An Investigation on the Extraction of High-Carbon Ferrochrome with an Environmental Approach

A. Anbarzadeh[1],*, M. S. Ghiyasi Nejad[2], S. Mirzamohammadi[2], S. Abbasi Geravand[3]

[1]*Department of Mechanical Engineering, Technical and Vocational University (TVU), Tehran, Iran.*
[2]*Department of Materials and Metallurgical Engineering, Technical and Vocational University (TVU), Tehran, Iran.*
[3]*Department of Biomedical Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran.*

Abstract

The main minerals containing chromium are chromite mineral compounds. Ferrochrome is divided into three groups: high carbon, medium carbon and low carbon. Chromite mineral has a cubic lattice and belongs to spinel category. In the present study, Fe-Cr-C three-component diagrams are presented along with chemical compounds of ferrochromium. In the following, the extraction of high carbon ferrochromium is further investigated. Fe-Cr-C ternary diagrams confirm that Cr_3C_2 decomposition at temperatures below 1600°C in minerals with 60 wt% Cr and 8 wt% C results in Cr_7C_3 composition. Finally, a solution to reduce the most toxic chromium ion (Cr^{6+}) in the leachate of the extraction process is presented. Cr^{6+} is the most toxic species among its different oxidation states. Cr^{6+} is also toxic to aquatic animals, plants, and bacteria. Cr^{3+} is 100 times less toxic than Cr^{6+}. In humans and in small quantities, chromium is an essential nutrient required for sugar and lipid metabolism, but in excess it may cause cancer and allergic skin reactions.

Keywords: High Carbon Ferrochrome, Extraction Process, Chromium Carbide, Cr^{6+}.

1. Introduction

Chromium is an important metallic element, known for high and low temperature corrosion and oxidation-resistance properties [1]. The thermodynamic activity of chromium in the Fe-Cr-C system has been measured for sixteen two- and three-phase compounds of these elements as a function of temperature using the X method by Castejón [2]. Fe-Cr-C system was investigated by Andersson and its elemental diagrams were developed by Dinsdale et al [3-4]. Fe-Cr-C ternary diagram is presented in fig. 1 and 2 [5-6].

The main minerals of chromium-containing ores are mineral formations of the chromite-type $FeO \cdot Cr_2O_3$ (68% Cr_2O_3 and 32% FeO), although pure chromite is not found in the earth's crust, but was found in meteorites. The chromite mineral belongs to the isomorphic minerals of the cubic system, the so-called spinels, with the general formula $MeO \cdot Me'_2O_3$, where Me—bivalent-(Mg^{2+}, Fe^{2+} etc.), Me/—are trivalent metals (Cr^{3+}, Al^{3+}, Fe^{3+}). In natural minerals, chromium is replaced by aluminum, and Fe^{2+} iron is replaced by magnesium. Chromites are minerals from the group of spinels of the composition $(Mg^{2+}, Fe^{2+}) (Cr^{3+}, Al^{3+}, Fe^{3+})_3 O_4$ [7]. Cr^{6+} is the most toxic species among its different oxidation states. It is considered a "human carcinogen" by the US EPA and the World Health Organization. It is also associated with other pathological effects such as Geno toxicity,

mutagenicity and dermatotoxicity. It may cause respiratory, cardiovascular, and gastrointestinal diseases, and it is related to reproductive and developmental pathologies. Cr^{6+} is also toxic to aquatic animals, plants, and bacteria. In different production processes, researchers seek to provide different solutions to reduce the damage of that process to the environment [8,9]. Cr^{3+} is 100 times less toxic than Cr^{6+}. In humans and in small quantities, chromium is an essential nutrient required for sugar and lipid metabolism, but in excess it may cause cancer and allergic skin reactions [8,9].
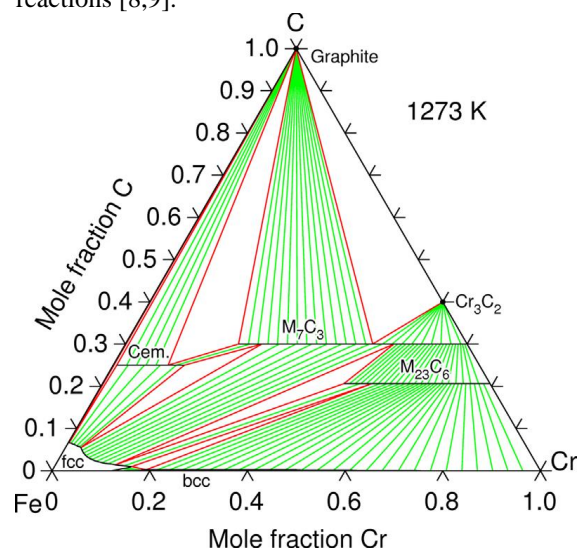

Fig. 1. Isothermal section of the Fe–Cr–C phase diagram at 1273 K calculated from the presently evaluated thermodynamic parameters [5].

