

Oxidation state of chromium in molten slags

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Abstract

To better understand chromium behaviour in slags under low oxygen potential, it is essential to clarify the existing form of chromium in slags. In an earlier work by the authors, oxidation state of chromium in $\text{CaO-SiO}_2\text{-CrO}_x$ slags was studied. However, due to the complications in the experiments and the analysis, the results were scattered. It was found that divalent and trivalent chromium co-exists in the slags related to ferrochromium and stainless steel production. The ratio of divalent to trivalent chromium increases with higher temperature, lower slag basicity and oxygen potential.

In the present work, to quantitatively verify the oxidation state of chromium in the slags, equilibrium experiments were conducted at 1590 °C. Molten slags were equilibrated with chromium crucible under Ar atmosphere. The oxidation state of chromium in the slags was determined with wet chemical analysis. It was concluded that the oxidation state of chromium in the slag system greatly varied from almost stoichiometric “CrO” to composition corresponding to Cr_3O_4 . The oxidation state depended on chromium oxide content in the slags as well as slag basicity. The results were consistent with those of the previous measurements by the authors.

In order to better characterise the slag phase, the microstructure of the quenched slags was examined. It revealed that with high chromium oxide slags “CrO” could partly disproportionate to metallic chromium and Cr_2O_3 during quenching.

INTRODUCTION

The steadily growing consumption of stainless steel in the world has an increasing demand on the production of ferrochromium alloy[1]. The research work in these fields has been greatly stimulated nowadays. From economic point of view, the optimisation of metal yield in the related smelting and refining processes in the ferroalloy production industry is very important. A successful operation to a large extent depends on the metal recovery. The most essential requirement in these processes is high chromium recovery from the slag to the metal phase. In the FeCr process, the slag is formed and prevails in reducing conditions. The slags in the stainless steelmaking process are subjected to both oxidising conditions during carbon removal and reducing conditions in the final refining stage. The discarded slags may expose to air or even more oxidising conditions. The transitional metallic ions of chromium in the slag will respond to such oxygen potential variations by changing the oxidation states. Chromium in the waste can be cycled among different oxidation states in nature, in which hexavalent chromium is highly mobile and toxic. Therefore, high chromium recovery would be beneficial in saving raw materials and energy as well as in reducing eventual chromium pollution from chromium containing slags and wastes.

Thermodynamic approach can define the effects of the various process variables on the chromium distribution between the slag and the metal phases. A quantitative evaluation on the oxidation state of chromium in slags and nature of chromium oxide in silicate melts is necessary. For an effective thermodynamic evaluation of chromium distributions, thermodynamic properties of the slag phase are required. The knowledge of the oxidation state of chromium will help to evaluate the thermodynamic properties and control the process for a higher metal recovery from the minerals.

Various efforts can be found in the literature to discuss the oxidation state of chromium in the metallurgical slags since the 1930's. However, the quantitative results are quite scattered and different from one to another. The fundamental nature and behaviour of chromium in slags still need to be clarified. The purpose of this study is to determine quantitatively the oxidation state of chromium in silicate melts, and to discuss the factors affecting the analysed results of divalent chromium. To do this, a literature review on the oxidation state of chromium in slags was firstly conducted. Then the oxidation state of chromium in $\text{CaO-SiO}_2\text{-CrO}_x$ slag system was experimentally investigated at 1590 °C. The slags were in equilibrium with metallic crucible under argon atmosphere. The quenched slag samples were examined by electron microprobe analysis, and further identified by X-ray diffraction.

LITERATURE REVIEW

In the slags for ferrochromium and stainless steel production, significant amount of chromium exists in the divalent state at high temperatures under low oxygen partial pressure. For the interests of the technology in metallurgical process, oxidation state of chromium in various slag systems under low oxygen partial pressure was reported in the literature by several researchers. Because the specific difficulties involved in the analysis for the divalent chromium in silicate slags, most analysing methods are limited to iron free slag systems[2]. In general, the slag systems investigated can be classified as the systems containing iron oxide, and the iron-free slag systems. For the slags containing iron oxide, the oxidation state was not directly quantified, but evaluated by measuring the distribution ratio of chromium and iron

between the slag and the metal phases. For the iron-free slag systems, the divalent chromium in the slags was mainly determined by wet-chemical analysing method. The studies were carried out under different oxygen partial pressure. In general, it can be roughly divided into moderate oxygen partial pressure ($P_{O_2}=10^{-5} - 10^{-10}$ atm) and low oxygen partial pressure ($P_{O_2}<10^{-10}$ atm).

