



The preparation of chromium metal by a sealed, cold-hearth, plasma-assisted aluminothermic method

by L.R. Nelson*

Synopsis

The efficiency and cost-effectiveness of the aluminothermic reduction process in the production of ferro-alloys and 'pure' metals depends strongly on appropriate balancing of the process energy required. Insufficient energy results in a poor metal yield, while over-supply can result in excessive fuming and possibly even ejection of the reactor contents in a potentially dangerous 'thermite bomb' reaction. This situation becomes even more critical when the suitability of limited quantities of oxide from new sources must be evaluated, dictating smaller-scale testwork. The resulting higher relative heat losses from the system complicates control of the energy balance, and usually requires the addition of thermal boosters or reactant preheating in order to sustain an autothermic process. This often detracts from the quality of the metal product, and adds to the hazards of batch aluminothermic-reduction testing.

The development of a small-scale method (producing less than 2,5 kg of metal) for the plasma-assisted aluminothermic reduction of chromium oxide that overcomes such difficulties is described. The technique involves the use of a sealed 50 kVA plasma-arc furnace to provide controlled electrical ignition and supplementary energy to the reactants contained in a water-cooled copper crucible. The application of the method to the evaluation of the aluminothermic production of pure chromium metal from a unique chromic oxide source is reported.

Introduction

The year 1995 is the centenary of Goldschmidt's original German patent on the aluminothermic 'thermite' reduction process¹. At that time, the process and its variations were applied to the preparation and commercial production of numerous 'pure' metals and ferro-alloys, including chromium²⁻⁷, manganese²⁻⁴, molybdenum^{2,3,5,8,9}, tungsten^{2,5,8}, vanadium^{2,3,5,10-16}, niobium^{2-5,8,17}, tantalum^{2,3,5,17-19}, titanium^{2,3,5,16,17,20,21}, zirconium^{3,17,21,22}, and boron^{2,3,5}.

The process has found frequent application in South Africa. Recent reports that Vantra, Vantech, and Vametco are to increase the local aluminothermic production of ferrovandium attest to this²³. Especially in view of the recent expansion of local aluminium production at the Hillside Smelter, potential exists for future

applications of aluminothermic-reduction technology to the production of metals.

Future expansion of aluminothermic metal production depends, in part, on the capability to prove that metal oxides from new sources are amenable to processing. For evaluation of the suitability to aluminothermic reduction of chromic oxide from a unique source, a sealed, cold-hearth, plasma-assisted test unit was developed. This provided a means of evaluating the aluminothermic preparation of 'pure' chromium metal from a chromic oxide source. This paper gives details of the technique and describes the experimental results.

Process energy required

General aluminothermic processes

The key factor common to highly exothermic aluminothermic reactions is the need for tight control over the energy balance and resultant temperatures in the process. This is, in fact, so critical that it usually determines the following:

- the form of the metal produced, i.e. 'pure' metal, or alloy (e.g. the 3407°C melting point of pure tungsten can be lowered through alloying with iron to ensure adequate metal-slag separation)
- the means of containment of the liquid products at temperatures in excess of 2000°C
- the form of any alloying additions, i.e. scrap iron if endothermic cooling is required, or mill scale (Fe₃O₄), and even hematite (Fe₂O₃), if the additional input of exothermic energy is required⁵
- the nature and sizing of the aluminium reactant, i.e. fine powder to ensure rapid reaction kinetics and an associated temperature rise in the autothermic thermite reactions (as planned by Vantech²³), or larger scrap in

* GENCOR Process Research, P.O. Box 658, Krugersdorp 1740.

© The South African Institute of Mining and Metallurgy, 1996. SA ISSN 0038-223X/3.00 + 0.00. Paper received Oct. 1995; revised paper received Mar. 1996.

The preparation of chromium metal

electrically-assisted furnace reactions (as planned by Vantra and Vametco²³)

- ▶ the need for, and form of, any supplementary energy additions through charge preheating, and the use of higher (more exothermic) oxides of the required metal or of chemical boosters
- ▶ the need for slag fluxing agents such as lime or fluorspar (and even soda ash¹⁰) to modify the physico-chemical properties of the slag and so promote metal-slag disengagement.

It should be appreciated that a specific metal's affinity for oxygen and aluminium (including any tendency to form aluminides) will frequently determine the need for, and extent of, secondary processing to yield a 'pure' metal product. In such cases, arc-^{5,18,19}, vacuum-^{5,12,13,18,19}, electron-beam^{5,12,13,14,18,19,21,22}, or even molten-salt electro-refining¹⁰ may be necessary to effect simultaneous refining of these (and other) impurities by vaporization (especially as Al₂O and AlO sub-oxides^{14,21,22}).

Special requirements for small-scale aluminothermic tests

Small-scale aluminothermic testwork normally has two aims:

- (1) to prove the purity and amenability of a metal oxide from a new source for aluminothermic production
- (2) to establish suitable charge recipes and production guidelines for a new commercial production lot.

In both cases, the rationale is to use the minimum source of metal oxide. In aim (1), there may be only a limited

quantity of product available, produced at great expense in a novel pilot-plant process. Aim (2) may arise from a need to reduce the costs of the raw materials. Prefect⁶ even suggests that 'using conventional processing procedures, frequently as much as a tenth of an entire production run might be consumed in experimenting to determine the characteristic of a particular lot of ore'.

Small-scale aluminothermic testwork (with less than 2,5 kg of product metal) is therefore frequently desirable, especially in the evaluation of metal grade and new oxide sources. However, by virtue of the higher ratio of surface area to volume in smaller reactors, the heat losses are proportionately higher than in larger vessels, requiring the addition of chemical boosters to provide supplementary energy. This introduces a safety risk since the system becomes increasingly unstable as proportionately more chemical boosters are added to smaller batches. This effectively limits⁵ thermite batch sizes to between 25 and 40 000 kg.

Aluminothermic reduction of chromic oxide

Source

The primary objective of the work described here was to evaluate the potential of a novel source of chromic oxide to yield commercial on-grade chromium metal. Two grades of chromic oxide (about 100 kg of each in total) were available for laboratory-scale investigation: chromic oxide 10 and chromic oxide 6000, having chromium-to-iron ratios of approximately 10:1 and 6000:1 respectively (Table I). The aim was to test the raw material in individual lots of under 5 kg each (Table II).