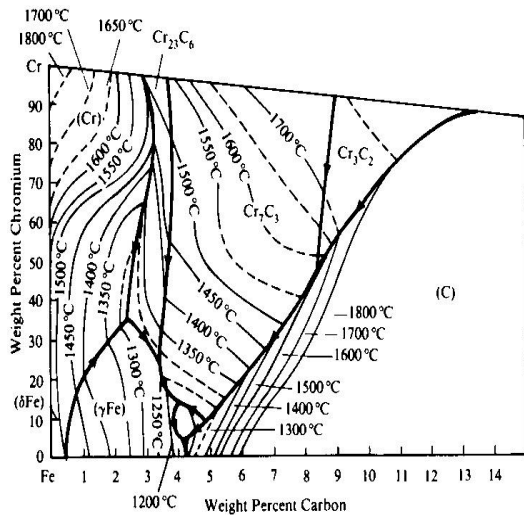*Corresponding author
Email address: aminanbarzadeh@yahoo.com*

Fig. 2. Isothermal section of the Fe–Cr–C phase diagram at 1273 K, (up to a maximum of 15 wt.%C) [6].

2- Chromium Minerals and Ores

The ores contain the following main mineral varieties of chromium-spinelides: magnesiochromite $(Mg, Fe)O \cdot Cr_2O_3$; chrompicotite $(Mg,Fe)O(Cr, Al)_2O_3$ and alumochromite $FeO \cdot (Cr,Al)_2O_3$. Grains of chromium spinels are cemented with serpentine of composition $3(Mg,Fe)O \cdot 2SiO_2 \cdot x2H_2O$ or ferruginous cement. The components of gangue in ores are serpentine, talc $Mg_6(Si_8O_{20})OH$, chlorite, magnesite, quartz, iron hydroxides, etc. [7].

In high-carbon ferrochromium for a state where solidification is very slow or equilibrium, M_7C_3 carbides are formed in the matrix from chromium ferrite compound. In the state of fast solidification (under water cooling), eutectic structure consisting of Cr_7C_3 and chromium ferrite is produced. As the percentage of carbon element decreases, M_7C_3 hexagonal carbides are replaced by $M_{23}C_6$ carbides. If dendritic carbides are observed in the eutectic microstructure of ferrochrome, it indicates a lower concentration of carbon in ferrochrome, which increases the commercial value of ferrochrome [10].

3. The Technology of Obtaining High-Carbon Ferrochromium

Ferrochromium is divided into three groups: high, medium and low carbon. The chemical composition of commodity high-carbon ferrochromium is given in Table 1, and *foundry* ferrochromium in Table 2. In this context, *foundry* means purposed for further processing [7].
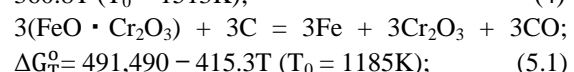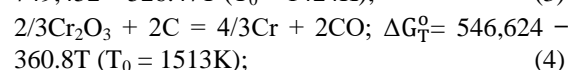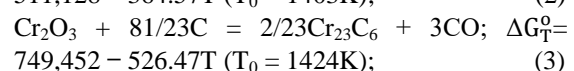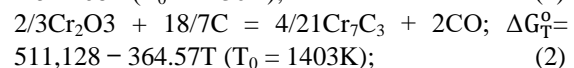
Table. 1. Chemical composition of high carbon ferrochromium, wt.%[7].

Grade	Cr, no less	C	Si	P	S
			No more		
FeCr 650A	65	6.5	2.0	0.03	0.06
FeCr 650B	65	6.5	2.1	0.05	0.08
FeCr 800A	65	8.0	2.0	0.03	0.06
FeCr 800B	65	8.0	2.0	0.05	0.08
FeCr 800CA	60	8.0	5.0–10.0	0.03	0.03
FeCr 800CB	60	8.0	5.0–10.0	0.05	0.05

Table. 2. Chemical composition of the foundry ferrochromium, wt.% [7].

