

PLASMA PROCESSING OF OXIDE SYSTEMS IN
THE TEMPERATURE RANGE 1000-3000 K

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Abstract - The chemistry of the use of a plasma reactor for the melting and reduction of oxides up to 3000°K is discussed.

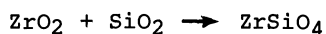
The development of plasma reactors which can be used to heat oxides up to temperatures as high as 3000 K during a relatively short time of exposure, has opened new pathways in high temperature processing on both the industrial and the laboratory scale. Such a capability only exists elsewhere in solar or arc-image heating, both of which can only provide heating which is external to the chemical system. The fact that plasma heating offers, in principle, the possibility of raising the temperature of a condensed phase to temperatures considerably above 3000 K, has given rise to speculations concerning the feasibility of carrying out chemical reactions at much higher temperatures than those which will be considered here, but it is suggested that such extreme temperature operations will very probably not be of industrial significance. An upper limit to practical operations will probably be set by a combination of several factors such as the residence time of particles which is necessary to achieve extreme temperatures, the increasing degree of volatilization of condensed phases and the limits which are set by the need for solid containers.

A number of proposals which have been made for the application of plasma heating devices have involved water-cooled sources, walls and collectors for the reacted products. Such schemes are attractive for laboratory studies, but with the rising cost of energy, plasma heating, which already suffers from the disadvantage at present of being wholly electrical in the source of energy, will almost certainly lose a significant industrial advantage if water-cooled containment is the only option. It is for these reasons that the studies which have been carried out in the University of Toronto have been designed to promote the most efficient utilization of electrical energy, together with the achievement of temperatures up to 3000 K in a furnace using the minimum amount of water cooling. Another and important consideration in the development of these reactors has been the

utilization of electrical power at domestic frequency with the simplest arrangement for power variation through transformers. Since the objective of all high temperature processes is to achieve high temperatures where the attainment of chemical equilibrium is very rapid, it is obvious that the exposure of particles to the heat-source which will also optimize reactions between condensed phase and gases, should be a major objective of high temperature processing. This requires that the residence time of particles in the heated zone should be prolonged either by use of a slowly moving gas phase to transport the particles, or through re-cycling of particles, such as may be achieved under fluid-bed conditions. Under the conditions of the operation of the extended-arc flash reactor (EAFR) (1) the flow rates of argon through the electrodes which are needed to sustain the electrical discharge permit the heating of particles of oxides to temperatures as high as 2800 K for particle sizes in the range 200-500 μm . Smaller particles than this have been used in reduction studies (see below) but evidence concerning the residence-time of very small particles in the plasma zone is at present not conclusive. The principal evidence that high temperatures have been achieved comes from observations of the spheroidization of oxide particles during transit in a 25 Kw furnace. Melting of particles in the range 350-500 μm . has been obtained to an extent of about 80% of the 40 g/min passed through the plasma zone with MgO, ZrO₂, CaO, Al₂O₃, TiO₂ and SiO₂ covering the fusion temperature range 1800-3000 K. In the case of silica a high percentage of spheroidization was achieved down to particle sizes around 125 μm . These results are quite similar to those obtained by Bonet, Vallabona and Foex using a plasma jet heater with silica particles (2). However, the generator used in that study was of 90 Kw power.

DECOMPOSITION AND FORMATION OF INTER-OXIDE COMPOUNDS AND SOLUTIONS

In some systems, the ability to attain temperatures up to 3000 K offers the possibility of the decomposition of complex oxides to their more simple components. The well established decomposition of zircon (ZrSiO₄) comes about because the free energy of formation of this compound from the component oxides reaches zero at about 1900 K (actually 1865 K)



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -10,630 + 5.7 T.$$

which is well within the plasma heating range for fine particles.

