Removal of Nitrogen and Phosphorus from Ferrochrome Powder with Ca-CaCl₂ and Mg-MgCl₂ Mixtures*

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Synopsis

Experiments were made in which ferrochrome particles of spherical form were treated with molten Ca-CaCl₂ and Mg-MgCl₂ mixtures in the temperature range of 900° to 1300°C under an inert atmosphere. The diameters of particles used were 0.09 to 1.1 mm. Nitrogen content of the ferrochrome was efficiently reduced to 10 ppm over the temperature range studied, whereas significant removal of phosphorus was observed at relatively higher temperatures and in longer reaction durations. The degree of removal was found to be expressed as a function of the reaction temperature and (t/d^2) , where t and d denote the reaction time and the diameter of particle, respectively. No fluid motion of the molten mixture affects the magnitude of the rate of removal. From these results, the rate-determining step was concluded to be the diffusion process in a ferrochrome particle. The obtained diffusion coefficient of nitrogen (e.g., $5.3 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 1080°C) was nearly close to that in chromium metal. The obtained diffusion coefficient of phosphorus was approximately one thousandth of that of nitrogen. Discussions were made on the practical availability of the present method for the production of low nitrogen ferrochrome and chromium metal.

I. Introduction

The purpose of the present work is to show a new way of making extremely low nitrogen ferrochrome powder which is expected to be used as a pure raw material in the production of high-purity ferritic stainless steels.

Recently, studies concerning new molybdenum stainless steels (high purity, high-chromium ferritic stainless steels with 25~30%Cr, 1~5%Mo, and extremely low levels of carbon and nitrogen) have been increasingly made for the purpose of using them as construction materials in the process industry.¹⁻⁸⁾ Works on these steels indicate that the contents of carbon and nitrogen should be kept below certain defined concentrations. The maximum limits of these elements depend on the selected corrosion forms and environments, the heat treatment, the contents of chromium and molybdenum, the amount of stabilizer used (Ti and Nb), the levels of sulfur and phosphorus contents, etc.; e.g., with 25~26%Cr-Mo-Fe alloys the tolerable sum of carbon and nitrogen contents are reported to be 100 to 130 ppm for intergranular corrosion after welding by Demo,³⁾ 60 to 80 ppm for rather severe pitting corrosion condition by Ogawa *et al.*,⁸⁾ and about 65 ppm for brittleness of the alloy with commercial levels of sulfur and phosphorus by Wright.⁶⁾ Unfortunately, there have been insufficient knowledges to define which of various properties required for actual process-plants determines the least levels of carbon and nitrogen. Steigh-

erwald and Shimodaira stated in their reviews^{9,10)} that the levels of carbon and nitrogen contents are to be kept as low as possible, even though stabilizing elements are added. It would, therefore, be presumed in the present work that both elements must be kept at a level below 50 ppm, respectively.

Carbon dissolved in liquid iron alloys containing 25~30%Cr can be readily reduced from a commercial level (100~400 ppm) to 10~20 ppm in high vacuum melting processes, such as vacuum induction melting,⁵⁾ electron-beam melting¹¹⁾ and vacuum arc remelting.¹²⁾ Kaneko *et al.*¹³⁾ reported that carbon can be removed from liquid 25%Cr-Fe alloy to an extremely low level by hydrogen plasma melting. On the contrary, no effective method has been developed for such liquid high-chromium iron-alloys, by which the content of nitrogen can be reduced to a level below 50 ppm from an ordinary level (100~300 ppm). The lowest level of nitrogen attainable by vacuum induction and electron-beam meltings^{14,15)} is regarded as being 80 to 100 ppm within practical limits of reaction time and evaporative loss of chromium. The work of Ban-ya *et al.*¹⁶⁾ revealed that no substantial change in nitrogen concentration at higher chromium contents occurs by argon blowing. The hydrogen plasma melting is effective for the removal of nitrogen as well as carbon. However, the limit of the nitrogen removal for 25%Cr-Fe alloy was reported to be 50 to 60 ppm.¹³⁾ Tokumitsu *et al.*¹⁷⁾ showed that Ca-CaF₂ refining process eliminates nitrogen from liquid 25%Cr-3%Mo-Fe alloy only by 30 to 50% of initial concentration of about 150 ppm.