Table I

Raw materials analyses in mass percentages

Type of feed	Cr ₂ O ₃	FeO	MgO	Al ₂ O ₃	CaO	TiO ₂	V ₂ O ₅	SiO ₂	S	P	C	Cu	Cr/Fe	Total
Chromic oxide 10	89.4	6.68	<0.1	0.37	1.03	0.44	0.74	0.28	0.01	0.011	<0.01	0.008	11.8	99.1
Chromic oxide 6000	97.3	0.014	<0.1	0.50	0.55	0.51	0.78	0.24	<0.01	0.007	<0.01	0.007	6120	100.0
Alumina	—	0.04	—	99.2	—	0.007	<0.01	0.15	—	—	—	—	—	99.4
Type of feed	Cr	Fe	Mg	Al	Ca	Ti	V	Si	S	P	C	Cu	O	Total
Al powder	—	0.25	0.11	99.35	—	0.018	0.010	0.13	—	—	—	0.041	0.11	99.9

Table II

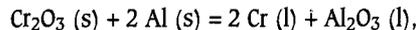
Charge recipes and key experimental conditions

Test	Design recipe			Duration of test min	Comments	
	Mass of Cr metal, kg	% excess 'Cr ₂ O ₃ '	% 'Cr ₂ O ₃ ' in heel			
Chromium oxide 10	I.1	0.5	10	20	10	No evacuation and Ar backfill No evacuation and Ar backfill — Al layer at base of heel Large batch—0.070 kg of unreacted feed
	I.2	1.0	10	10	18	
	II.1	1.5	10	20	15	
	II.2	1.5	10	30	15	
	II.3	2.5	10	20	14	
Chromium oxide 6000	1	1.5	13	30	18	Feed pipe melt—0.143 kg of unreacted feed 0.538 kg of unreacted feed 'Bomb'—0.322 kg of unreacted feed
	2	1.5	8	30	15	
	3	1.0	13	100	7	

The preparation of chromium metal

Fundamentals

The reduction of chromic oxide displays all the key characteristics of a typical aluminothermic process, including those related to the energy requirements, and to the fact that the purity of the final product is strongly determined by the purity of the reactants. The key reaction is as follows:



where, the equilibrium constant,

$$K_r = (a_{\text{Cr}}^2 \cdot a_{\text{Al}_2\text{O}_3}) / (a_{\text{Cr}_2\text{O}_3} \cdot a_{\text{Al}}^2).$$

The complete reaction in production batches of up to 40 000 kg is exceptionally rapid, typically occurring within 1 to 10 minutes^{3,4}. During this time, the process temperatures must exceed 2100°C to permit adequate separation of the product metal and slag (pure chromium and alumina melt at 1857°C and 2072°C respectively, Table III).

Table III
Basic physical data pertinent to the aluminothermic production of chromium metal

Species	Melting point °C	Boiling point °C	Vapour pressure (2100°C) atm	Density (25°C) kg/m ³
Metal				
Al	660	2467	0.121	2.7 × 10 ³
Cr	1857	2672	0.032	7.2 × 10 ³
Oxide				
Al ₂ O ₃	2072	2980	Volatile sub-oxides	3.7 × 10 ³
Cr ₂ O ₃	2266	4000		5.2 × 10 ³
CrO ₃	196	Decomposes	Decomposes	2.7 × 10 ³

Basic thermodynamics

The reaction is highly exothermic ($\Delta H^\circ_{25^\circ\text{C}} = -272,80 \text{ kJ}/(\text{mol Al})$, Table IV), but insufficiently exothermic to be autothermic, requiring the input of additional energy. As a general rule, Volkert² suggests that, for a self-sustaining reaction and adequate product metal-slag separation, $\Delta H^\circ_{25^\circ\text{C}}$ should be less than $-302 \text{ kJ}/(\text{mol Al})$.

The standard change in the free energy of the reaction is strongly negative ($\Delta G^\circ_{25^\circ\text{C}} = -266,89 \text{ kJ}/(\text{mol Al})$, Table IV), which yields a high value of K . An analysis of the type presented by Alcock²⁴, involving the application of Raoult's law to the alloy phase and Temkin's law to the slag phase, suggests that the extent of the aluminothermic reaction is sufficient to permit 'pure' chromium metal to be produced concurrently with an alumina-rich slag (Figure 1). The analysis also shows that, for the ASTM aluminium specification in chromium (less than 0,3 per cent Al) to be met²⁵, some chromium loss to the slag is inevitable. As would be expected from the application of Le Chatelier's principle to an exothermic reaction, K decreases with increasing temperature, so that the equilibrium extent of the reaction is most favourable at lower temperatures (Figure 2).

Basic kinetics: metal-slag

As liquid-phase mass-transfer kinetics (which are promoted at higher temperatures) play a significant role in aluminothermic reactions, especially at the metal-slag interface, the attainment of true equilibrium conditions should not be expected in reactions of typically less than 10 minutes' duration. Consequently, there should be some optimum processing temperature at which the kinetic and thermodynamic equilibrium effects can be ameliorated to yield the highest possible practical extent of reaction.

Table IV
Basic thermodynamics of the aluminothermic reactions in the production of chromium metal

Reactant	Product	$\Delta H^\circ_{25^\circ\text{C}}$ kJ/mol Al	$\Delta G^\circ_{25^\circ\text{C}}$ kJ/mol Al	Disadvantages
Cr ₂ O ₃ + 2 Al =	2 Cr + Al ₂ O ₃	-272.80	-266.89	
CrO ₃ + 2 Al =	Cr + Al ₂ O ₃	-548.52	-540.47	Deliquescent ⁴ , carcinogenic
K ₂ Cr ₂ O ₇ + 4 Al =	2 Cr + 2 Al ₂ O ₃ + K ₂ O↑	-429.70	-404.59	Carcinogenic
Na ₂ Cr ₂ O ₇ + 4 Al =	2 Cr + 2 Al ₂ O ₃ + Na ₂ O↑	-449.45	-429.41	Hygroscopic ⁴ , carcinogenic
3 BaO ₂ + 2 Al =	Ba ₃ Al ₂ O ₆	-766.52	-758.25	Toxic, strong oxidant
KClO ₃ + 2 Al =	Al ₂ O ₃ + KCl↑	-859.39 ²	-	Oxidant in explosives
3KClO ₄ + 8 Al =	4 Al ₂ O ₃ + 3 KCl↑	-840.10	-831.59	Oxidant in explosives
NaClO ₃ + 2 Al =	Al ₂ O ₃ + NaCl↑	-868.18 ²	-	Oxidant in explosives
3 NaClO ₄ + 8 Al =	4 Al ₂ O ₃ + 3 NaCl↑	-847.44	-838.76	Oxidant in explosives
6 NaNO ₃ + 10 Al =	5 Al ₂ O ₃ + 3 Na ₂ O↑ + 3 N ₂ ↑	-683.12	-685.31	Explosives, N source
6 KNO ₃ + 10 Al =	5 Al ₂ O ₃ + 3 K ₂ O↑ + 3 N ₂ ↑	-651.12	-652.04	Explosives, N source