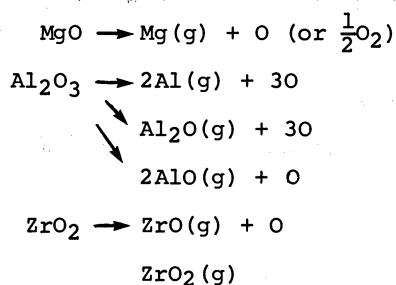
The scope of these decomposition reactions is determined by several factors, the principal among these being the entropy of formation of the compound oxide from its component oxides. The heat of formation of a stable compound will almost certainly be negative at low temperatures, and unless there are unusual features in the heat capacity of the compound at high temperatures, the achievement of zero free energy of formation, and hence of decomposition, will depend upon the balance of this negative heat of formation with a negative entropy of formation. Usually this latter term is quite small, less than one entropy unit, in the formation of a solid from two solids, and hence very high temperatures must be achieved for decomposition to occur. A further factor is that if the temperature which is achieved in the reactor leads to the fusion of both component oxides, then it is very probable that a single liquid phase will be formed thus destroying any phase separation which may occur at lower temperatures. The zirconia-silica system, where the melting points of the component oxides are separated by 1000°C seems to be a particularly good example of the circumstances under which separation could be achieved.

The formation of refractory interoxide solid solutions and compounds is best achieved via the liquid state. This comes about because the formation reaction from the simple oxides normally occurs by the counter-migration of cations through these oxides. In the solid state, where sintering reactions must be used, the low diffusion coefficients of many cations make sintering reactions times very long. However, in the liquid state diffusion coefficients are normally much higher being in the range 10^{-5} - 10^{-7} cm²/sec. The difficulties which are usually associated with the heating of oxide particles to high temperatures can clearly be overcome with the use of plasma heating devices in the light of the evidence of fusion given above. To date, no significant industrial application of this nature appears to have been considered. An example will be given below where the almost unique properties of plasma heating systems can be used to advantage in forming steelmaking slags with a high calcium oxide activity. The products here were required in the liquid state during the course of the experiment, but in the synthesis of new solid materials, a great deal of thought will have to be given to the solidification of molten oxide products

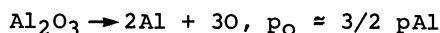
if the plasma preparation route is to be applied. Laboratory experiments which have been made with a 25 Kw. EAFR, have shown that molten material can be readily collected on a base which is slowly removed from the heated zone to form a column of solid material. Rods of alumina have been formed in this way, and experiments with alkaline earth oxides are under way.

VAPORIZATION OF OXIDES

Refractory oxides all achieve significant vapour pressures at temperatures between 2000 and 3000 K. The mechanisms of vaporization in vacuum or in an inert atmosphere change from one oxide to another and typical examples are



The compounds of elements which form only one simple oxide in the condensed phase e.g. Al_2O_3 , must vaporize with the formation of the gaseous species in accord with the oxide stoichiometry. It follows that, as an approximation, the pressure of each species can be calculated from a knowledge of the free energy of vaporization using the stoichiometry ratio in the calculation thus:



$$\Delta G^\circ_{\text{evap}} = -RT \ln K = - (2 RT \ln p_{\text{Al}} + 3RT \ln p_{\text{O}}).$$

$$\approx - 5 RT \ln p_{\text{Al}}$$

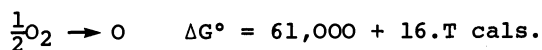
From the data which have been assembled for the common refractory oxides (Table 1) it can be calculated that the oxides MgO , Al_2O_3 , SiO_2 and ZrO_2 will all have vapour pressures greater than 10^{-4} atmos at temperatures below 3000 K. Thus the vaporization products of these oxides will become significant components of the plasma/gas phase system in a reactor which contains particles of these materials, the surfaces of which have reached 3000 K. The vaporization coefficients which yield the free evaporated rate from the equilibrium rate which was calculated above have been found to be between 0.1 and 1 for most refractory oxides at temperatures around