Iron-containing slags

Körber and Oelsen[3] studied SiO_2 saturated chromium containing FeO-MnO- SiO_2 slags which were equilibrated with Fe-Cr melt. When the chromium content in the alloy was within 17 – 60 %, the divalent chromium was the main existing form in the slags in the temperature range of 1600 to 1640°C. Some other researchers[4-6] reported the oxidation state of chromium in SiO_2 saturated slag, and concluded that most of the chromium presents in divalent state in the slags. For the CaO- Al_2O_3 -FeO- CrO_x - SiO_2 slag equilibrated with Fe-Cr-Si alloy, under Ar protecting atmosphere at 1600°C, $CrO_{1.07}$ was the average chromium oxide composition in these low oxygen partial pressure conditions. It is equivalent to 86% Cr^{2+} and 14% Cr^{3+} in the slags.

Iron-free slags under moderate oxygen partial pressure

Frohberg and Richter[7] studied the equilibrium between Cr^{2+} and Cr^{3+} in CaO- SiO_2 - CrO_x slags in platinum boats at the oxygen partial pressure ranging from 10^{-6} to 10^{-9} atm at 1600°C and 1650°C. Morita et al.[8] investigated MgO- Al_2O_3 - SiO_2 -CaO- CrO_x slags saturated with MgO. Cr_2O_3 at 1600 °C under reducing conditions. Under similar oxygen partial pressure, the results of divalent to trivalent chromium ratio in the slag saturated with MgO. Cr_2O_3 [8] is much lower than that in the CaO- SiO_2 - CrO_x slags with the basicity of 1.3 – 1.5[7]. It proves that the slag composition has very significant effect on the oxidation state of chromium.

Iron-free slags under low oxygen partial pressure

McCoy and Philbrook[9] studied the reduction behavior of divalent chromium oxide from CaO- SiO_2 - Al_2O_3 based slags with carbon-saturated iron at the temperature range from 1500°C to 1650°C, and with the oxygen partial pressure of the order 10^{-15} atm. About 89 to 99% of the total chromium was considered to be divalent chromium. Pretorius and Muan[10] examined oxidation state of chromium in CaO- Al_2O_3 - CrO_x - SiO_2 melts under oxygen partial pressures from $10^{-9.56}$ to $10^{-12.50}$ atm at 1500 °C. They observed that under such conditions chromium was dominantly present in the divalent state in slag melts. The Cr-Si-O system at low oxygen partial pressure was investigated in tungsten crucible under H_2 - H_2O atmosphere at 1600 – 1750°C by Healy and Schottmiller[11]. Cr^{2+} fraction was found to be between 0.7 and 0.8. Xiao[12] studied the equilibrium of chromium containing slags in metallic chromium crucible at 1500 - 1600°C. The effects of temperature, slag basicity, as well as additions of MgO and Al_2O_3 were investigated. The results showed that the divalent chromium fraction increased with increasing temperature and lowering slag basicity. Morita et al.[13] studied the CaO- SiO_2 - CrO_x system at 1873K under oxygen partial pressure of 6.95×10^{-11} atm, and found that the ratio of Cr^{3+}/Cr^{2+} significantly increases with basicity. Both chromium oxides of $CrO_{1.5}$ and CrO behave as basic ones. The solubility of chromium oxide in the slag system drastically decreased with increasing X_{CaO}/X_{SiO_2} . For the high slag basicity, chromium behaviour was studied in MgO saturated CaO- SiO_2 - Al_2O_3 -MgO- CrO_x slags which were in equilibrium with Ni-Cr alloy at 1550 – 1650°C[14]. The system oxygen partial pressure was controlled by steam-hydrogen ratio in the gas phase. A similar conclusion was drawn that the ratio of divalent chromium in proportion to total chromium content in the slag was increased by decreasing the slag basicity, increasing temperature and decreasing oxygen partial pressure.

Further, Maeda and Sano[15] studied the chromium oxide reduction with solid carbon in CaO-MgO-Al₂O₃-SiO₂-CrO_x slags under carbon monoxide atmosphere at 1500°C and 1650°C. The phase diagram was constructed for the SiO₂-CrO-MgO-Al₂O₃ slag in equilibrium with chromium crucible. They assumed that all the chromium existed as divalent chromium.