↑ = Vaporizes at reaction temperatures

The preparation of chromium metal

Basic kinetics: solid-state

The reactant aluminium and chromic oxide should be thoroughly mixed to ensure intimate contact. Particle sizes must be carefully chosen since they impact strongly on the safety and reaction kinetics of the process²⁻⁸. Especially with too coarse an aluminium (with a median particle diameter, d_p , of more than 350 μm), the reaction kinetics may be

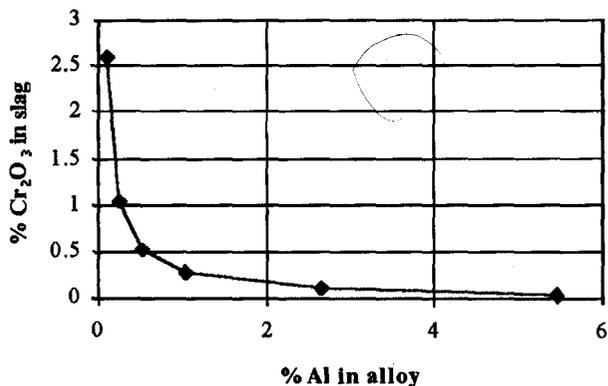


Figure 1—Equilibrium relationship between the aluminium in the alloy and the slag in the Cr_2O_3 at a temperature of 2100°C

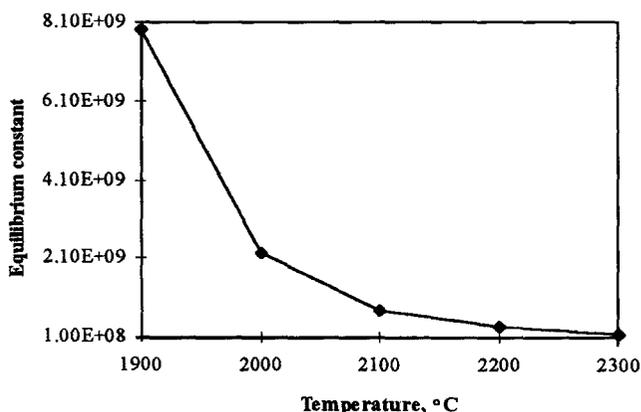


Figure 2—Effect of temperature on the equilibrium constant of the reaction $\text{Cr}_2\text{O}_3 + 2 \text{Al} = 2 \text{Cr} + \text{Al}_2\text{O}_3$

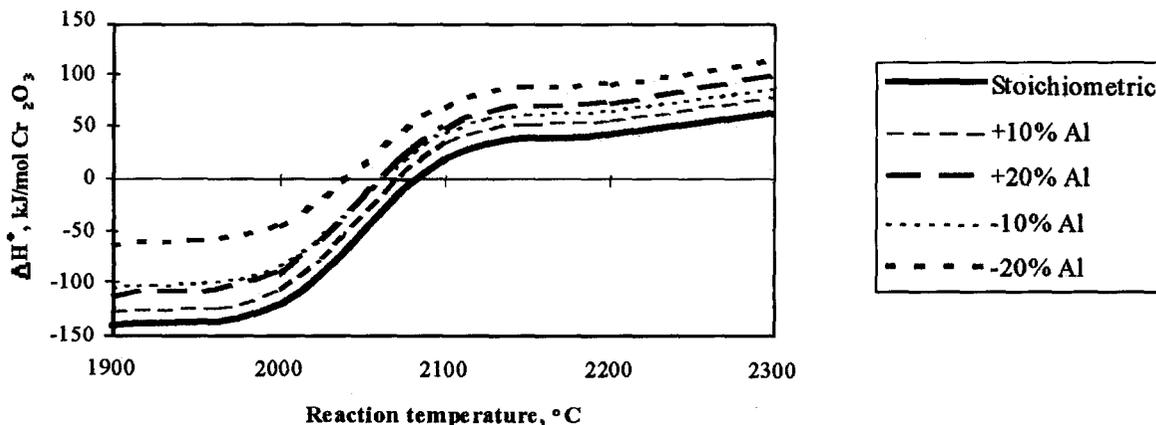


Figure 3—Effect of the aluminium–chromic oxide stoichiometry on the enthalpy of the reaction

impeded to the extent that the ignition of an autothermic thermite reaction becomes impossible⁸. Too fine an aluminium (with a d_p of less than 7.5 μm), on the other hand, leads to the fastest reaction kinetics and the highest peak temperature, but this is not always conducive to optimum metal recoveries because^{4,8}

- fast-reacting fine aluminium does not necessarily yield the longest time above product liquidus temperatures, which is more critical to efficient metal–slag separation than the peak temperature obtained *per se*
- vapour losses are higher
- dust losses are greater in a more violent reaction.

Moreover, the use of too fine an aluminium introduces a safety hazard owing to its increased potential for an uncontrolled explosion (ultrafine aluminium finds application as a 'booster in propellant compositions'²⁶, which can include its use as a component of solid-state rocket fuels). Belitskus⁸ therefore recommends the use of a medium-sized aluminium powder (with a d_p of about 100 μm) as the reactant, and thorough mixing of the reactants to yield an autothermic process.

Aluminium–chromic oxide stoichiometry

The aluminium–chromic oxide stoichiometry affects both the equilibrium distribution of the products and the exothermicity of an autothermic process. As close to a stoichiometric aluminium addition as possible will ensure maximum thermal efficiency (Figure 3). Under-stoichiometric or over-stoichiometric aluminium additions respectively should therefore be used only in investigations of the enhanced refining of aluminium from the metal (at the expense of poorer chromium yield), or of improved chromium recoveries from the slag (potentially resulting in contamination of the metal product by aluminium).

Energy balance

The need for an additional energy source to initiate and sustain the aluminothermic reduction of chromic oxide has already been noted. Standard methods² employed to achieve this include the following:

- preheating of the reactants (theoretically to 135°C ignoring heat losses, but practically to between 400 and 600°C for commercial production^{4,6})

The preparation of chromium metal

- addition of the higher oxide Cr_2O_3 ($\Delta H_f^\circ_{25^\circ\text{C}}(\text{Cr}_2\text{O}_3) = -548.52 \text{ kJ}/(\text{mol Al})$, Table IV)
- use of dichromate oxidants (e.g. $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Na}_2\text{Cr}_2\text{O}_7$, Table IV)
- use of a peroxide oxidant reacting to form a lower oxide in the slag (e.g. BaO_2 , Table IV)
- use of oxidant salts (e.g. sodium and potassium chlorates, perchlorates, or nitrates, Table IV)
- supply of 'clean' electrical energy from an external source (e.g. an electric-arc or induction furnace^{2,3,15-17,21,22}).