As a whole, alternative methods would be necessary in order to make high-purity ferritic stainless steels with nitrogen content below 50 ppm. One of the methods is to use raw materials of relatively higher purity. A major source of nitrogen present in the raw materials is originated from ferrochrome which contains ordinarily 100 to 400 ppm nitrogen. Calculation of material balance indicates that the nitrogen content of ferrochrome must be kept below 60 to 70 ppm for the purpose. A problem, thus, is how to produce such low nitrogen ferrochrome from ordinary one. This is a main objective of the present work.

II. Purification Method

Calcium and magnesium metals are known to have strong affinity for nitrogen¹⁸⁾ as well as for phos-

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phorus.^{18,19)} Little works, however, have been reported on the removal of nitrogen from ferrochrome by using these alkaline-earth metals. Nakamura *et al.*²⁰⁾ reported that Ca-CaF₂ solution can remove efficiently and simultaneously phosphorus and nitrogen from liquid 18%Cr-8%Ni-Fe alloy. Nevertheless, as for liquid 65%Cr-Ni-C-Fe alloys,²¹⁾ no significant removal of nitrogen was observed, whereas phosphorus was easily reduced to a low level. The work of Koloyartsev *et al.*²²⁾ showed that under the streams of calcium and magnesium vapours phosphorus content of solid high-carbon ferrochrome powder changes from about 0.08% to a steady value of about 0.02% at 1 100°C. Their work, however, contained no remarks on the behaviour of nitrogen.

A new purification method to be proposed in the present works is that ferrochrome powder is treated with molten $X-XCl_2$ mixture ($X=Ca$ or Mg) at temperature between the melting point of XCl_2 and the boiling point of X . The overall reaction scheme is:

where, (X) : X metal in the molten $X-XCl_2$ mixture

$\langle N \rangle$: nitrogen in the ferrochrome powder

(X_3N_2) : hypothetical constituent of the reaction product dissolved in the molten $X-XCl_2$ mixture. Probably, the reaction product might be separately present in the form of ions such as N^{-3} and X^{+2} .

This purification method would be expected to remove not only nitrogen from ferrochrome powder but also phosphorus according to a similar reaction scheme to Eq. (1). Simultaneous removal of phosphorus, therefore, is also examined in the present work.

The values of the free energy changes for the formations of calcium and magnesium nitrides increase with increasing temperature and reach zero ($\Delta G_f^0=0$) at about 1 600°C. This means that low nitrogen ferrochrome would be obtained at temperatures relatively lower than the steel-making range. From the standpoint of kinetics, the rapid rate of nitrogen removal would be achieved under the following conditions.

- (A) Higher reaction temperature
- (B) Higher concentration of the reagent (Ca and Mg metals)
- (C) Shorter distance through which the reactant moves
- (D) Quicker removal of the reaction product formed on the ferrochrome surface

The condition (A) is expected to make the rates of mass transfer and chemical reaction higher. However, the upper limit of the reaction temperature depends on the condition (B). Calcium and magnesium metal in a liquid state or in concentrated solu-

tions would be more effective for the chemical reaction rather than those in a gaseous phase. The boiling point of calcium (1 492°C) or magnesium (1 117°C), thus, is the upper limit of the reaction temperature. Ferrochrome is in a solid state at the temperatures concerned. The condition (C), therefore, means that ferrochrome to be treated must be in the form of fine particle (thin plate and wire are impractical).

In the present experiment, molten $CaCl_2$ and $MgCl_2$ salts of ionic character are used as a solvent of the reaction product (Condition (D)). It is, thus, necessary that ferrochrome particles to be treated are sufficiently immersed in these molten salts in order to quickly dissolve the reaction product (formed on the surface of them). The minimum value of the salt/ferrochrome ratio in weight is estimated to be about 0.3. The solubilities of calcium and magnesium metals in their corresponding chlorides²³⁻²⁷⁾ are small: * that is, about 1.6wt% at 950°C for calcium²³⁾ and 0.2wt% at 1 000°C for magnesium.²⁷⁾

In the present experiments, the $X-XCl_2$ mixture used contained 10 to 40% of X metal in weight. Therefore, the mixture would be separated into two melts at the reaction temperatures: chloride-rich and metal (or metal rich) phases. The density of the former is slightly higher than that of the latter. Hence, the ferrochrome powder would be at least in contact with alkaline-earth metal in solution in its molten chloride salt, unless the mixture is agitated.

