PRODUCTION OF MOLYBDENUM-, NICKEL-, CHROMIUM-CONTAINING IRON-BASED ALLOYS VIA METALLOTHERMIC PROCESS

Meryem Nis Gungor, Kagan Benzesik, Mehmet Bugdayci, Onuralp Yucel

İstanbul Technical University, Kimya-Metalurji Fakültesi, Metalurji ve Malzeme Mühendisliği Bölümü, Maslak, İstanbul, 34469, Türkiye; nismer@itu.edu.tr, kaganbenzesik@gmail.com, mbugdayci@itu.edu.tr, yucel@itu.edu.tr

ABSTRACT

The main usage area of chromium in metallurgy is ferrochromium, and FeCr covers 95% of the total chromium production. 90% of this ferrochromium is used as an alloying addition in stainless and heat-resistant steels. Although Turkey does not have large reserves of chromite, these ores are preferred to be used in metallurgical sector due to the fact that they have high quality.

This study was aimed at producing molybdenum-, nickel-, chromium-containing iron-based alloys via metallothermic process. In Turkey, Eti Krom A.Ş. produces high carbon ferrochromium by consuming 2700 kWh/t energy. In the case of the low carbon ferrochromium production in Antalya, the energy consumption can increase up to 8200 kWh/t. Instead of the electrical energy, aluminum scrap and powder are used for reduction and smelting of low carbon FeCr as the concept of the energy efficiency. Thus, energy consumption and pollution is decreased.

In our first experimental set, low carbon FeCr was produced which contains 66%Cr and 0.2% C. Additionally, low carbon iron-based alloys were also produced by metallothermic process. In the second set of the study, millscale was used as iron source. MoO3, Cr2O3, NiO were used as alloying elements. Mg, Si and Al were used as reductants. Millscale is a layer of iron oxide which forms on ferrous materials cooling after being processed in hot rolling or continuous casting plants. Millscale contains iron, iron I, iron II and iron III oxides which results in a 70% total iron content in oxide form.

In the millscale studies, Mo 76%, Ni 91%, Cr 62.5% are recovered with these recovery rates, respectively. The samples were characterized by using chemical analysis, AAS, XRD, XRF techniques.

INTRODUCTION

Chrome is one of the natural components of the earth crusts and one of the basic elements of metallurgy, chemical and refractory industry. In metallurgical industry, the most important usage of chromium ore is ferrochromium production which is used in making stainless steel. Ferrochromium is crucial ingredient of stainless steel, metal and also arms industry. Because of its high resistance to corrosion, chemical effects and abrasion, besides hard structure, it is widely used for coating of steel and other materials [1].

This study proposed a metallothermic process to produce iron based alloys using a mixture of millscale and Fe_2O_3 as an iron source, NiO, Cr_2O_3, MoO_3 and chromic acid as alloying elements, Al as the main reductant, Mg and Si were added as reductants for higher Cr recovery.

In the world, chromite resources level is totally 7.6 billion tons but just 3.6 billion tones can be classified as a reserve. Chromium ore deposits that can be economically operated; they are mainly located in South Africa, Kazakhstan, Zimbabwe, Finland, India, Turkey, Iran, the Philippines, Cuba and Brazil [2]. Ferrochrome is an alloy of iron and chromium, with chromium containing rate of 45-95%, usually used for rust and corrosion prevention and resistance increasing in the iron and steel industry. According to the amount of C contained, it is divided into three groups; high carbon (4-10% C), medium carbon (0.5-4% C), low-carbon (0.01 to 0.5% C) ferrochromium. For the first time in 1820, it was produced by chromium and oxide mixture reducing by charcoal in a crucible. The usage of electrothermal process in ferrochromium production was a turning point for development. In 1893, Moisson obtained ferrochromium containing 60% Cr and 6% C, in an electric furnace. In 1907, low carbon ferrochromium production was carried out by F. M. Becket [3]. Metallothermic process is distinguished from the other production methods by characterized several features. Some of them are listed as easy applicability, high reaction rate, low power requirements and low cost [4, 5].