It can be seen that the oxidation state of chromium in the slags was investigated under various conditions by different researchers. The available investigations on chromium oxidation states in different slag systems are summarised in Table I. Direct comparison of these results is still difficult. However, in general, it can be concluded that in silicate slags under low oxygen partial pressure, both Cr²⁺ and Cr³⁺ are present in all slags. The equilibrium exists between these two valences depending on the equilibrium oxygen partial pressure, slag composition including chromium oxide content, and temperature. It is agreed that qualitatively the ratio of Cr²⁺/Cr³⁺ in the slags increased with higher temperature, lower oxygen partial pressure as well as lower slag basicity. Some of the experimental results from different researchers were compared and drawn in Fig.1 Due to the other factors (basicity, CrO_x content, temperature) influencing the oxidation state the Figure gives us only a qualitative description. However a certain discrepancy in the results is quite evident. Therefore, further study is still needed to quantitatively specify the oxidation state of chromium in slags.

EXPERIMENTAL

The equilibrium experiments were carried out in a SiC electrical resistance furnace under argon atmosphere. Metallic chromium crucible was used, 28 mm in inner diameter, 34 mm in outer diameter and 45 mm in height. The charged crucible was put in a protecting crucible of corundum, and placed on a supporting pedestal of mullite in the furnace. The experimental temperature was controlled and measured with a PtRh10-Pt thermocouple. The oxide mixtures were reacted and equilibrated at 1590 °C for about 20 h in the furnace. The overall error in the measurement and control of the temperature was estimated to be less than ± 4 °C. The reaction system was protected by a purified argon gas with a flow rate of 0.25 l/min. The purification system for argon consisted of KOH for removing CO₂, silica gel and phosphorus pentoxide for removing moisture, and sponge titanium heated at 850 °C in a resistance furnace for lowering the oxygen partial pressure.

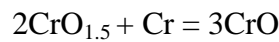
The compositions of the oxide mixtures were chosen within the liquid region of the system. Laboratory reagent-grade oxides were used as raw materials in the experiments. CaO was calcinated at 1400 °C for 24 hours, crushed and ground into powder and then kept in a desiccator ready for use. To reduce the equilibrating time of the reaction system, CrO was added to the slag systems with a stoichiometric mixture of Cr₂O₃ and chromium metal powder based on proper divalent chromium fractions. 30g of the required powders was homogeneously mixed and pressed into tablets, and then packed in the chromium working crucible.

The slag samples were taken with an alumina tube under controlled suction, and were quickly pulled out and quenched in water within a few seconds. The colour of the slags varied from deep blue to bluish green with increasing the total amount of the chromium oxides and slag basicity. The slag was carefully removed from the sampling tubes, ground and screened to particle size less than 122 μ m for slag analysis. The weight percentage of divalent chromium

in slags was analysed with wet-chemical method of indirect chemical redox titration[12]. The total chromium and the other slag components CaO and SiO₂ were determined by X-ray fluorescence. In addition, the slag samples were examined by scanning electron microprobe and X-ray diffraction.

RESULTS AND DISCUSSION

The slags containing chromium oxides have a similar problem like the iron containing slags, in which the non-stoichiometry of CrO_x varies with temperature, slag basicity and even total chromium oxides content in the system equilibrated with metallic chromium. When Cr₂O₃ is mixed with other slagging oxide components at high temperatures in contact with chromium metal, the following equilibrium of chromium oxides is expected:



Chromium is therefore distributed in slag both as divalent and trivalent states in different fractions, depending on the experimental conditions. The analysed slag compositions are presented in Table II. The results of the oxidation state of chromium in the slag are represented in Fig.2 by comparing to the previous results from the author[12]. It can be seen that generally the present results are in a reasonable agreement with the previous ones. Under the present experimental conditions, the oxygen partial pressure is determined by the slag compositions, and mostly by the total chromium oxide content in the slags. Therefore, the ratio of Cr²⁺/Cr³⁺ is dependent on the total chromium oxides content and the slag basicity. From the results in Fig.2 it is clear that higher slag basicity and higher concentration of the total chromium oxide will lead to lower divalent chromium fraction in the slag. The oxidation state of chromium in the CaO-SiO₂-CrO_x slags changed from almost stoichiometric “CrO” to composition corresponding to Cr₃O₄ (divalent to trivalent ratio 1:2).