Grade	Cr, no less	C	S	Si	P
		No more			
FeCrF	65	-	-	-	0.04
FeCrF 850	65	8.5	0.07	2.0	0.04
FeCrF 850A	65	8.5	0.06	2.0	0.04
FeCrF 900	65	9.0	0.06	2.0	0.04

For the smelting of high-carbon ferrochromium, chromite ore and carbonaceous reducing agents—coke, semi-coke and gas coal—are used. Alloy's recycled waste is also introduced into charge. Ferrochromium can also be smelted using sinter and/or pellets from chromite ores. When calculating the charge, it is assumed that the extraction of chromium is 92%, iron 95%, and the excess reducing agent for melting in closed furnaces is 2%, open—10%. The mixture contains: chromite ore, slag from the production of ferrosilicon-chromium, quartzite, coke, own metal wastes. The production of high-carbon ferrochromium is based on the reduction of chromium and iron from chromite ores by carbon in a continuous way in ore-smelting circular closed electric furnaces with a capacity of 16.5–33 MV A with magnesite lining (Fig. 3) [7]. Below are the main reactions for the reduction of chromium from carbon oxides [1, 7]:

$$Cr_2O_3 + 13/3C = 2/3Cr_3C_2 + 3CO; \Delta G_T^o = 730,940 - 511.68T \ (T_0 = 1430K); \tag{1}$$

$$2/3Cr_2O_3 + 18/7C = 4/21Cr_7C_3 + 2CO; \Delta G_T^o = 511,128 - 364.57T \ (T_0 = 1403K); \tag{2}$$

$$Cr_2O_3 + 81/23C = 2/23Cr_{23}C_6 + 3CO; \Delta G_T^o = 749,452 - 526.47T \ (T_0 = 1424K); \tag{3}$$

$$2/3Cr_2O_3 + 2C = 4/3Cr + 2CO; \Delta G_T^o = 546,624 - 360.8T \ (T_0 = 1513K); \tag{4}$$

$$3(FeO \cdot Cr_2O_3) + 3C = 3Fe + 3Cr_2O_3 + 3CO; \Delta G_T^o = 491,490 - 415.3T \ (T_0 = 1185K); \tag{5.1}$$

Or

$$FeCr_2O_4 + Na_2CO_3 + 2C = Fe + Na_2Cr_2O_4 + 3CO (g); \Delta G_T^o = 466,491-44.3T \ (T_0 = 1048K); \tag{5.2}$$

$$MgO \cdot Cr_2O_3 + 3C = 2Cr + MgO + 3CO; \Delta G_T^o = 720,350 - 465.94T \ (T_0 = 1546K); \tag{6.1}$$

Or

$$MgCr_2O_4 + Na_2CO_3 + C = MgO + Na_2Cr_2O_4 + 2CO \text{ (g); } \Delta G_T^o = 321105 - 289.2T \text{ (1110K);} \qquad (6.2)$$
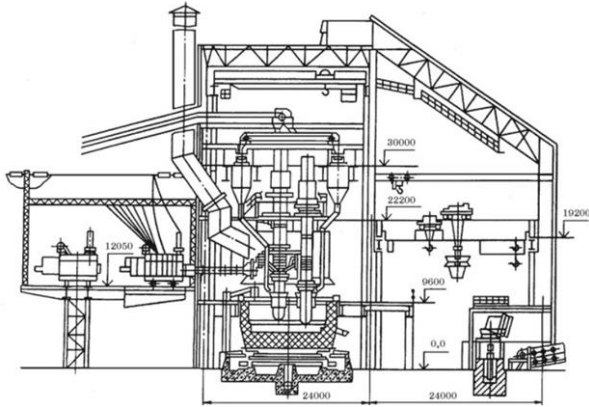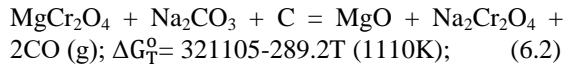

Fig. 3. Cross section of a melting unit with closed electric furnaces 33 MV A for the smelting of high-carbon ferrochromium [7].

The technological scheme for the production of high-carbon ferrochromium is shown in Fig. 4. Metal and slag are discharged from the furnace together 3–4 times per shift. Slag dump contains %: 4–6 Cr_2O_3; 30 SiO_2; 45 MgO; 15 Al_2O_3; 1 FeO; 1CaO. The high MgO content in the slag is associated with its high content in ore. Slag ratio 1. Specific consumption of charge materials in the smelting of high carbon ferrochromium, kg/t: 2000–2200 chromite ore; 30–100 quartzite; 200–400 coke. Electricity consumption 3400–3600 kWh/t [7].
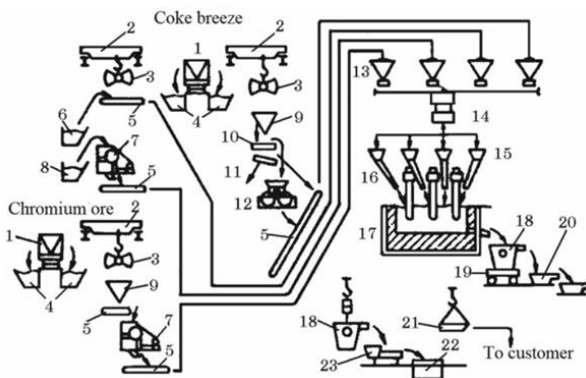