The first part of this study was aimed at producing low carbon ferrochromium with using Eti Krom A.Ş. concentrate via metallothermic process. The second part of this study was aimed at producing iron-based alloys with low carbon content (chromium, nickel and molybdenum) by metallothermic process.

EXPERIMENTAL STUDY

In the first set of experimental studies, low-carbon ferrochromium production from chromite was aimed and Eti Krom A.Ş. concentrate is given in Table 1. 98% purity Al powder was used as a reductant and minimum 99.7% CrO3 containing chromic acid was added into the charge.

Table 1: Composition of Eti Krom A.Ş. concentrate (%)

Cr_2O_3	47.16
Fe_2O_3	16.00
SiO_2	6.5
Al_2O_3	10.63
CaO	0.32
MgO	19.05

In the first experiments set, grinded CrO3 and chromite concentrate were dried at 105^0C in an oven for about 30 minutes. Ratio of concentrate and chromic acid are fixed by using FactSage 6.2 Thermochemical Software data. Addition of Al used as reductant was calculated according to calculation mixture scale with using assay balance. Then base mixture was prepared in turbula mixer.

Table 2. Experimental data for mixture compound

Experiment No	Chromite-CrO_3(%)	Chromite	CrO_3	Al(%)
1	50–50	50	50	100
2	55 - 45	55	45	100
3	60–40	60	40	100
4	65 - 35	65	35	100
5	70 - 30	70	30	100
6	65–35	195	105	100
7	65–35	65	35	90
8	65–35	65	35	110
9	65–35	65	35	120

In the second set of metallothermic experiments, a mixture of Mill scale, NiO, Cr_2O_3, MoO_3 and Al powders were used in order to produce metallic Fe, Fe-Ni, Fe-Ni-Cr, and Fe-Ni-Cr-Mo alloys. The metal oxide powders have over 96% purity and 150 μm average grain sizes. Table 3 displays purity and grain size of powders. Chemical analysis of mill scale is given in Table 4. The advanced thermochemical simulations of the reactions were investigated in detail including different ratios of initial mixtures, appropriate flux, heat sinker or increaser additions as well as different initial temperatures in order to reduce the number of experiments.

Table 3: Purity and Grain Size of Raw Materials

Raw Materials	Purity, %	Grain Size
Al	> 96.0	< 150 micron
Cr_2O_3	> 99.0	< 150 micron
NiO	> 99.0	< 150 micron
Fe	> 98.0	< 150 micron
Mill Scale	>70.95*	< 150 micron

*iron oxide content

Table 4: Chemical Analysis of the Dried Mill Scale

Component	Ratio, wt. %
Total Iron	70.95
Fe^{2+}	24.59
Fe^{3+}	42.80
Fe^{0}	3.65
Mn	0.14
Cu	0.75
SiO_2	0.39

For both experimental sets, the reaction mixtures were mixed thoroughly for 15 minutes in a turbula mixer and powder mixtures (approximately 150 g) were charged into Cu crucible and compacted. W (tungsten) wire was placed at the top of copper crucible and the reaction was realized by passing current through the wire. After initiation, a highly exothermic reaction became self-sustaining and propagated throughout the metallothermic mixture. The obtained metallothermic products were discharged from the crucible after cooling.

RESULT AND DISCUSSION

By using metallothermic method for the first set of experiments, total metal recovery, the scattering ratio parameters, calculated results are shown below in table form. Besides concentrate and chromic acid ratio, the amount of Al was changed. In the case where the high yields obtained, the stoichiometric ratio was changed and this change is shown in Table 5. Effects were observed by varying experimental parameters. Also parameters where high yield was obtained are increasing by 3 times to observe the test result. In Figure 1, the efficiency of Cr is illustrated; and Figure 2 presents metal gain and scattering ratio.