III. Experiment

1. Apparatus

A reaction tube made of SUS304 type stainless steel is schematically shown in Fig. 1. The outer shell of the reaction tube was 67 mm in diameter and about 1 200 mm in length. The lower portion of the reaction tube was set in a resistance-heating furnace (a heating zone). The upper portion was composed of a cooling zone, gas in-let and out-let tubes, and O-ring joint for a holding pipe suspending a crucible

Fig. 1. Experimental apparatus used

* These solubilities are apparently increased due to the presence of impurities such as oxide and hydride; e.g., calcium solubility in $CaCl_2$ containing trace of water is reported to be about 8% at 950°C.

of cylindrical form. The gas in-let tube was connected with argon gas flow and vacuum pump systems. The holding pipe of 12 mm in diameter was movable upward and downward, and equipped with a powder reservoir made of glass. A rotating tube including a thermocouple was set inside the holding pipe. A stirrer was jointed with the lower end of the rotating tube. The crucible and the stirrer were made of SUS 304 type alloy containing 0.003%P and 0.006%N. They had beforehand been treated with Ca-CaCl₂ melt at 1 000°C for 10 hr for further decrease in nitrogen content. The size of the crucible was 33 mm in inner diameter, 87 mm in height and 1 mm in thickness. Electric power for the heating furnace was supplied from a power supplier of 12 kVA which included an on-off regulator connected with a thermocouple set on the outer shell of the reaction tube.

2. Materials

1. Ferrochrome

Ferrochrome particles of almost spherical form was prepared by an atomizing method. Commercial low-carbon ferrochrome of about 10 kg was melted in an induction furnace and then poured into an atomizing chamber. The downward stream of liquid ferrochrome was broken into powder by an argon jet. The ferrochrome powder thus made was sieved to make the size of particle even. The values of the size were 0.09 ± 0.02 , 0.13 ± 0.02 , 0.27 ± 0.03 , 0.55 ± 0.05 and 1.1 ± 0.1 mm. The film of dark green oxide formed on the surface of ferrochrome was peeled off. The cross-section of an as-atomized particle is shown in Photo. 1. In some of the experiments, the powder was heat-treated at 1 100°C for 4 hr before the experiment. The chemical compositions of ferrochrome powders studied are shown in Table 1.

2. Reaction Reagents

Calcium and magnesium metals of 99.9% purity were used. The calcium metal was of granular form with 2 to 3 mm diameter. The magnesium chip used was prepared from a commercial rod by machine-cutting. Anhydrous CaCl₂ and MgCl₂

salts of reagent purity were heated at 900°C for 1 hr under an inert atmosphere and stocked in a desiccator prior to the experiment. Further precaution for impurities was not taken.

3. Procedure

1. Nitrogen

Experiments on the removal of nitrogen were made as follows. The crucible, containing alkaline-earth metal (Ca or Mg) of 4 g and its chloride (CaCl₂ or MgCl₂) of 15 g, was first set at the cooling zone. The air inside the reaction tube was pumped out, and argon of commercial high purity was flowed into it at the rate of 100 cm³/min. Then, the crucible was lowered and suspended in the heating zone. After the crucible temperature had reached a given reaction temperature (900°, 1 000°, 1 080°C), the ferrochrome powder of 2.5 to 5 g in the reservoir was fed into the crucible. The diameter of the powder was 0.55 and 1.1 mm. The addition of ferrochrome powder made the crucible temperature immediately dropped by 30°C, but the temperature reached again the given value within 30 sec. Thereafter, the fluctuation of the reaction temperature was kept within