Fig. 4. Technological scheme for the production of high-carbon ferrochromium. 1-railway carriage; 2-overhead crane; 3- grab; 4- bins; 5- plate feeder; 6-screenings of quartzite; 7- jaw crusher; 8- own returns; 9- hopper; 10- double screening screen; 11-screenings; 12- two-roll crusher; 13- dosing hopper with feeder; 14- dosage trolley; 15- furnace bunkers; 16- pipe-chute; 17- ore-smelting furnace; 18- ladle for receiving alloy; 19- trolley; 20—slag; 21- box; 22-tank for granulation of the alloy; 23- trough [7].

Guidelines for the reduction of chromium ore simultaneously with the reduction of chromium ions in the reaction products, by Escudero-Castejón et al. [1]:

Each ore is poured at a weight of 100 grams and mixed with analytical grade (99.9% pure) Na_2CO_3 and activated charcoal in a weight ratio of chromite: Na_2CO_3: charcoal equivalent to 1:1:0.2. The reactants are mixed by grinding using a mortar for 10 minutes. Then, the ground mixture of reactants is pressed into 2 g pellets using a steel mold. After pressing the pellets are placed inside an alumina crucible. Before starting the isothermal reduction test at a predetermined isothermal temperature for a fixed time, e.g. 1050 ∘C for 2.5 hours, a thermogravimetrically balanced vertical furnace, purged with argon gas and maintained at a flow rate of 2 L/min for 15 minutes. Allow the mixture to cool to room temperature. the spent leachate is a dilute sulphonic acid with 0.05 M-0.5 M strength at the end of the process, which contains little or no Cr^{6+}-ions immediately after processing. By leaving the acid leachate in air for several weeks, the residual Cr^{3+}-ions oxidize and yield Cr^{6+}-ions up to 140 ppm. For reductive roasting of chromite ores with alkali, the presence of a reducing agent, e.g. carbon is necessary, which is in contrast with the oxidation process. Under the reducing condition, the alkali complexes with chromium oxide in 3+-state and forms water insoluble sodium chromite ($Na_2O \cdot Cr_2O_3$). Iron oxide present in the chromite spinel is reduced to a metallic state by forming Fe-Cr alloy, whereas the alumina forms water-soluble $NaAlO_2$. The water-insoluble sodium chromite may be separated during leaching from the soluble $NaAlO_2$. The residual oxides, MgO, Al_2O_3 and silica form complex silicates during leaching.

4. Conclusion

Fe-Cr-C ternary diagrams confirm the formation of Cr_7C_3 in minerals with 60 wt. % of chromium and 8 wt. % of carbon at temperatures below 1600°C; And Cr_7C_3 is obtained from the decomposition of Cr_3C_2. By the decarburization process, the hexagonal Cr_7C_3 carbides are replaced by $Cr_{23}C_6$ carbides. If dendritic carbides are detected in the eutectic microstructure of ferrochrome, it indicates a lower concentration of carbon in ferrochrome structurally. By melting high-carbon ferrochrome in a plasma furnace, ferrochrome losses can be reduced. This makes it economical to extract chromium from chromite ore with lower concentrations of chromium. Because by this method, 92% of chromium in the furnace charge can be extracted. By using the presented reaction equations as well as the described method, the amount of Cr^{6+} ions in the leachate of the extraction process can be reduced.

References
[1] L. E. Castejón, J. Taylor, S. S. Segado, A. Jha and J. Hazard, Mater., 403(2021), 123589.

[2] L.D. Teng, R.E. Aune, M. Selleby and S. Seetharaman, Metall. Mater. Trans., B 36B(2005), 263.

[3] J.-O. Andersson, Metall. Trans., A 19A, (1988), 627.

[4] A.T. Dinsdale, Calphad., 15(1991), 317.

[5] A.V. Khvan, B. Hallstedt and C. Broeckmann, Comput. Coupling Phase Diagrams Thermochem., 46(2014), 24.

[6] H. Baker, ASM Handbook, Vol3(1993), Chap 3, 24.

[7] M. Gasik, V. Dashevskii and A. Bizhanow: Ferroalloys-Theory and practice, Speringer (book).

[8] S. Mirzamohammadi, M Velashjerdi and A. Anbarzadeh, JEFM, 5, 2(2021), 11.

[9] A. G. Carnota, J. L. Barriada and R. Herrero, J. Environ. Chem. Eng., 10, 5(2022), 108258.

[10] A. Lesko and E. Navara, Mater. Charact., 36(1996), 349.