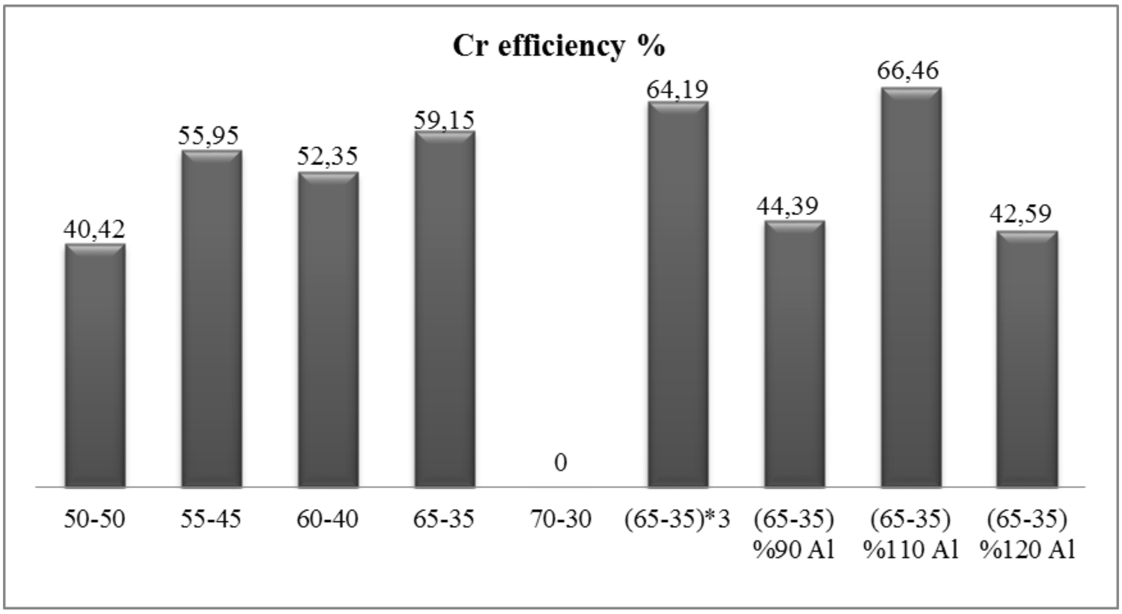

Figure 1: Efficiency of test parameter to Cr yield

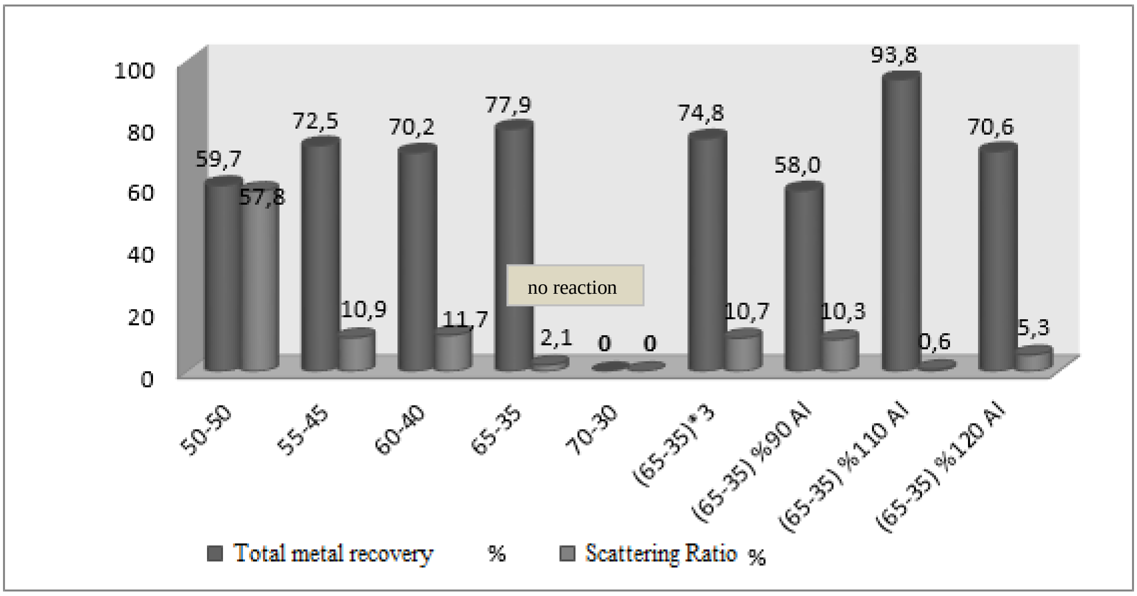

Figure 2: Metal gain ratio and scattering ratio according to the test parameter

In the second series, productions of Fe-Ni and Fe-Cr-Ni alloys was investigated by using a mixture of Mill scale, NiO, Al and Mill scale, NiO, Cr_2O_3, Al with using Cu crucible. The list of experiment parameters, weight of the initial mixtures and final products are given in Table 5. NiO addition into the green mixtures decreased the total metal recovery. On the other hand, Cr_2O_3 addition into the green mixtures decreased the scattered ratio due to the lower exothermicity of Cr_2O_3 reduction. The second series of experiments aimed at producing some similar alloys, alike stainless steel (S.S.) which contains the same ratio of Cr, Ni, Mo of standard stainless steels.

Table 5: Weight of the Initial Mixtures and Final Products (Stainless Steel "S.S.").

Experiment Parameters	Initial Mixture, (g)				Final Products		Total Metal Recovery, %	Scattered Ratio, %
	Mill Scale	Al	NiO	Cr_2O_3	Alloy	Slag		
Fe Ni	100	37.7	25.4	x	73.2	68.8	78	10.9
304 S.S.	83.6	34.1	10.5	21.7	65.2	81.4	79	6.7
304 S.S.	100	40.8	12.5	25.9	88	86.6	89	3.0
305 S.S.	100	41.8	15.4	26.6	89.7	80.1	88	1.7
305 S.S.	50	20.9	8	13.3	46.4	43.3	91	1.8
201 S.S.	100	38	5.7	22.5	80.2	85	88	6.8
201 S.S.	50	19	2.9	11.3	44.9	21.1	98	3.5
301 S.S.	100	38.8	8.3	23.2	81.5	88.7	87	2.4
316 S.S.	100	42.2	14.2	25.2	88.5	82.3	87	2.8