Photo. 1. Cross-section of an as-atomized ferrochrome particle

Table 1. Compositions of ferrochrome powders

Powder No.*	Diameter (mm)	Element (%)						
		Cr	N	P	C	O	S	Si
7-10-S	0.27	60.7	0.16	0.030	0.053	0.46	0.011	0.65
7-12-S	0.13		0.16	0.033	0.050	0.61		
7-13-S	0.09		0.16	0.033	—	—		
8-5-S	1.1	59.9	0.074	0.029	0.016	0.18	0.019	0.72
8-5-T	1.1		0.065	0.029	0.009	0.15		
8-8-S	0.55		0.075	0.029	0.018	0.17		
8-8-T	0.55		0.062	0.027	0.009	0.15		
8-12-S	0.13		0.078	0.030	—	—		
15-5-S	1.1	61.7	0.051	0.037	0.26	0.41	0.014	0.57
15-5-T	1.1		0.047	0.039	0.25			

* S=as-atomized, T=heat-treated

$\pm 5^{\circ}\text{C}$ by using the on-off regulator. After a specified reaction duration had elapsed, electric power was turned off. Then, the crucible was rapidly lifted to the cooling zone. The cooling rate was approximately $150^{\circ}\text{C}/\text{min}$.

Visual observation shows that fine particles of alkaline-earth metal together with the ferrochrome powder is dispersed in a block of chloride salt in the cooled crucible. A small amount of calcium and a somewhat large amount of magnesium (about 1 g at $1\,000^{\circ}\text{C}$ for 1 hr) were deposited on the surfaces of the feeding and rotating tubes owing to the evaporation. The ferrochrome powder was separated by dissolving the alkaline-earth metal and its chloride with hot water and was used as the samples for chemical analysis of nitrogen.

2. Phosphorus

The experiments concerning phosphorus were made at higher reaction temperatures ($1\,080^{\circ}$, $1\,200^{\circ}$, $1\,300^{\circ}\text{C}$) and for smaller sizes of ferrochrome particles (0.09, 0.13, 0.27 mm). The experimental procedure was as follows. The charge added into the crucible was composed of ferrochrome powder of 7 to 10 g, alkaline-earth metal of 4 g, and its chloride salt of 6 g. The crucible was heated to a given reaction temperature in 4 min. Neither supply of ferrochrome from the reservoir nor stirring was done. Subsequent procedure was the same as that conducted in the experiment on the removal of nitrogen. Both contents of nitrogen and phosphorus were determined by chemical analyses.

4. Chemical Analyses

The nitrogen content of the ferrochrome powder was determined with Kjeldahl method. Total uncertainties in the measurement were ± 5 ppm. The samples were dissolved with hydrogen chloride solution. Residual undissolved by hydrogen chloride was separately decomposed with $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-CuSO}_4$ solution for the determination of its nitrogen content ("insoluble nitrogen"). However, nitrogen in the residual was found to be negligibly small, as shown in Table 2. The phosphorus content was determined with molybdenum-blue absorption method with total uncertainties of ± 10 ppm. It should be noted that the value chemically determined is equivalent to the mean value of concentration distribution of element in a ferrochrome particle.

IV. Results

The obtained values of nitrogen content of ferrochrome powder are plotted against the reaction time. Typical examples are shown in Figs. 2 to 4. The nitrogen content is found to be eliminated from 500~

1 600 ppm to an extremely low level. As shown in Fig. 2, the rate of nitrogen removal is independent of the stirring and the composition of molten mixture. Figure 3 shows that the removal rate increases with increasing the reaction temperature. It is also shown in Figure 3 that the rate for the as-atomized ferrochrome powder is almost the same as that for the heat-treated one.

Figure 4 also shows a plot of the obtained values of

Fig. 2. Plots of the observed values of nitrogen content against the reaction time

Fig. 3. Dependence of the nitrogen content on the reaction time and temperature

Fig. 4. Phosphorus and nitrogen behaviours at higher reaction temperatures

Table 2. Insoluble nitrogen content

Ferrochrome powder	Sol. N (%)	Insol. N (%)
As-atomized	0.079	<0.0005
ELNA-treated at 900°C for 85 min	0.0005	<0.0005

phosphorus content against the reaction time. The rate of phosphorus removal is much lower than that of nitrogen, though the temperature is higher and the size of ferrochrome particle smaller. In the case of Ca-CaCl₂ mixture, phosphorus is gradually removed to a low level with reaction time. Such a behaviour of phosphorus is in contrast with that under the gas stream of alkaline-earth metal observed by Koloyartsev *et al.*²²⁾ The discrepancy would result from the use of molten salt as a solvent of reaction product in the present work. Mg-MgCl₂ mixture is found to remove phosphorus at a similar rate to that for Ca-CaCl₂ in the early stage of reaction. However, the reaction in the later stage becomes slower. This tendency is possibly due to a large evaporative loss of magnesium metal occurring for a long time.

