the other hand microstructure of ESR ingots was very fine and well distributed and austenite grain are impeding between lath martensite

4. Mechanical properties:

- ESR process has a positive effect on tensile strength properties of maraging steel. This is due to its effect on reducing the NMI content, improving the homogeneity of matrix composition, minimizing the zone segregation of alloying elements and improving the NMI distribution.
- Retained austenite inter-lath film can increase the strength by transforming to martensite during tensile test similar to behavior of trip steel. For these steel, retained austenite has a positive effect on all tensile ductility properties.

ACKNOWLEDGMENT:

Authors express their grateful thanks to Prof. Dr. Eng. Mamdouh Eissa, Head of Steel Technology Dept. for his valuable discussion and encouragement. Thanks are also due to Prof. Dr Hoda El - Faramawy and Ass. Prof Dr. Taha Mattar, CMRDI, Cairo, Egypt, for their continuous help. The authors are deeply grateful for many years of inspiring interactions with all steel technology members, Steel Technology Dept., CMRDI, Cairo, Egypt.

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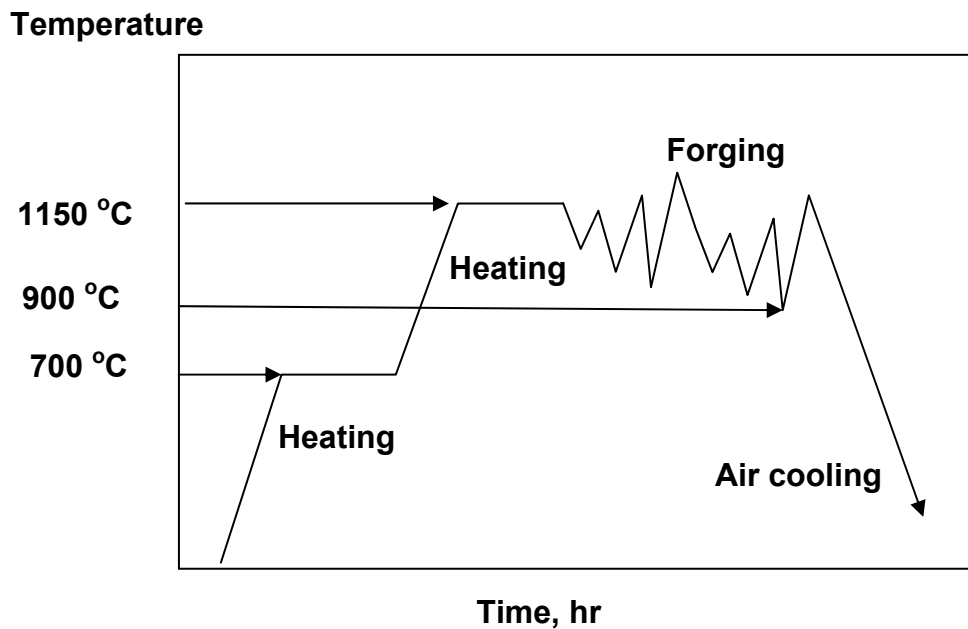
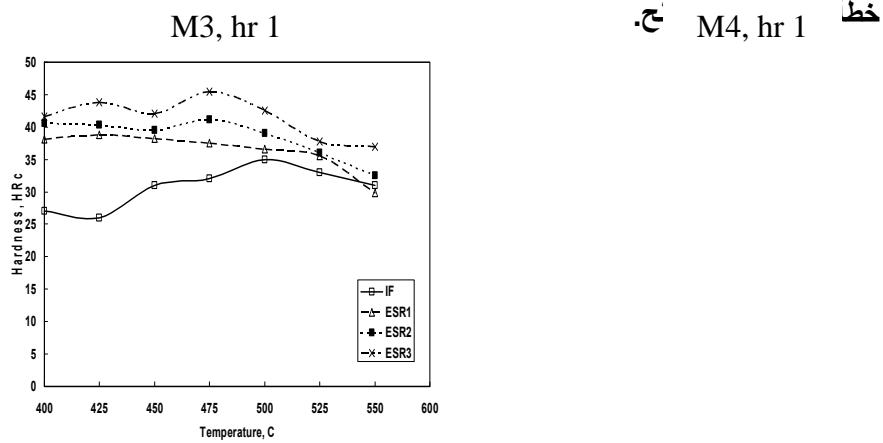


