VACUUM-THERMAL METHOD OF DEEP REFINING OF FERROCHROMIUM IN SOLID STATE

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ABSTRACT

Refining of ferrochromium to remove carbon and oxygen as well as other impurities to very low levels is possible via heat-treatment in vacuum. In this work, thermodynamic analysis of the Cr-C-O equilibria at normal and reduced pressures is carried out and the industrial practice of the method is described to achieve 10-100 ppm of carbon, hydrogen, oxygen and nitrogen. Such process is advantageous compared to smelting operations as liquid ferrochromium cannot be easily degassed to such purity levels due to excessive vaporization of chromium.

1. INTRODUCTION

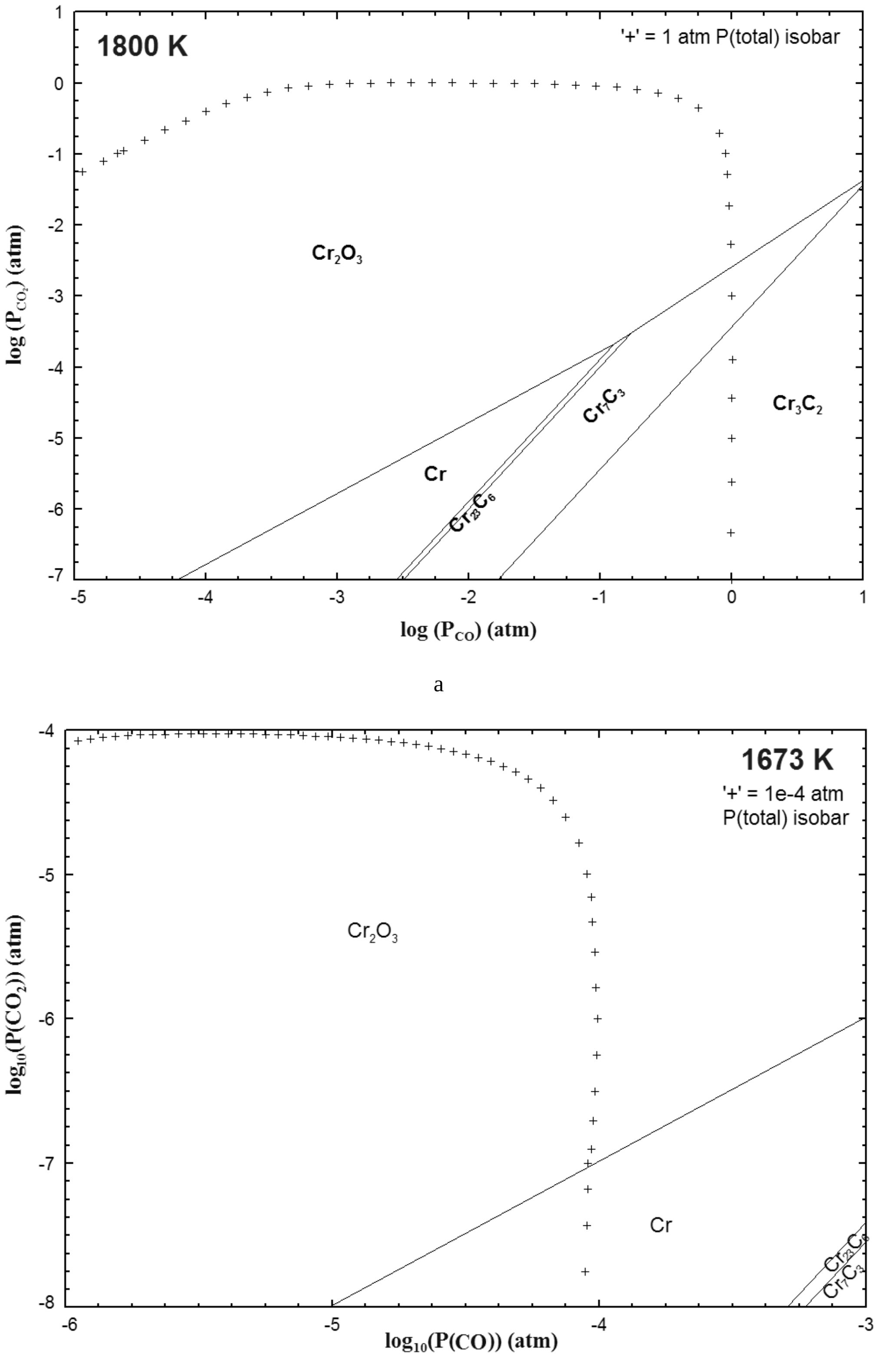
Production of some specific steels and alloys with chromium requires ultra-low level of impurities, especially carbon and gases (oxygen, hydrogen, nitrogen). It is known that significant amount of such impurities in steel and alloys production is brought with ferroalloys where impurities solubility and affinity to alloying elements is usually higher than to that to iron [1,2]. Low-carbon FeCr with <0.03% C still has too high nitrogen content, significantly reducing corrosion stability of Cr-Ni-Mo stainless steels even when carbon in the steel does not exceed 0.015%. The purpose of deep refining of ferrochromium, a method of the vacuum treatment, has been developed [1, 3], which includes heating of solid ferrochromium batch under reduced pressure. In this work, thermodynamics of the Cr-C-O system is first considered to evaluate the operational window of the process, and later industrial practice of the refining is outlined.