Precise control over the initiation of the reaction is not possible when preheating is used. The chemical methods are generally expensive, increase the consumption of aluminium, and are more chemically unstable and less environmentally acceptable, often being inherently toxic and carcinogenic, or releasing byproducts with these properties (Table IV). Furthermore, inevitably contained impurities further contaminate the metal. The latter fact complicates the identification of those chromium metal contaminants specifically derived from a novel source of chromic oxide, detracting from the primary objective of establishing its inherent suitability to industrial aluminothermic processing. Consequently, the option of an external supply of 'clean' electrical energy appears attractive.

Fluxes

The effect of chromic oxide on an alumina slag is to increase its liquidus temperature (Figure 4), which also increases the energy required to ensure adequate metal-slag separation. In autothermic processes, lime (or fluorspar) additions are frequently made to depress the liquidus temperatures³ (Figure 4) and viscosities²⁴ of the slag (Figure 5), thus effecting the metal-slag disengagement at lower process temperatures. The disadvantages of fluxing chromic oxide from a unique source include the following:

- increased overall losses of metal oxide through increased slag volumes
- inevitable introduction of still further impurities in the product metal
- contamination of the alumina slag product, rendering it less suitable for direct use in the production of high-alumina refractories.

Experimental method

Design of the reactor

Design, operational, and safety issues addressed in past investigations^{6-14,16-19,21} guided the development of the final reactor design. Nonetheless, the unit is considered unique in the respect that no previous design incorporated quite the same combination of features. The reactor comprised a 50 kVA sealed plasma-furnace shell (Figure 6) that had originally been designed for the investigation of a magnesium production process.

Within the shell, a water-cooled copper-crucible 'cold hearth' was supported over a bed of alumina bubble on graphite disks. The cold hearth (with a working volume of about 3 litres) comprised independent cylindrical and base water-cooled copper sections, which were electrically insulated from each other by a thin layer of aluminosilicate

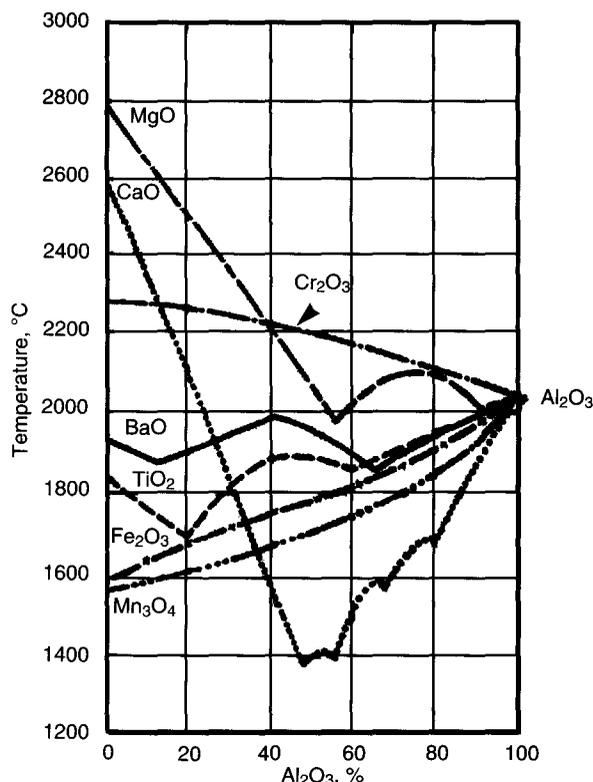


Figure 4—Liquidus temperatures in some binary Al_2O_3 oxide systems³

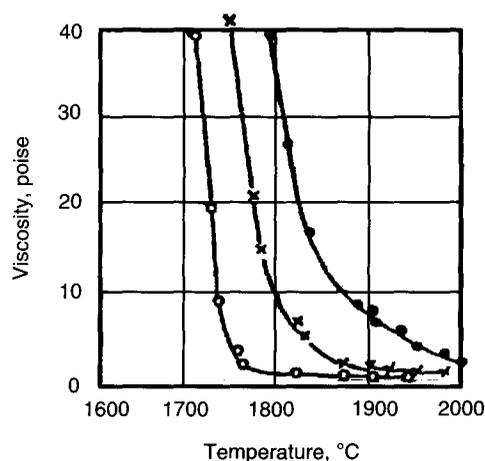


Figure 5—Effects of temperature and composition on some slags formed in the aluminothermic production of ferrovanadium²⁴

- = 86.9% Al_2O_3 , 2.2% CaO , and 1.4% MgO
- * = 84.5% Al_2O_3 , 6.6% CaO , and 1% MgO
- = 80.2% Al_2O_3 , 6.4% CaO , and 4.7% MgO

wool. The graphite disks provided the anodic electrical connection to the base section for the d.c. plasma arc, whilst the alumina bubble provided some furnace protection and safety in the event of an unplanned breakout.

Above the cold hearth, gaseous products were continuously evacuated through a side condenser unit. Argon was introduced above the charge through a 6 mm axial hole in a water-cooled copper-graphite composite electrode (with a tapered graphite tip of 30 mm outside diameter), which acted concurrently as the cathodic connection of the argon-stabilized d.c. plasma arc. An electrically insulated feed pipe

The preparation of chromium metal

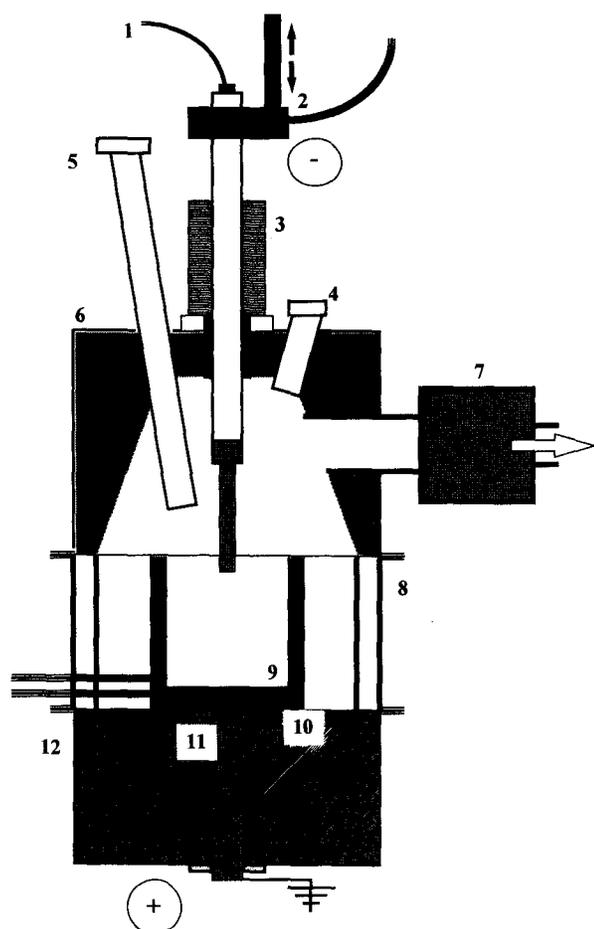


Figure 6—Schematic representation of the sealed 50 kW furnace

- 1 Argon supplied to water-cooled copper-graphite tip composite electrode
- 2 Electrode support mechanism, clamp, and power cable
- 3 Stainless-steel bellows and electrode seal
- 4 Observation window
- 5 Extended feed pipe from sealed hopper
- 6 Refractory-lined upper portion of furnace
- 7 Condenser
- 8 Water-cooled middle furnace section
- 9 Water-cooled copper crucible
- 10 Alumina bubble
- 11 Graphite anode connection
- 12 Refractory-lined bottom portion of furnace with anodic external connection