For the slags of CrO_x-SiO₂ system, and the slags with lower chromium oxide contents (about < 20 wt%) in CaO – SiO₂ – CrO_x system, the slag samples have a deep blue glassy nature after quenching. The inhomogeneous feature in micro-level exists possibly due to the different interaction forces of the ions, and different ratio of divalent to trivalent chromium, as shown in Figs.3 and 4. For the Cr-Si-O system, chromium oxide exists mainly in combination with silica as Cr₂SiO₄ according to the X-ray diffraction analysis. The liquid matrix may be depleted of chromium oxides and becomes richer in SiO₂. Based on the electron microprobe analysis, the Cr/Si ratio in the darker phase is slightly lower than that in the lighter phase. Due to the amorphous structure, the existing form of chromium in sample B1 is difficult to establish from the analysis of X-ray diffraction. The qualitative analysis showed that in Fig.4, the amount of chromium and calcium in the light phase might be a little higher than that in the dark matrix.

For the CaO-SiO₂-CrO_x slag system with higher CrO_x content, the disproportion of CrO in the slag seems to occur, as demonstrated in Fig.5. With the reaction of 3CrO=2CrO_{1.5}+Cr, the precipitated Cr₂O₃ is in the needle shape and the metallic chromium inclusions are normally associated with these precipitates. For the same slag compositions, the microstructure is quite different if the slag was cooled naturally in the furnace under the argon gas protection, the Cr₂O₃ and chromium metal phase were normally concomitant and dispersed in the silicate phase, as observed in Fig.6. The disproportionation of CrO to Cr₂O₃ and chromium proceeded

to a greater or lesser extent, depending upon the slag compositions. As it is known, the structure of the silicate is very complicated. For the slags with low chromium oxides concentration and high SiO₂ content, the nuclei formation and growth of the new phase during cooling may be slow, the solidified silicate slag may still keep its characteristics of the structure in the molten state. Therefore, no significant disproportion of CrO was found in the quenched slags. For the slag with high concentration of chromium oxide, it is not appropriate to conclude and extend the results to the molten slag due to the precipitation of quench crystals and the presence of metal droplets in the slag. However, in the wet chemical analysis[12] oxidation of one mole Cr consumes the same amount of Fe³⁺ as the oxidation of 3 mole Cr²⁺ which is just equivalent to the consumption of CrO and the formation of metallic chromium during the disproportionation reaction. Therefore, it can be concluded that the disproportionation may have complicated the divalent chromium analysis of the slags, but its effect on the determination of divalent chromium in molten slags can be compensated in the wet-chemical analysis.

The disproportionation reaction would have introduced certain random error for the analysed results of divalent chromium oxides. In addition, the difficulties encountered in the wet-chemical analysing method may also add uncertainties in the divalent chromium determination. A complete reaction and dissolution of chromium containing slags without oxidising the divalent chromium ion by atmosphere and/or by any other undesirable factors are very important for a less scattered results, for which the sample preparation and the ground slag powder size should be well controlled.

CONCLUSIONS

The oxidation state of chromium in CaO-SiO₂-CrO_x slag system was investigated. The slag was equilibrated with solid metallic chromium at 1590 °C under argon atmosphere. The results obtained were compared with the previous results under similar conditions, and a reasonable agreement was achieved. It can be concluded that at low oxygen partial pressures divalent and trivalent chromium is the major existing form. Low slag basicity favours the presence of divalent chromium in the slags.

For the evaluation of the experimental results, it seems that the quenching speed may still not be fast enough to maintain the initial liquid structure of the slag. During the cooling period, even for only a few seconds, the disproportionation reaction can occur: $3\text{CrO}=\text{Cr}+2\text{CrO}_{1.5}$. The slag may change from homogeneous to heterogeneous.