Fig. 1 Illustration of the schedule of forging process

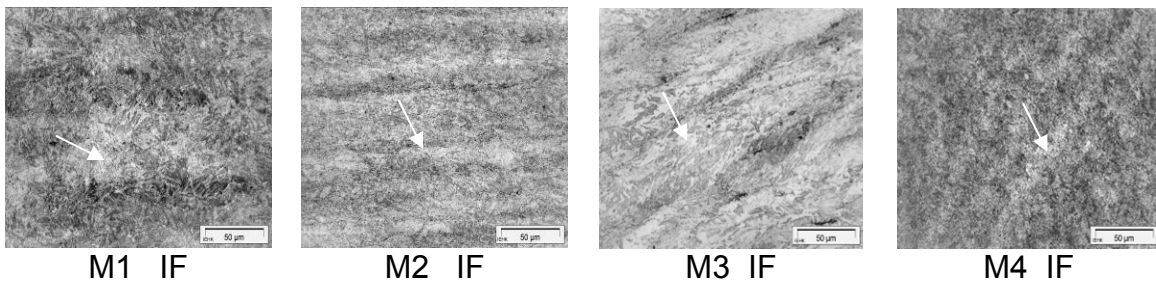
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Fig. 2.a Aging curves for different Maraging steels under investigation at different aging temperatures and at different times.



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Fig. 2.b Aging curves for different Maraging steels under investigation at different aging temperatures and at different times.



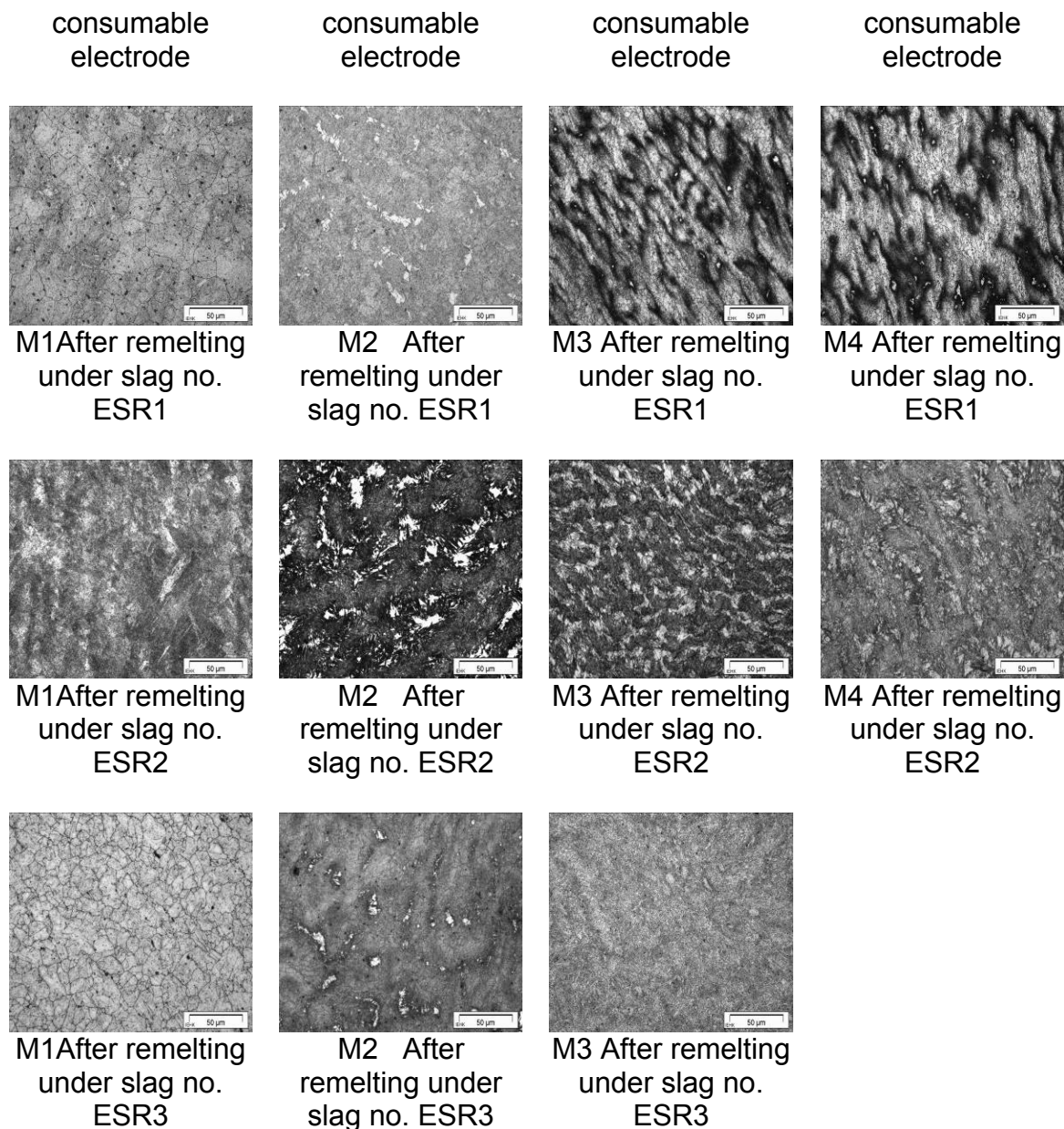


Fig. 3: Metallographical microscope observation of steels under investigation before and after ESR.