2. PHASE EQUILIBRIA IN THE Cr-C-O SYSTEM

Carbon and chromium form several carbides [1, 2], which have been a subject of many investigations. The commonly observed carbides in the Cr-C system are $Cr_{23}C_6$ (5.68 wt. %C; sometimes also referred as Cr_4C), Cr_7C_3 (9.0 %C) and Cr_3C_2 (13.3 %C). The types of crystalline lattices and their parameters for chromium carbides have been determined as complex BCC for $Cr_{23}C_6$, hexagonal for Cr_7C_3 and orthorhombic for Cr_3C_2. The solubility of carbon in solid chromium is rather low [1, 4], so carbides are the main form of carbon in chromium and ferrochromium.

Among chromium oxides, trivalent chromium oxide Cr_2O_3 is the most stable in the solid state and wide temperature range. Oxides Cr_3O_4 (tetragonal lattice of rutile-type) and CrO (cubic) are stable at high temperatures only [1, 2]. Upon cooling they usually decompose to Cr and Cr_2O_3. Oxide Cr_3O_4 might be also considered as a chromium chromite, $CrCr_2O_4$ or $CrO{\cdot}Cr_2O_3$. The practically relevant oxide Cr_2O_3 has the structure of corundum -Al_2O_3 type. Oxygen solubility in solid chromium is also low (~0.013 wt. %O at 1500°C), lowering the chromium melting point. Oxide liquid phase may form over 1663°C in equilibrium with either chromium or chromium oxides.

For chromium reduction from oxides and the refining process design, thermodynamics of the Cr-O-C equilibria is of a high importance. In Fig. 1, the isothermal sections of the phase dominance diagram are shown for two different temperatures and pressures. Here cross marks (+) indicate the isobar line – the total pressure in the system, which was fixed to be 1 atm (Fig. 1, a) or 10^{-4} atm (Fig. 1, b). If these cross marks exist in any of the phase stability field, this means thermodynamic possibility of obtaining of this phase in the system.



a

b

Fig. 1. Phase dominance diagram at 1800 K and 1 atm (a) and 1673 K and 10^{-4} atm (b)

The conclusions one could draw on the basis of these diagrams are as follows. First, at 1800 K it is not possible to get metallic chromium in the Cr-C-O system but only oxide Cr_2O_3 (at high CO_2 fractions) or carbides $Cr_{23}C_6$ and Cr_3C_2 (at high CO fractions) if the total system pressure of 1 bar (atm) is maintained. Therefore, though chromium might be reduced by carbon at high temperatures and normal pressure, it is unlikely to be practically feasible for pure metal production due to difficulties in local control of the gas atmosphere.