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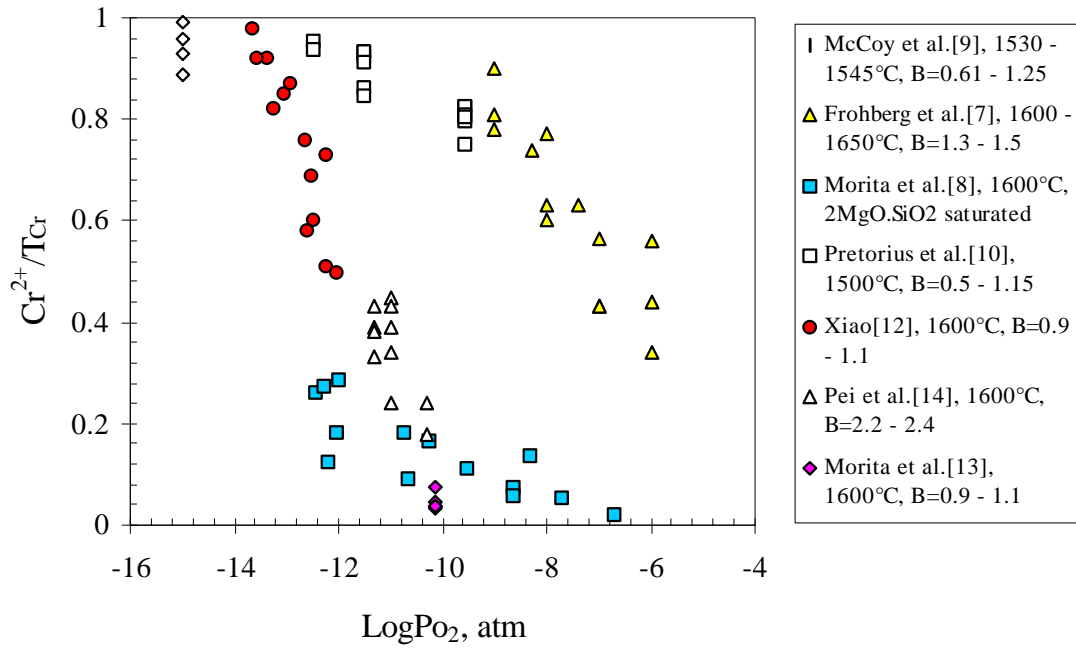


Fig.1 Comparison of the oxidation state of chromium in the CaO-SiO₂-CrO_x based slags from different researchers