located just above the cold hearth, and connected to an externally sealed feeding system, could deliver feed directly into the arc-attachment zone (AAZ) of the plasma reactor.

Operating procedure

Preparation of the charge

The junction of the water-cooled crucible base and shell was first lined with a little pure alumina (Table II) to provide an 'inert' freeze-lining to protect the junction against the possibility of a liquid breakout (which never happened). When high-purity chromic oxide 6000 was reacted, a thin (100 g) layer of pure electrolytic chromium metal (Table II) was placed to form a bottom freeze-lining, thus effectively freeing the remaining reactor volume for the reaction of the

remaining charge batch. The premixed charge was then placed in the crucible. The low bulk density of the charge mixture relative to the densities of the final products (Table III), dictated that, in most tests, the whole charge batch could not be accommodated within the crucible at start-up. Consequently, all the aluminium, but only 30 per cent of the chromic oxide, was pre-charged. The remaining chromic oxide was typically fed from the sealed hopper over a period of 7 minutes. The addition of about 30 per cent of the chromic oxide to the aluminium heel before ignition was found to help to reduce aluminium losses due to fuming, which otherwise became excessive when the process was started in the presence of only a heel of pure aluminium. Also, to simulate a commercial 'thermite' reaction, the total mass was pre-charged in one test (Test 3 of Table II).

The unusually low density of aluminium (Table III) meant that it tended to 'float' on the Cr_2O_3 - Al_2O_3 slag, which covered the product chromium metal (Figure 7). This provided the rationale for the pre-charging of the total aluminium requirement, the perceived advantages being as follows.

- ▶ The denser top-charged Cr_2O_3 would experience a 'transitory' reduction reaction in its downward passage through the upper aluminium layer, in addition to subsequent reduction at the 'permanent contact' interface between the liquid aluminium and the slag.
- ▶ The chromium metal (and dissolved aluminium) so produced would similarly experience a 'transitory' refining reaction in its downward passage through the intermediate slag layer, in addition to final refining at the 'permanent contact' interface between the liquid chromium and the slag.
- ▶ The potential dangers associated with the handling of aluminium in the feed system would be eliminated.
- ▶ At startup, an electrically conducting pathway would be provided to the bottom anode contact.

The primary objective of the testwork was to evaluate the potential for the production of on-grade chromium metal from the chromic oxide source, rather than optimization of the chromium recoveries. Consequently, an addition of 10 per cent excess chromic oxide was typically made to ensure the production of chromium metal that was essentially refined of aluminium (Table VI).

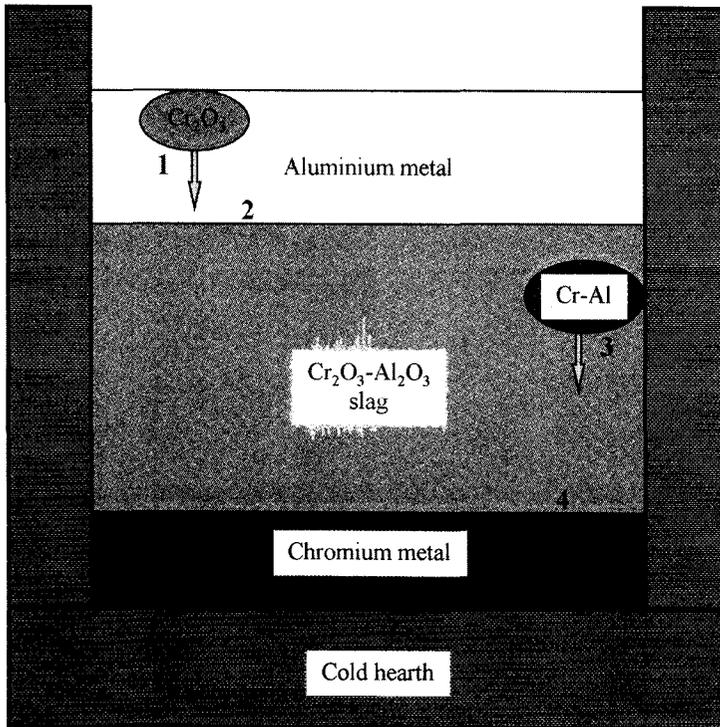
Startup of the reactor

The integrity of water cooling on the crucible was checked first. (The operation was immediately terminated if the water pressures dropped excessively, or if the outlet temperatures exceeded 50°C .) The plasma furnace was sealed, evacuated to 50 kPa in a check for leaks, and back-filled with argon (supplied through the shaped graphite electrode) at least three times before startup.

Ignition was then simply effected by switching on the d.c. power supply and lowering the electrode onto the charge to strike an arc. This defined the instant of reaction initiation. Full power of 45 to 50 kW was applied immediately, the argon-stabilized plasma arc being drawn out to about 50 mm in length to prevent undue contamination of the reacting material with graphite.

After one minute's operation, a molten pool was clearly visible in the crucible. Further chromic oxide was typically fed at a controlled rate over 7 minutes, before the bath was

The preparation of chromium metal



Key reaction sites:

- 1 'Transitory' reduction of Cr_2O_3 feed by Al metal
- 2 'Permanent contact' Al metal–slag interfacial reduction of Cr_2O_3
- 3 'Transitory' refining of Al (in Cr metal) by Cr_2O_3
- 4 'Permanent contact' slag–Cr metal interfacial refining of Al

Figure 7—Schematic diagram of the possible influences of different phase densities on potential reaction sites in the aluminothermic reduction of chromium

allowed to 'stew' for a further 7 minutes in order to help melt the unreacted feed and to promote the separation of metal and slag.

To terminate a test, the power was cut while water-cooling of the cold hearth was maintained. The reaction products cooled very quickly, permitting at least four 2,5 kg batches of chromium metal to be generated in a working day. Thus, meaningful testwork could be conducted rapidly.