When pressure and temperature decreased (Fig. 1, b), the isobar lines are appearing also in the chromium region, indicating that formation of carbides is not anymore thermodynamically favoured, even at high CO concentrations. This gives an opportunity to design a process of simultaneous removal of carbon and oxygen from solid ferrochromium or metallic chromium at reasonable conditions in the solid state. Similarly to oxygen, nitrogen and hydrogen can also be removed from the metal, although their process is different, as it goes over decomposition of nitrides or just removal of dissolved gases [1].

3. VACUUM REFINING IMPLEMENTATION

Based on the thermodynamic analysis, a method for removal of these impurities and oxide inclusions by subjecting solid FeCr lumps to high-temperature treatment in vacuum has been developed [1, 3]. This patented method has received widespread recognition, allowing production of FeCr with <100-150 ppm C and 150-250 ppm N. The principle of the method is in solid-phase decarburization and degassing of FeCr lumps with starting carbon content of 0.10-0.15%C in a vacuum (residual pressure 1.3-13 Pa) at l350-1450°C in three-chambered resistance furnaces, Fig. 2, 3. During the treatment carbon content drops from 0.10% to 0.02% C and nitrogen from 0.06-0.07% to <0.02% N [2]. The ferrochrome degassed by this process is also characterized by low concentrations of hydrogen (≤ 7 ppm), oxygen (≤ 300-400 ppm) and non-metallic inclusions [1, 3].

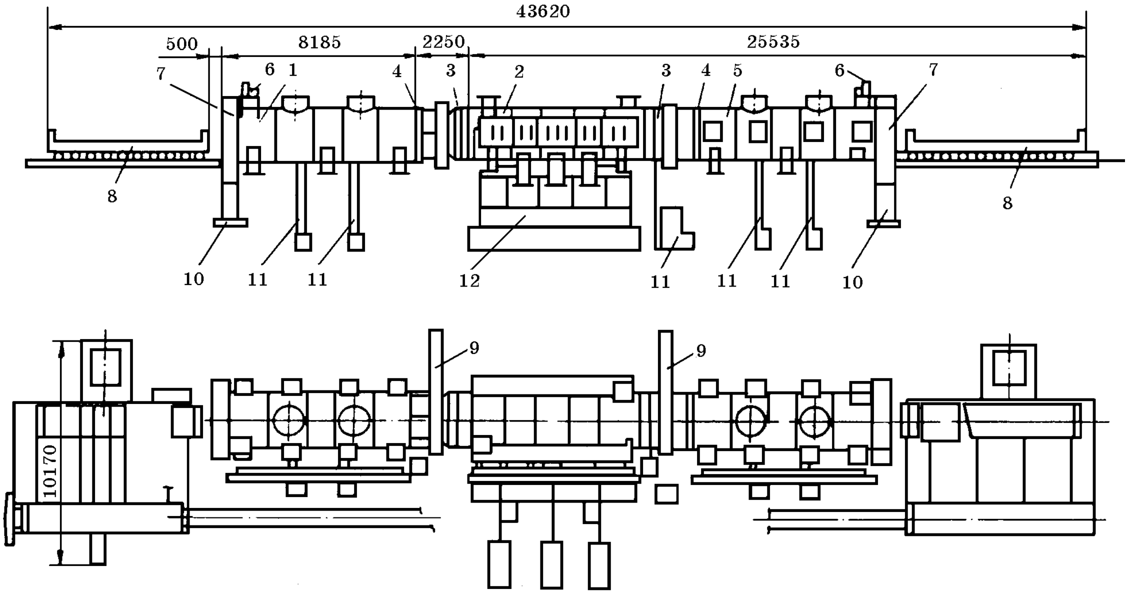


Fig. 2. Vacuum furnace layout for processing of ultra-low carbon ferrochromium by method designed in Dnipropetrovsk Metallurgical Institute [1-3]: 1 – FeCr cooling chamber, 2 – isothermal soaking chamber, 3 – vacuum gates, 4 – compensators, 5 – preheating chamber, 6 – cover lift, 7 – cover, 8 – carrier, 9 – vacuum shields, 10 – support, 11 – low-vacuum pumps, 12 – acceleration pumps.