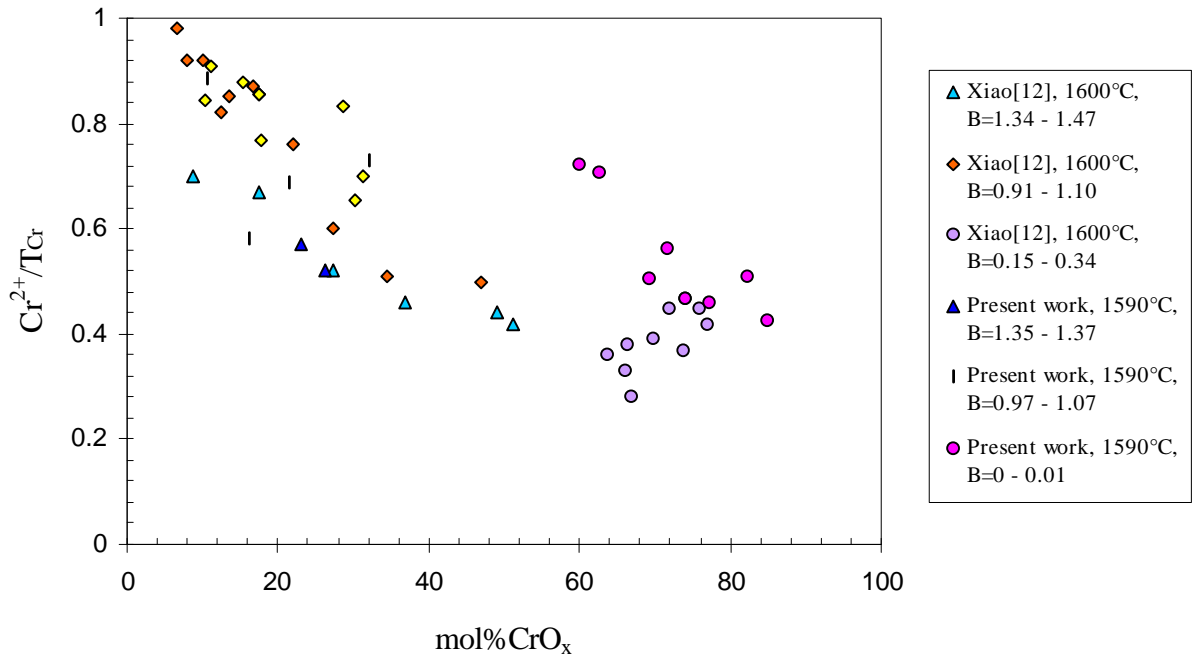


Fig.2 Oxidation state of chromium in CaO-SiO₂-CrO_x slag system

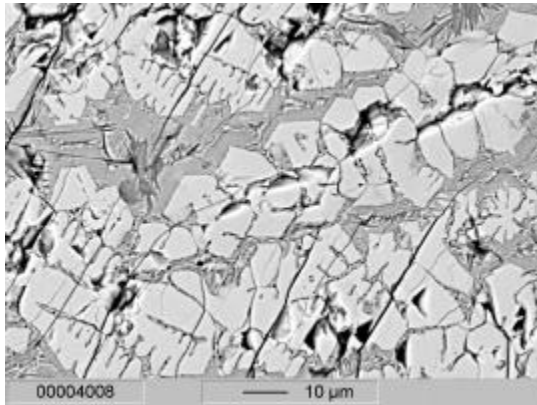


Fig.3 Microstructure of sample A1 quenched from 1590°C with compositions of 0.28 mol% CaO – 39.66 mol% SiO₂ – 45.69 mol% CrO – 14.37 mol% CrO_{1.5}

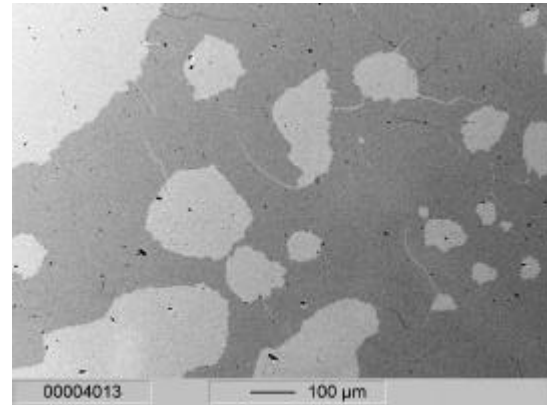


Fig.4 Microstructure of sample B1 quenched from 1590°C with compositions of 46.05 mol% CaO – 43.60 mol% SiO₂ – 8.72 mol% CrO – 1.62 mol% CrO_{1.5}

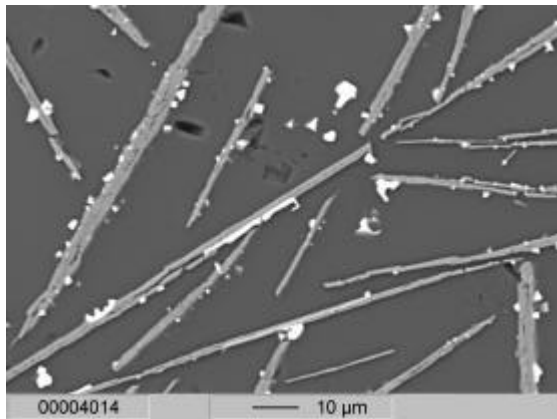


Fig.5 Microstructure of sample B6 quenched from 1590°C with compositions of 34.65 mol% CaO – 34.09 mol% SiO₂ – 21.90 mol% CrO – 9.36 mol% CrO_{1.5}

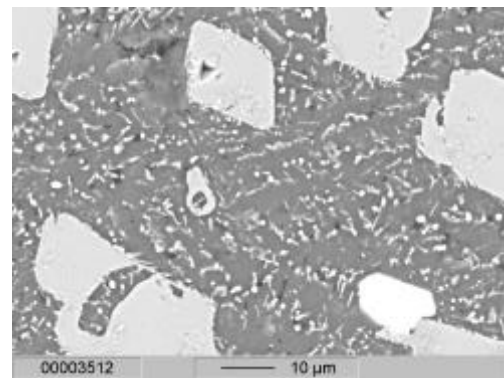


Fig.6 Microstructure of sample B6 naturally cooled in the furnace from 1590°C

Table I. Summary of the investigations on chromium oxidation state in slags under different conditions