Processing advantages

The specific design adopted for the testwork was considered to hold numerous processing advantages over prior designs (Table V).

Results

For the 23 tests performed in total, the representative conditions and results are presented in Tables II, VI, and VII for five tests on chromic oxide 10 and three on chromic oxide 6000. Thermodynamic simulations of typical charges by use of a free-energy minimization routine (PYROSIM²⁸) showed that there was generally good agreement between the predicted equilibrium and the experimentally achieved results (Tables VI and VII). Moreover, the simulations confirmed that the process was not autothermic, theoretically requiring an input of 0,116 kWh/(kg Al) ignoring any heat losses.

The ability to supplement the process energy independently of the aluminothermic reaction, through the application of a 'clean' plasma arc, ensured good metal–slag separation. The cold hearth effected a simple containment of the melt at high temperatures (estimated to be at least 2100°C) through the development of a protective freeze-lining at the crucible wall. This permitted easy removal of a

Table V

Perceived processing advantages of the sealed, cold-hearth, plasma-assisted method

Ignition	Plasma-assisted
<ol style="list-style-type: none"> 1. Safe, precise, and controllable 2. 'Clean' plasma-arc ignition 3. Eliminates contamination by chemicals or filament wires 4. Eliminates need for unstable chemical boosters 5. Eliminates imprecise ignition associated with charge preheating 	<ol style="list-style-type: none"> 1. 'Clean' external energy source introduces additional degree of freedom to processing 2. Independent temperature control to provide time for improved metal–slag separation 3. Better approach to equilibrium conditions with reduced dependence on reaction kinetics to dictate process conditions 4. Reaction kinetics effectively decoupled from sizing of raw materials and mixing effects 5. Eliminates use of less stable ultrafine aluminium powders 6. Permits fluxless operation even with highly refractory oxides 7. Provides bath stirring, enhancing interfacial metal–slag mass-transfer rates
<p style="text-align: center;"><i>Cold hearth</i></p> <ol style="list-style-type: none"> 1. 'Clean' containment with little product contamination 2. Fast test turnaround as products cool in the cold hearth (conventional batch tests take several hours to cool⁴) 3. Accommodates progressive feeding to utilize full reactor volume in batch operation 4. Fairly precise reaction termination achievable 5. Facilitates tight closure of the mass balance on a small-scale batch test 	<p style="text-align: center;"><i>Sealed reactor</i></p> <ol style="list-style-type: none"> 1. Improves control over gaseous interstitial impurity levels 2. Improves capture and containment of fugitive emissions

The preparation of chromium metal

Table VI

Analyses of the chromium metal in mass percentages

ASTM specifications for chromium metal	Cr	Al	Fe	C	Si	Ti	V	Cu	S	P	O	N
A	99.0	0.30	0.35	0.05	0.15	0.05	0.05	0.01	0.03	0.01	0.50	0.05
B	99.4	0.10	0.35	0.05	0.10	0.003	0.05	0.01	0.01	0.01	0.10	0.02

	Mass kg	Cr	Al	Fe	C	Si	Ti	V	Cu	S	P	O	N	Total
Tests on chromic oxide 10														
I.1	0.375	89.0	<0.02	8.90	0.54	0.037	<0.01	0.48	0.41	n.a.	0.02	0.90	0.8	101.1
I.2	0.584	91.0	<0.02	9.79	0.14	<0.02	<0.01	0.41	<0.02	n.a.	0.02	0.60	0.5	102.5
II.1	1.314	90.9	0.022	8.65	0.04	0.080	<0.008	0.51	<0.02	0.01	0.02	0.60	0.04	100.9
II.2	1.257	90.0	<0.02	9.16	0.05	0.085	<0.008	0.48	<0.02	0.01	0.02	0.79	0.05	100.7
II.3	1.857	89.6	0.027	10.5	0.04	<0.04	<0.008	0.34	<0.02	0.01	0.02	0.56	0.04	101.2
Simulation of test II.1	1.482	90.569	0.057	8.516	0.001	0.122	0.008	0.657	0.035	0.016	0.018	-	-	100
Tests on chromic oxide 6000														
1*	1.198	97.7	0.11	0.30	0.03	0.03	<0.02	0.48	0.02	<0.01	<0.01	0.74	0.09	99.5
2	1.293	97.4	0.58	0.24	0.07	0.03	0.03	0.50	0.01	<0.01	<0.01	0.18	0.06	99.1
3	0.805	96.3	0.29	0.37	0.14	n.a.	0.01	0.26	0.01	<0.005	0.011	0.90	0.18	98.5
Simulation of test 2	1.428	98.917	0.051	0.153	0.001	0.110	0.008	0.698	0.034	0.017	0.012	-	-	100

* Corrected for contamination by 0.018 kg of iron

Predicted process energy requirements: Both simulations II.1 and 2 required 0.116 kWh/kg Cr metal

Test I was without repeated prior furnace evacuation and Ar backfill

Test II was with repeated prior furnace evacuation and Ar backfill

n.a. = Not analysed

Table VII

Analyses of the slag in mass percentages

	Mass kg	Al ₂ O ₃	Cr ₂ O ₃ *	Fe ₂ O ₃ *	SiO ₂	TiO ₂ *	V ₂ O ₅ *	CaO	MgO	C	Total
Tests on chromic oxide 10											
I.1	0.792	76.33	19.50	2.00	0.25	0.10	0.05	0.14	0.02	0.05	98.4
I.2	1.341	62.1	37.5	4.66	0.42	0.11	0.04	0.38	0.05	0.04	105.3
II.1	1.905	68.5	29.2	2.12	0.10	0.09	0.04	0.22	0.02	0.03	100.3
II.2	1.993	66.6	32.1	2.51	0.34	0.12	0.07	0.46	0.01	0.03	102.2
II.3	3.228	57.7	42.9	1.64	0.38	0.12	0.05	0.34	0.01	0.02	103.2
Simulation of Test II.1	1.667	87.41	11.20	0.07	0.24	0.64	0.04	1.51	0.08	-	101.2†
Tests on chromic oxide 6000											
1	1.474	71.4	20.5	1.10	1.14	<0.2	<0.05	0.22	0.01	0.03	94.7
2	1.462	79.0	11.4	1.06	0.13	<0.2	<0.05	0.22	0.01	0.03	92.1
3	1.145	76.1	14.5	0.78	0.10	<0.2	<0.05	0.15	0.02	0.02	91.9
Simulation of Test 2	1.709	86.41	13.49	0.001	0.21	0.71	0.05	0.79	0.08	-	101.7†

* Cr, Fe, Ti, and V reported as Cr₂O₃, Fe₂O₃, TiO₂, and V₂O₅ respectively

† The simulation totals reported for the above species exceeded 100%, but the actual simulations totalled 100%, since these species contained lower oxides

clean reaction product, which greatly facilitated the closure of the mass balance, which is especially important when the charge batches are small.