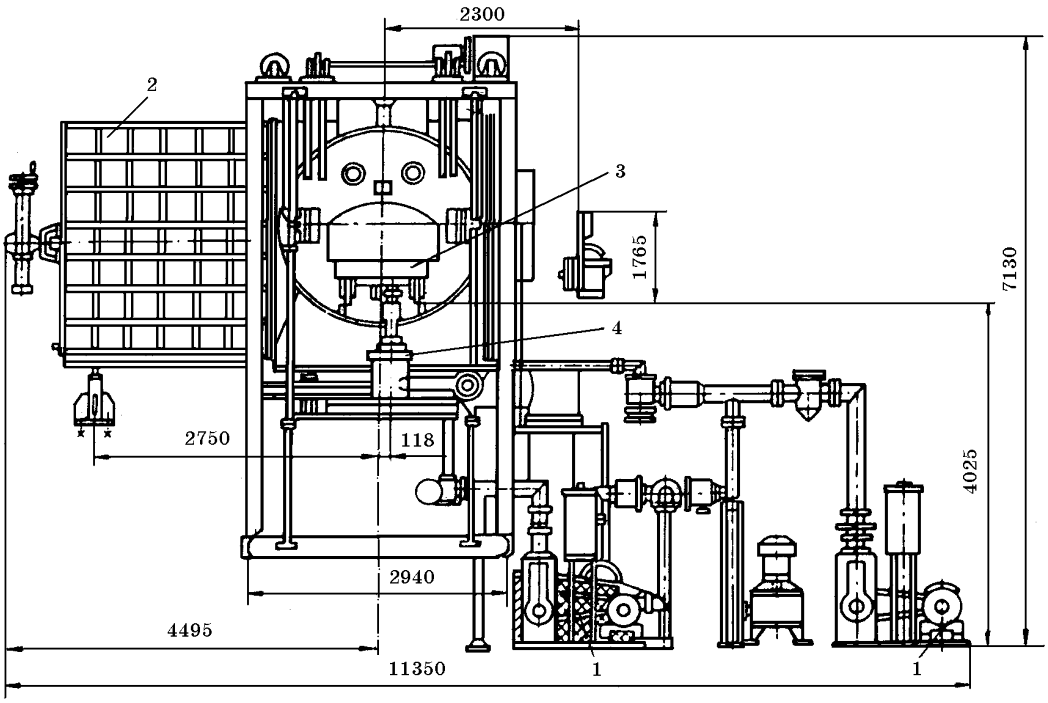


Fig. 3. Cross section of the vacuum furnace for ultra-low carbon FeCr processing (Fig. 2): 1 – pumps, 2 – vacuum slag, 3 – carrier, 4 – carrier moving mechanism [1, 2].

The furnace of 1.5 MW operates at 1050°C in the first chamber and 1350-1450°C in the second chamber (the third chamber is used for cooling). The whole cycle time is 24 h. Dissolved nitrogen, hydrogen and oxygen is being removed by diffusion mechanism, whereas oxide inclusions might be partially reduced in vacuum. Carbon removal is expected to proceed as a result of the reaction between chromium carbides with oxygen or chromium oxide at reduced pressures.

The method of deep refining of ferrochromium and chromium in the solid-state is very efficient and often the only practical alternative vs. liquid ferrochromium purification, as the latter has too much losses of chromium with vapors.

References:

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