System investigated	Temperature, °C	(N _{CaO} +N _{MgO})/N _{SiO₂}	pO ₂ , atm	(CrO _x) in slag	Cr ²⁺ /T _{Cr}	Reference
CaO-SiO ₂ -Al ₂ O ₃ -CrO _x in graphite crucible	1530 - 1545	0.61 – 1.25	10 ⁻¹⁵	2.3 – 3.7 wt%	0.89 – 0.99	McCoy and Philbrook (1958)
CaO-SiO ₂ -CrO _x in H ₂ -steam - Ar	1600 - 1650	1.39 – 1.61	10 ⁻⁶ – 10 ⁻⁹	0.62 – 6.48 wt%	0.34 – 0.90	Frohberg and Richter (1968)
CrO _x -SiO ₂ in steam-hydrogen in tungsten crucible	1750	---	H ₂ O/H ₂ < 0.05	64 wt%	0.7 – 0.8	Healy and Schottmiller (1964)
CaO-SiO ₂ -Al ₂ O ₃ -FeO-CrO _x with Fe-Cr-Si in Al ₂ O ₃ or SiO ₂ crucible	1600	0.28 – 2.42	10 ^{-13.8} – 10 ^{-16.6}	0.50 - 14 wt%	0.86	Rankin and Biswas(1978)
CaO-SiO ₂ -Al ₂ O ₃ -MgO-CrO _x with NiCr	1600	2MgO.SiO ₂ sat.	10 ^{-7.5} – 10 ^{-12.5}	0.5 - 8 wt%	0 - 0.25	Morita and Sano (1988)
CaO-SiO ₂ -Al ₂ O ₃ -CrO _{xx} and PtCr alloy in (H ₂ +CO ₂)	1500	0.03 - 1.2	10 ^{-9.56} – 10 ^{-12.4}	3.79 - 23.15 mol%	0.79 - 0.98	Pretorius et al. (1992)
CaO-MgO-SiO ₂ -Al ₂ O ₃ -CrO _x with Cr metal in Ar	1500 - 1600	0.2 - 1.5	10 ⁻¹³ – 10 ⁻¹⁵	4.5wt%-saturation	0.15 - 1.0	Xiao (1993)
CaO-MgO-SiO ₂ -Al ₂ O ₃ -CrO _x with MgO sat. in (H ₂ O+H ₂)	1600 - 1650	1.74 - 2.41	5×10 ⁻¹¹ - 4×10 ⁻¹²	0.7 - 4.75 wt%	0.19 - 0.49	Pei and Wijk (1994)
CaO-SiO ₂ -CaF ₂ with Ag in (CO+CO ₂)	1275 - 1400	1 - 5	10 ^{-10.22} – 10 ^{-12.22}	0.38 -0.62 wt%	0.03 - 0.96	Okabe et al. (1998)
CaO-SiO ₂ -CrO _x and Cu-Cr alloy in Mo crucible in (CO-CO ₂)	1530 - 1650	0.5 – 1.5	6.95×10 ⁻¹¹	2.4 – 64 wt%	0.02 – 0.17	Morita et al. (1999)

Table II. Slag compositions of CaO – SiO₂ – CrO – CrO_{1.5} oxide system in equilibrium with metallic chromium in argon atmosphere at 1590 °C

Samples	CaO, mol%	SiO ₂ , mol%	CrO, mol%	CrO _{1.5} , mol%	N _{CaO} /N _{SiO₂}
A1	0.28	39.66	45.69	14.37	0.01
A2	0.00	36.80	29.06	34.14	0.00
A3	0.11	37.33	45.37	17.18	0.00
A4	0.63	17.65	41.63	40.09	0.04
A5	0.64	14.97	35.93	48.46	0.04
A6	1.05	25.78	34.29	38.88	0.04
A7	1.11	25.79	34.26	38.85	0.04
A8	0.74	37.57	31.13	30.56	0.02
A9	0.85	28.09	39.98	31.08	0.03
B1	46.05	43.60	8.72	1.62	1.06
B2	46.00	43.39	9.40	1.20	1.06
B3	46.04	42.88	10.08	0.99	1.07
B4	43.72	40.98	13.46	1.84	1.07
B5	35.36	34.50	19.71	10.42	1.02
B6	34.65	34.09	21.90	9.36	1.02
B7	36.90	34.48	23.80	4.81	1.07
B8	41.49	41.05	14.91	2.55	1.01
B9	41.08	41.22	13.58	4.13	1.00
B10	40.72	41.79	14.98	2.51	0.97
C1	42.38	31.34	13.73	12.55	1.35
C2	44.48	32.53	13.11	9.88	1.37