The increase in particle size of ferrochrome is found to decrease the both removal rates of nitrogen and phosphorus. As shown in Fig. 5, the observed values of the degree of nitrogen removal at each reaction temperature is approximately determined as a function of (t/d^2) alone, where t and d denote the reaction time and the diameter of ferrochrome particle, respectively. Similar results are obtained for the removal of phosphorus, as shown in Fig. 6. The dependence of the removal degree on the variable of (t/d^2) means that the removal rate at a given concen-

Solid curve: the theoretical relation (see in the text)

Fig. 5. Relation between the observed degree of nitrogen removal and the ratio of the reaction time (t) to the square of particle diameter (d)

Solid curves: the theoretical relation (see in the text)

Fig. 6. Relation between the observed degree of phosphorus removal and the ratio of the reaction time (t) to the square of particle diameter (d)

tration is inversely proportional to the square of particle diameter.

V. Discussion

1. Rate-determining Step

The transfer of nitrogen and phosphorus from a ferrochrome particle to the $X-XCl_2$ solution may proceed through the following sequent steps.

Step (1): Dissolution of chemical compound, such as chromium nitride, initially dispersed in the ferrochrome matrix

Step (2): Diffusion of solute element (P and N) dissolved in a solid ferrochrome particle toward its surface

Step (3): Chemical reaction occurring on the surface

Step (4): Transfer of reaction product in the boundary layer in the $X-XCl_2$ solution adjacent to the ferrochrome surface

The "insoluble nitrogen" content of the ferrochrome powder is negligibly small (Table 2), and the heat-treatment gives little effect on the rate of nitrogen removal (Fig. 3). Phosphorus is unlikely to form a dispersed compound in the ferrochrome matrix. Therefore, Step (1) seems not so important.

If the removal rate is assumed to be controlled by either Step (3) or (4), the rate equation may be given by Eq. (2).

$$\rho(4\pi/3)(d/2)^3(dN/dt) = 4\pi(d/2)^2k\Phi \quad \dots\dots\dots(2)$$

or

$$(1/\Phi)(dN/dt) = (6/\rho)(k/d) \quad \dots\dots\dots(2)'$$

where, ρ : the density of ferrochrome

N : the solute concentration in ferrochrome

k : the rate constant.

The term of Φ is the driving force which is expressed as a function of N ; *e.g.*, $\Phi = KN$ for Step (4), where K is the equilibrium constant. Equation (2) indicates that the removal rate at a given value of N is inversely proportional to the value of d . This relation is inconsistent with that obtained from the present experiments. Neither Step (3) nor (4), therefore, is concluded to be a rate-determining step. Another proof for excluding Step (4) may be obtained from the results shown in Fig. 2, indicating little effect of stirring on the rate. The value of k for the Step (4) is approximately proportional to D'/δ , where D' and δ are the diffusion coefficient of the reaction product in the molten $X-XCl_2$ mixture and the thickness of the boundary layer, respectively. The value of δ decreases with increasing degree of fluid motion. Thus, the rate in a stirring state should be higher than that in a quiescent one. This conclusion is not in accordance with the observed result.

We, now, consider the diffusion process in a sphere (Step (2)). If the initial concentration of diffusing element is uniform and the surface concentration is kept constant, the removal degree of diffusing element may be expressed as follows.²⁸⁾

$$[N_0/(N_0 - N_e)]\eta = (N_0 - N)/(N_0 - N_e)$$

$$= 1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-4n^2\pi^2 Dt/d^2)$$

.....(3)

where, $\eta = (N_0 - N)/N_0$: the removal degree
 N : the average concentration in the sphere at the time of t
 N_e : the surface concentration (in other words, the equilibrium concentration)
 N_0 : the initial concentration
 D : the diffusion coefficient.

Equation (3) shows that η should depend only on the variable of (t/d^2) at a given temperature. This dependence of η is in agreement with that observed. As a whole, Step (2) may be deduced to be the slowest of the sequet reaction steps concerned.