Tests on chromic oxide 10

Owing to the low chromium-to-iron ratio of the chromic oxide (Table I) and the critical dependence of the product purity on the purity of the input raw materials, on-grade chromium metal was not expected. The trials were therefore

conducted with the aim of establishing a suitable operating procedure for aluminothermic testwork on the plasma facility.

Metal

The agreement between the predicted and the achieved metal masses and chemical analyses was remarkably good (Table VI). Key results included the following.

- Chromium contents between 89 and 91 per cent were achieved, compared with the 90.6 per cent Cr predicted.

The preparation of chromium metal

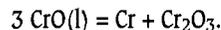
- Iron (about 9 per cent Fe) was the main contaminant, as expected.
- Highly efficient refining of the aluminium was achieved (typically 0,02 per cent Al, compared with the 0,06 per cent Al predicted).
- Both the predicted and the experimental vanadium contents (0,7 per cent V and 0,5 per cent V respectively) were about an order of magnitude higher than the ASTM specification of 0,05 per cent V.
- In the initial process development (Series I), the metal was contaminated by carbon, nitrogen, and oxygen to levels exceeding the least stringent ASTM A grade by one order of magnitude for carbon and nitrogen, and by a factor of two for oxygen. In later tests (Series II), in which greater care was taken to strictly control the furnace atmosphere and the length of the plasma arc, on-grade metal in terms of these three elements was achieved.
- Initial indications were that Prefect⁷ may be correct in suggesting that a water-cooled copper crucible cannot be operated above 1650°C in the aluminothermic production of 'pure' chromium if copper pick-up is to be prevented. (Test I.1 in Table VI had a copper content of 0,41 per cent.) However, with improved charge preparation to promote the formation of a freeze-lining, and with generally more controlled operation, copper contents of less than 0,02 per cent were obtained. Moreover, the aluminium reductant proved to be contaminated with copper (0,041 per cent, Table I), from which the simulations predicted a copper content of 0,035 per cent in the metal. Clearly, the pick-up of copper from the crucible was not a problem and, if anything, the plasma-assisted technique promoted the refining of some of the copper (possibly by vaporization).
- On-grade metal in terms of sulphur was produced (0,01 per cent S).
- The phosphorus specification of 0,01 per cent could not be met, but this was not too surprising since it had been predicted by simulation (0,018 per cent P predicted, compared with 0,02 per cent P achieved).
- The total chemical analyses were close to 100 per cent, suggesting that they were reliable.

Slag

Agreement between the predicted and the experimental results for the slag was not as good as for the metal (Table VII). The contents of chromic oxide, in particular, were higher than predicted (30 per cent compared with 11,2 per cent Cr₂O₃), which tended to dilute the alumina content (65 per cent compared with 87,4 per cent Al₂O₃). This also limited the chromium yield to 81 per cent. There are two possible explanations for this.

- (1) A little unreacted feed (predominantly hopper-fed chromic oxide) was sometimes observed to form a skull on the crucible.
- (2) The total chemical analyses were consistently higher than 100 per cent, suggesting that the oxides were in a lower oxidation state than reported. Mineralogical examination of the slags revealed high contents of finely dispersed metal. Thermodynamic simulations

predicted that 88,6 per cent of the chromium in the slag at equilibrium (at a temperature of 2100°C) would be present as CrO(l), and not as the Cr₂O₃ reported. As in many other chromium-bearing slags²⁹⁻³¹, the observation of dispersed metal in close proximity to Cr₂O₃ could well be explained as being due to the following disproportionation reaction as the samples cooled:



Chromic oxide 6000

The experimental results, which were well supported by the thermodynamic simulations, showed that the chromic oxide 6000 was not sufficiently pure for the production of commercial-grade chromium metal. Both progressive feeding and 'bomb' tests yielded similar results (Table VI).

Metal

The key findings for the metal produced can be summarized as follows.

- The total chromium contents were too low (97,7 per cent Cr was the best achieved, compared with a minimum 99,0 per cent Cr content for ASTM grade A).
- The aluminium grade was generally met, and it seemed that it would be possible to achieve the most stringent ASTM grade B specification of 0,01 per cent Al under tightly controlled conditions.
- The chromium-to-iron ratio of 6000:1 in the feedstock was sufficient to yield metal that met the specifications of 0,35 per cent Fe.
- The vanadium contents were at least an order of magnitude higher than the specification of 0,05 per cent V.
- The less stringent ASTM grade A specification (0,05 per cent Ti) could be met, but the more stringent ASTM grade B specification (0,003 per cent Ti) could not.
- With tight operational control, the specifications for carbon, copper, nitrogen, oxygen, sulphur, and phosphorus appeared to be achievable.

Slag

The agreement between the simulation and the experimental results for chromic oxide 6000 was better than that obtained for chromic oxide 10. The chromic oxide contents agreed well (typically close to the 13,5 per cent Cr₂O₃ predicted), but the alumina contents were somewhat lower than the 86,4 per cent Al₂O₃ predicted. The best chromium yield to the metal was 80 per cent.

However, the results were somewhat anomalous, in that the analyses typically totalled only 92 per cent (in contrast to the slag analyses for chromic oxide 10, which typically exceeded 100 per cent). Much less entrained metal was observed in the slags from chromic oxide 6000 since feeding problems had resulted in a somewhat higher incidence of unreacted feed. A spectrographic scan of chromic oxide 6000 identified boron, cobalt, gallium, molybdenum, nickel, lead, strontium, zinc, and zirconium as trace constituents (less than 0,01 per cent), but none could have been present in sufficient quantity to account for the shortfall. At this stage, it can only be suggested that some analytical error may have been responsible for the consistently low total chemical analyses.

The preparation of chromium metal

Conclusions

A bench-scale method using a sealed cold-hearth assisted by a plasma arc was successfully developed for use in the assessment of the amenability of small quantities of metal oxides to aluminothermic processing. The application of the technique to chromic oxide from a novel source resulted in the production of small ingots of chromium metal (0,5 to 2,5 kg in mass). It was proved that the chromic oxide was insufficiently pure to yield on-grade metal, especially in terms of total chromium content (the maximum achieved was 97,7 per cent Cr, compared with the more than 99,0 per cent Cr required), and of impurity vanadium content (the lowest achieved was 0,26 per cent V, compared with the specified 0,05 per cent V).