317 S.S.	100	44.7	16.6	28.6	94	86.5	87	4.2

Metallic distributions in alloy, slag and scattered parts obtained after metallothermic experiments are given in Table 6. Fe recovery was reduced with the NiO addition into the green mixture, but it was ascended with the Cr_2O_3 addition. Highest metal recoveries were measured as 100% Fe, 99.75 % Ni, 75 % Cr, 91 % Mo, respectively.

Table 6. Metallothermic Products, Metal Recoveries

Experiment Parameters	Fe, %	Al, %	Cr, %	Ni, %	Mo, %
Fe Ni	93.80	X	X	86.30	x
304 S.S.	100.0	X	67.20	95.00	x
304 S.S.	100.0	X	72.00	100.0	x
305 S.S.	94.30	X	59.40	99.75	x
305 S.S.	99.00	X	74.30	92.16	x
201 S.S.	95.70	X	75.00	94.80	x
201 S.S.	96.00	X	72.30	86.30	x
301 S.S.	97.00	X	66.80	100.0	x
316 S.S.	95.00	X	61.50	99.00	91.00
317 S.S.	95.70	X	62.45	88.00	78.12

In the last series of metallothermic experiment, reductant effect has been investigated by adding Mg and Si. 316 and 201 stainless steel standards were selected for this experiments to reach higher Cr recovery, because 316 series Cr recovery was the worst of experiments and 201 series had the highest Cr recoveries in the same series. Both Mg and Si additives positively affected the Cr recovery, the best result has been detected in 100% Millscale, 95% Al, 5% Si system. The Cr recovery was increased from 61.5% to 69.4% but the same effect has not been seen in 201 stainless steel standard experiment. The list of experiment parameters, weight of the initial mixtures and final products are given in Table 7.