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

Flux No.	Chemical Composition, wt. %	Physical Properties
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	CaF₂	CaO	Al₂O₃	TiO₂	Density gm/cm³	Viscosity poise	Interfacial Tension mN/m
F1	70	15	15	-	2.55	0.25	1375
F2	52.5	-	22.5	25	2.75	0.8	1050
F3	70	-	-	30	2.8	3.0	700

Table 2. Chemical composition of ESR slag raw material.

Material	Chemical composition, wt. %											
	CaO	CaF₂	Al₂O₃	SiO₃	FeO	MnO₂	Cr₂O₃	V₂O₃	Co₃O₄	W₃O₄	TiO₂	C
Fluorspare	4	92	.089	1.27	.115	.007	.019	-	.004	.009	-	-
limestone	69.6	-	1.34	4.13	2.26	.067	.024	.008	.004	-	-	0.6
alumina	1.65	-	94.3	1.85	1.44	.081	.118	-	-	-	-	-
Rutile	-	-	0.5	3	4	0.5	4	-	-		88	-

Table 4 Recovery* of different elements during ESR process

Steel No.	Condition	Recovery, %													
		C	Si	Mn	P	S	Cr	Mo	Ni	Al	Ti	N			
M1	ESR1	161.60	35.56	4.95	100.56	58.87	90.34	100.68	89.84	68.51	36.52	571.43			
	ESR2	164.20	145.77	21.38	102.22	68.79	93.56	99.66	90.81	90.06	113.26	1433.3			
	ESR3	160.40	66.55	8.29	162.22	81.56	108.15	102.03	91.19	111.05	141.96	646.67			
M2	ESR1	95.88	64.00	109.13	75.60	51.03	102.16	98.04	96.59	38.39	40.58	119.44			
	ESR2	92.74	144.00	113.31	62.50	62.55	105.63	95.42	96.82	36.14	25.87	344.17			
	ESR3	83.29	37.00	46.86	191.07	77.78	106.71	96.24	97.21	44.92	38.77	221.39			
M3	ESR1	155.44	118.87	61.45	146.92	41.03	90.95	89.13	88.52	33.10	17.28	104.26			
	ESR2	146.89	108.49	83.48	115.38	61.38	101.21	98.76	87.40	108.85	17.43	406.23			
	ESR3	150.26	135.85	94.20	226.92	76.55	96.78	99.07	94.90	55.66	39.88	302.92			
M4	ESR1	201.73	178.96	90.34	65.93	27.27	97.11	94.36	89.32	63.68	46.94	16.50			
	ESR2	181.56	102.52	81.72	135.16	54.55	91.53	96.87	92.94	490.55	53.19	236.00			
	ESR3	-	-	-	-	-	-	-	-	-	-	-			

* Recovery = Metal output / Metal input * 100

Table 5. Comparing the retained austenite measurements by X-ray and magnetic methods.

Steel No.	Condition	Net Austenite, Wt %	
		X-ray	Magnetic
M3	IF	7	7.1
	ESR1	7.12	7.1
	ESR2	7.2	7.6
	ESR3	1.5	1.9

Table 6. Retained austenite measurements (magnetic method).

Steel No.	Condition	Net Austenite, Wt %	Non Magnetic Particle, Wt %
M1	IF	4.6	10.5
	ESR1	19.7	20.5
	ESR2	4.4	5.0
	ESR3	8.0	9.2
M2	IF	14.5	19.8
	ESR1	13.7	14.0
	ESR2	7.6	8.1
	ESR3	0.7	1.4
M3	IF	7.1	10.7
	ESR1	7.1	7.4
	ESR2	7.6	7.9
	ESR3	1.9	2.4
M4	IF	9.1	12.9
	ESR1	11.3	11.5
	ESR2	6.5	8.1
	ESR3	-	-

*non magnetic particle : retained austenite + non metallic inclusion

Table7. Tensile ductility properties of different steels under investigation.

Steel No.	Condition	Heat Treatment Condition		Mechanical Properties Measurements			
		Temp. °C	Time, hr	Yield (MPa)	UTS (MPa)	Elong., %	Reduction of area, %
M1	IF	400	2	1141	1229	12	40
	ESR1	450	2	1495	1508	17.5	55.2
	ESR2	450	2	1554	1569	17.9	56.2
	ESR3	450	4	1428	1449	12.5	42.1
M2	IF	500	4	1277	1288	14	42
	ESR1	475	1	1434	1453	16.6	58.0
	ESR2	475	1	1414	1450	11.6	36.3
	ESR3	475	1	1380	1400	14.5	45
M3	IF	400	1	1211	1225	15	45.51
	ESR1	425	2	1224	1239	13.7	63.3
	ESR2	425	2	1327	1334	14.1	53
	ESR3	425	4	1114	1149	11.7	45.5
M4	IF	450	4	1400	1420	10	35
	ESR1	500	1	1235	1254	15	52
	ESR2	500	1	1406	1418	13.4	47.2

**All reading is average of three measurements **