The bench-scale method developed is applicable to the testing of metal oxides from other novel sources for their amenability to aluminothermic processing. It should also prove useful in the characterization of widely varying production lots of metal oxides, since it requires only a small mass of metal oxide for each batch test. For non-autothermic aluminothermic reduction processes, the flexibility of supplementary electrical energy afforded through the plasma-assisted approach may prove to be a process benefit that can be exploited in a commercial environment.

Acknowledgements

This paper is published by permission of Samancor Ltd and Mintek.

References

1. GOLDSCHMIDT, H. Verfahren zur herstellung von metallen oder metalloiden oder legierungen derselben. *German pat.*, no. 96317. 13th Mar., 1895.
2. VOLKERT, G., and FRANK, K.D. (eds.). *The metallurgy of ferroalloys*. 2nd edn. Berlin, Springer, 1972.
3. ELYUTIN, V.P., et al. *Production of ferroalloys. Electrometallurgy*. 2nd edn. Moscow, State Scientific and Technical Publishing House, 1957.
4. BURCHELL, T. The aluminothermic process and the preparation of commercially pure chromium, manganese and special alloys such as ferro columbium. *The refining of non-ferrous metals—a symposium*. London, Institution of Mining and Metallurgy, 1950. pp. 477–495.
5. BELITSKUS, D. Aluminothermic production of metals and alloys. *J.O.M.*, Jan. 1972. pp. 30–34.
6. PREFECT, F.H. Metallothermic reduction of oxides in water-cooled copper furnaces. *Trans. Metall. Soc. AIME*, vol. 239. Sep. 1967. pp. 1282–1286.
7. PREFECT, F.H. Aluminothermic chromium and chromium alloys low in nitrogen. *Communications. Metall. Trans. B*, vol. 12B. Sep. 1981. pp. 611–613.
8. BELITSKUS, D. Aluminothermic production of ferroalloys. *J.O.M.*, May 1973. pp. 39–44.
9. PATTNAIK, S.P., et al. Ferromolybdenum from ferrimolybdate. *Metall. Trans. B*, vol. 12B. Dec. 1981. pp. 770–773.
10. WYPARTOWICZ, J., et al. An aluminothermic reduction of vanadium pentoxide. *Archiwum Hutnictwa*, vol. 28, no. 3. 1983. pp. 341–349.
11. POLYAKOV, A.Y. Development of method for melting ferrovanadium by aluminothermic method. *BISI Trans.* no. 22117. Sep. 1983. 10pp.
12. CARLSON, O.N., et al. A process for preparing high-purity vanadium. *J.O.M.*, Mar. 1966. pp. 320–323.
13. CARLSON, O.N., and SCHMIDT, F.A. Preparation of low-silicon vanadium metal. *Proceedings, Vacuum metallurgy conference on specialty metals*. Pittsburgh, TMS-AIME, Jun. 1984. pp. 129–136.
14. REINHARD, H., and KRUGER, J. Refining of vanadium-aluminium alloys to vanadium 99.9 per cent by electron beam melting. *Electron beam melting and refining, state of the art 1986*. Bakish, R. (ed.). 1986. pp. 53–62.
15. HESS, H.G., and SATTELBERGER, S. Vanadium production and application. *INFACON 5*. New Orleans, Apr. 1986. vol. 1, pp. 44–49.
16. SLATTER, D., et al. Technology for the production of new grades and types of ferroalloys using thermal plasma. *INFACON 4*. Rio de Janeiro, Sep. 1986. pp. 191–204.
17. BARCZA, N.A., et al. The aluminothermic reduction of the oxide of reactive metal. *S. Afr. Pat.*, no. 84/0245. 1984. 19pp.
18. GUPTA, C.K., and JENA, P.K. Production of tantalum metal by aluminothermic reduction of its pentoxide. *J.O.M.*, May 1986. pp. 25–28.
19. WILHELM, H.A., et al. Tantalum metal by bomb reduction of Ta₂O₅. *J.O.M.*, Jan. 1970. pp. 45–49.
20. FREITAS, L.R., et al. Aluminothermic reduction of anatase concentrates. *INFACON 4*. Rio de Janeiro, Sep. 1986. pp. 349–362.
21. FLETCHER, G.W. Aluminothermic process. *U.S. pat.*, no. 4,169,722. 2nd Oct. 1979. 10pp.
22. SMITH, D.DE.W., and DIPPENAAR, R.J. A thermal analysis of the liquid-pool purification of zirconium metal in a high-energy beam facility. *XVth CMMI Congress*. Glen, H.W. (ed.). Johannesburg, South African Institute of Mining and Metallurgy, 1994, vol. 2, pp. 73–80.
23. ANON. Vanadium industry being swung by launching into Fe-V production in South Africa. *TEX Report*, vol. 27, no. 6440. 19th Sep. 1995. p. 9.
24. ALCOCK, C.B. *Principles of pyrometallurgy*. London, Academic Press, 1976. pp. 231–235.
25. AMERICAN SOCIETY FOR TESTING AND MATERIALS. *Annual book of ASTM standards A481-73*. 1986.
26. HULETT METALS (PTY) LTD. *SUPRAMEX 2000 aluminium powder data sheet*. 7th Jul., 1986.
27. ARKHIPOV, O.A., et al. Influence of the physicochemical properties of the slag on the separation of liquid phases in the production of high-percentage ferrovanadium by the aluminothermic method. *Surface phenomena in metallurgical processes*. Belyaev, A.I. (ed.). New York, Consultants Bureau, 1969. pp. 224–226. (Translation).
28. JONES, R.T. (Convenor). PYROSIM seminar. Randburg, Mintek, Mar. 1991.
29. RANKIN, W.J., and BISWAS, A.K. The nature and behaviour of chromium in stainless-steelmaking slags. *Mineral Sci. Engng.* vol. 7, no. 2. Apr. 1975. pp. 89–98.
30. BARCZA, N.A., et al. The production of ferrochromium in a transferred-arc plasma furnace. *39th electric furnace conference* ISS. Dec. 1981. pp. 243–259.
31. TOKER, N.Y. Equilibrium phase relations and thermodynamics for the systems chromium-oxygen and iron-chromium-oxygen in the temperature range from 1500 to 1825°C. Pennsylvania State University, Ph.D. dissertation. 1978. ◆

Chamber of Mines post at Wits*

Professor Wolter te Riele has been appointed to a Chamber of Mines post in minerals processing at the University of the Witwatersrand.

Professor te Riele obtained his B.Sc., M.Sc., and Ph.D. degrees at the University of Natal before joining Mintek, where he worked for 26 years in both hydrometallurgy and minerals engineering and rose to a very senior level. He will concentrate on minerals engineering in his new position. ◆

* Issued by Lynne Hancock Communications,
P.O. Box 180, Witkoppen 2068.