Table 7: Weight of the Initial Mixtures and Final Products

Initial Mixture, (g)							Final Products		Total Metal Recovery, %	Scattered Ratio, %	Additives Stoichiometric Ratio, %
Mill Scale	Al (g)	Mg (g)	Si (g)	NiO (g)	Cr_2O_3 (g)	MoO_3 (g)	Alloy	Slag			
100	42.2	2.1	x	14.2	25.2	3.3	88.1	87	87	2.6	100 Al, 5 Mg
100	40.1	2.2	x	14.2	25.2	3.3	89.2	73.7	88	1.8	95 Al, 5 Mg
100	38.0	4.2	x	14.2	25.2	3.3	88	70.3	87	4.4	90 Al, 10 Mg
100	38.0	4.2	x	14.2	27.7	3.3	94.5	86.5	92	0.3	110 Cr
100	42.2	x	2.1	14.2	25.2	3.3	89.5	83	89	2.9	100 Al, 5 Si
100	40.1	x	2.2	14.2	25.2	3.3	90.3	83	89	4.9	95 Al, 5 Si
100	40.1	1.0	1.0	14.2	25.2	3.3	83.8	84.3	85	8.7	95 Al, 5 Mg-Si
100	36.1	1.9	x	5.7	22.5	x	85.6	12.3	94	0.8	95 Al, 5 Mg
50	18	1	x	2.9	11.3	x	41.8	31.4	92	1.5	95 Al, 5 Mg

Metallic distributions in alloy, slag and scattered parts obtained after metallothermic experiments were given in Table X. Fe recovery was reduced with the NiO addition into the green mixture, but it was ascended with the Cr_2O_3 addition. Highest metal recoveries were measured as 99% Fe, 98 % Ni, 72 % Cr, 95.4 % Mo, respectively.

Table 8: Metallothermic Products, Metal Recoveries

Additives Stoichiometric Ratio, %	Fe, %	Al, %	Cr, %	Ni,%	Mo, %	Alloy
100 Al, 5 Mg	95.90	x	64.70	98.10	95.40	316 S.S.
95 Al, 5 Mg	95.80	x	68.80	96.50	93.20	316 S.S.
90 Al, 10 Mg	95.60	x	63.00	92.70	91.30	316 S.S.
110 Cr	90.50	x	54.00	92.00	80.00	316 S.S.
100 Al, 5 Si	96.00	x	69.41	94.00	92.70	316 S.S.
95 Al, 5 Si	99.00	x	67.20	83.60	78.10	316 S.S.
95 Al, 5 Mg-Si	99.00	x	68.70	99.50	92.20	316 S.S.
95 Al, 5 Mg	96.00	x	71.00	98.00	x	201 S.S.
95 Al, 5 Mg	97.00	x	72.00	96.00	x	201 S.S.

CONCLUSION

The study shows that production of low-carbon ferrochromium is possible by metallothermic process. For the chromite concentrate experiments, the optimum condition was detected in stoichiometric 110% Al and 65-35% concentrate-CrO3 mixture. This mixture's Cr recovery is calculated approximately at 66.46%. In our future study, additional Al and charge amount optimization will be attempted. In the mill scale based experimental set the highest Cr recovery is calculated 72 % at stoichiometric 95%Al, 5%Mg mixture.

REFERENCES

[1] www.mta.gov.tr , Madenlerin Kullanım Alanları
[2] www.jmo.org.tr, TMMOB Jeoloji Mühendisleri Odası, Krom
[3] Fichte, R., Habashi, F., Hall, F. W., 1997. Ferroalloys, in Handbook of Extractive Metallurgy III, Ed. F. Habashi, Wiley VCH, Weinheim, Germany. pp. 438-453
[4] O. Yücel, F.C. Sahin, A. Tekin, High. Temp. Mater. Proc., 15 No.1-2 (1996) 103–106.
[5] Merzhanov, A.G., 2002. Self-propagating High-temperature Synthesis (SHS), ISMAN, Russia
[6] FactSage 6.2 Thermochemical Software for WindowsTM. Thermfact and GTT-Technologies (2010).
[7] Gruner W, Stolle S, Wetzig K (2000) Int J Refract Metals Hard Mater 18:137
[8] Lee GG, Kim BK (2003) Mater Trans 44:2145
[9] Lim YS, Park JW, Kim MS, Kim J (2006) Appl Surf Sci 253:1601
[10] Luo M, Gao JQ, Zhang X, Hou GY, Yang JF, Ouyang D, Wang HJ, Jin ZH (2007) J Mater Sci 42:3761. doi:10.1007/s10853-006-0425-9
[11] Sacks MD, Wang C, Yang Z, Jain A (2004) J Mater Sci 39:6057.doi:10.1023/B:JMSC. 0000041702.76858.a7