2. Diffusion Coefficient

The magnitude of D in Eq. (3) is calculated from each observed result with the aid of a numerical table for Eq. (3) and the assumption of $N_e \ll N$. Semi-logarithmic plots of the calculated values against the reciprocal of reaction temperature for nitrogen and phosphorus are shown in Figs. 7 and 8, respectively. The calculated values of D are found to be fairly represented by a straight line over the temperature range studied: that is,

$$D_N = 3.5 \times 10^{-1} \exp[-36\,100/RT] \text{(4)}$$

$$D_P = 5.5 \times 10^{-4} \exp[-37\,900/RT] \text{(5)}$$

where, the subscript to D denotes the diffusion element, and R and T have their usual meaning.* Figures (5) and (6) show examples of theoretical η -(t/d^2) profiles corresponding to D_N and D_P given by Eqs. (4) and (5). The theoretical and experimental values are in good agreement over the range of (t/d^2) examined. In other words, the observed results are thus consistent with the rate equation for the diffusion process in a sphere (Eq. (3)), if the values of D for nitrogen and phosphorus in ferrochrome are defined by Eqs. (4) and (5), respectively. It should be noted that the value of D_N is thousand times of that of D_P ; i.g., $D_N/D_P = 1.2 \times 10^{+3}$ at 1 080°C.

No diffusion data are available for ferrochrome in order to check whether the calculated value of D is reasonable or not. Accordingly, the calculated value are to be compared with the diffusion coefficient in chromium and α -iron metals, because these metals are major component of ferrochrome and have the same crystal structure (body-center). Unfortunately, the diffusion coefficients of phosphorus in these metals have not been reported. Further discussion, thus, will be limited to nitrogen.

Fig. 7. Plots of the calculated values of the diffusion coefficient of nitrogen against the reaction temperature

Fig. 8. Plots of the calculated values of the diffusion coefficient of phosphorus against the reaction temperature

The work of Fast and Verrijp²⁹⁾ shows that the diffusion coefficient of nitrogen in α -iron is expressed as $D = 6.6 \times 10^{-3} \exp[-18\,600/RT]$. This relation and its extrapolation over the α - γ transition temperature are represented as a dotted line in Fig. 7. The diffusion coefficient of nitrogen in chromium metal at 1 000° to 1 400°C measured by Arnold and Hagel³⁰⁾ is also shown in Fig. 7: that is, $D = 9.6 \times 10^{-3} \exp[-28\,500/RT]$. The calculated values of D for ferrochrome are found to distribute nearly above those for chromium metal, but comparatively far below those for α -iron. The activation energy for ferrochrome is relatively close to that for chromium metal. Such similarities between the diffusions of nitrogen in ferrochrome and chromium seem to be reasonable, because the diffusion process in solid ferrochrome (65%Cr-Fe alloy) would be for the most part governed by interactions among chromium and nitrogen atoms. It may be, therefore, concluded that the

* Estimated standard deviation ($\hat{\sigma}$) for the calculated values of $\log D$ are 0.092 for nitrogen and 0.17 for phosphorus.

Rather large value of $\hat{\sigma}$ for phosphorus originates from the assumption of $N_e \ll N$. Qualitatively, N_e increases with increasing temperature.¹⁹⁾ Thus, the calculated values of D for higher temperatures and higher removal degrees should be smaller than the correct one.

As for nitrogen, the value of N_e is expected to be very small (below 10 ppm, as shown in Fig. 4). Therefore, the assumption of $N_e \ll N$ may be regarded as valid for whole experimental conditions.

calculated value of D given by Eq. (4) is regarded as being actual.

3. Significance and Availability

The experimental results reveal that Ca–CaCl₂ and Mg–MgCl₂ mixtures can reduce efficiently the nitrogen content of solid ferrochrome to a very low level in the temperature range of 900° to 1 300°C. Significant removal of phosphorus is observed only at relatively higher temperature (1 080°~1 300°C) and in longer reaction durations. Such selective elimination of nitrogen results from great difference between the magnitudes of the diffusion coefficients of nitrogen and phosphorus in ferrochrome. On the other hand, in the treatment of liquid ferrochrome with Ca–CaF₂ (MSR*) and CaC₂–CaF₂ (CAR*) solution, phosphorus can be preferentially eliminated rather than nitrogen.^{21,31)} The present authors, thus, proposed to name the Ca–CaCl₂ and Mg–MgCl₂ treatment of solid alloy “ELNA (Extremely Low Nitrogen Alloy)” process in order to distinguish the refining feature of this process from these of MSR and CAR.

Holding time enough to achieve a desired low value of nitrogen content (below 60~70 ppm) depends on the temperature and the diameter of ferrochrome particle. At relatively lower temperatures (900°~1 000°C), the holding time is less than 3 hr for ferrochrome particles of 0.55 to 1.1 mm in diameter. This particle-size distribution can be practically obtainable by atomizing and mechanical-crushing methods. The reaction temperatures ranging from 900° to 1 000°C would not be so high to give serious problems in the selection of materials composing a reaction vessel. Since insignificant removal of phosphorus takes place, emission of poisonous gas, such as phosphine, from the reagents used in the experiments may be kept least (if any) during the washing of treated ferrochrome particles with hot water. ELNA process at 900° to 1 000°C will, therefore, be developed as a practical and promising way for the production of low-nitrogen ferrochrome which is suitable as a raw material for high-purity ferritic stainless steels.

Apart from the ferrochrome problem, ELNA process is expected to be available for the production of extremely low nitrogen-chromium metal. Chro-

mium-base alloys have superior oxidation-resistance at high temperatures. One of deterrents in the use of chromium-base alloys in structural applications is the lack of low temperature ductility. The brittle-ductile fracture temperature is very sensitive to the amount of impurities such as carbon, oxygen, sulfur, and nitrogen.³²⁻³⁴⁾ In particular, nitrogen is known to be so detrimental that its content must be kept below 10 ppm. Electrolytic chromium of commercial grade contains nitrogen of 80 to 150 ppm. Iodide chromium, which is made by the thermal decomposition of chromium iodide vapour, is reported to contain nitrogen of only 3 ppm.³³⁻³⁴⁾ However, it is very expensive. Preliminary experiments were thus made in which electrolytic chromium powder of flake form was treated with Ca–CaCl₂ mixture. The result is shown in Table 3, indicating that the nitrogen content is reduced to 5 ppm.

VI. Summary

Experiments are made in which ferrochrome powder is treated with molten Ca–CaCl₂ and Mg–MgCl₂ mixtures in the temperature range of 900° to 1 300°C under an argon atmosphere. The result shows that the nitrogen content of ferrochrome particle with diameter below 1.1 mm is efficiently reduced from 500~1 600 ppm to an extremely low level. On the other hand, the removal of phosphorus from the ferrochrome particles of 0.09 to 0.33 mm diameter becomes significant at higher temperatures (1 080°~1 300°C) and in longer reaction durations. Thus, at relatively lower temperatures (900°~1 000°C) selective elimination of nitrogen is possible. These results will give a powerful means of making low nitrogen powder of chromium-base alloys such as ferrochrome and chromium metal.

The removal degrees of nitrogen and phosphorus at a given temperature are found to be determined as a function of (t/d^2) alone. Neither chemical composition nor agitation of molten mixture affects the rate of nitrogen removal. From these results the diffusion process of both elements in ferrochrome are concluded to control their removal rates. With the aid of the theoretical relation, the diffusion coefficients of nitrogen and phosphorus are calculated as follows.

$$D_N = 3.5 \times 10^{-1} \exp [-36\,100/RT]$$

$$D_P = 5.5 \times 10^{-3} \exp [-37\,900/RT]$$

Table 3. Chemical composition of chromium metal (%)

	N	P	C	O	S
Electrolytic Cr*	0.032	0.002	0.01	0.36	0.029
Iodide Cr ³³⁾	0.0003	—	0.0003	0.0025	<0.001
Iodide Cr ³⁴⁾	<0.0003	—	0.0010	0.0032	0.001
Cr ELNA-treated					
at 1 100°C for 1 h	<0.0005	0.003	—	0.66	0.009
at 1 000°C for 2 h	<0.0005	0.003	—	0.83	0.009

* before ELNA treatment

* MSR and CAR are acronyms of “Metal Bearing Solution Refining” and “Carbide Refining”, respectively.

The obtained value for nitrogen is found to be nearly close to that in chromium metal.

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