TABLE 1

Thermodynamic Data for Oxide Vaporization

<u>Oxide</u>	<u>Vapour Species</u>	<u>Free Energy of Vaporization (Cals.)</u>	
Alumina	Al + O	$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 3\text{O}$	$\Delta G^\circ = 74200 - 176T.$
	$\text{Al}_2\text{O} + \text{O}$	$\text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{O} + 2\text{O}$	$\Delta G^\circ = 483,000 - 120T.$
Calcium Oxide	Ca + O	$\text{CaO} \rightarrow \text{Ca} + \text{O}$	$\Delta G^\circ = 251,100 - 62.7T.$
Magnesia	Mg + O	$\text{MgO} \rightarrow \text{Mg} + \text{O}$	$\Delta G^\circ = 240,800 - 67.4T.$
Silica	SiO + O	$\text{SiO}_2 \rightarrow \text{SiO} + \text{O}$	$\Delta G^\circ = 244,400 - 76.2T.$
Zirconia	ZrO_2	$\text{ZrO}_2 \rightarrow \text{ZrO}_2(\text{g})$	$\Delta G^\circ = 327,000 - 75.0T.$

To change the equations to represent diatomic rather than monatomic oxygen, add the equation



proportionately to the number of oxygen atoms in the evaporation reaction.

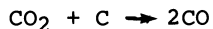
2000 K (3) and these values appear to approach unity as the temperature increases, or as melting occurs. It can be concluded, therefore, that the equilibrium rates which are calculated wholly from thermodynamic data will give a fairly accurate guide to evaporation behaviour in the range 2000-3000 K.

OXIDE REDUCTION REACTIONS

The absorption of energy from a plasma source by oxides depends to a large extent on the valence states of cations in the oxides. Materials such as silica and alumina become more conductive to heat at higher temperatures, their thermal conductivities showing a wellknown minimum in the temperature range where heat transfer by radiation starts to be more significant than that by phonons. In oxide systems such as those of iron, chromium and manganese, the presence of more than one valence states of the cation makes energy absorption more probable than in the transparent single valency cation oxides. The concentrations of the valency states of a variable valency cation are a function not only of temperature but also of the oxygen partial pressure in the surrounding gas phase. When carbon monoxide can be generated in a neutral gas atmosphere, then reduction reactions can occur which lead to enhanced radiation absorption by oxide materials and thus more efficient plasma heating. Since the extended arc in the EAFR can be sustained by carbon monoxide as well as by argon, it is a comparatively simple matter to bring about such reducing conditions.

It is part of the design of the EAFR that material which is charged to the reactor is pre-heated to about 900°C in a rotary kiln and then allowed to fall under gravity, in counter current flow to the rising hot gases leaving the plasma zone. At the point of entry into the plasma zone it has been found by sampling, that particles of chromite have been reduced to liquid iron (M.pt. 1535°C) and a chromium-rich solid or slag when CO is added to the arc gas, and hence these particles must have reached 1600°C at this early stage of treatment (4).

The conditions for reduction are of course obtained from the thermodynamic data for the reduction reaction with carbon, and it has been established that this usually occurs via a Boudouard reaction in the gas phase between the metal oxide and carbon particles.



Since direct reduction would involve physical contact between the oxide and carbon particles this is likely to be a rare event. The degree to which reduction of an oxide by carbon in a given system can be carried out is therefore a function of the capacity of the gas to transport oxygen from the oxide to carbon in the form of a CO₂/CO mixture. This capacity can be readily judged by comparing the CO₂/CO ratio in equilibrium with the metal oxide phase in the original and reduced stage with that in equilibrium with carbon at the reaction temperature. The Ellingham diagram for the free energy of formation of oxides as modified by Richardson and Jeffes (5) shows this factor very clearly. The free energy of the carbon/oxygen reaction to form CO becomes more negative as the temperature increases, and from the temperature at which this line intersects the various metal/metal oxide lines, it is possible to estimate the temperature required for the reduction of oxide to metal when this is in contact with carbon. The CO/CO₂ ratio in equilibrium with pure carbon becomes very large as the temperature increases as does that in equilibrium with the metal/oxide systems which are crossed by this free energy line at high temperatures. Hence in these regions of high chemical stability, the capacity of the gas to transport oxygen from oxide to carbon as CO₂ becomes very small, and hence although reduction is, in principle, feasible, the rate of reduction will be extremely small. As an example of this, at 1600°C the CO₂/CO ratio in equilibrium with FeO/Fe is about 1/10 whereas that in equilibrium with CO/C is less than 1/10⁴. Hence carbon particles readily reduce iron oxide particles via the gas phase at this temperature. On the other hand, the CO₂/CO ratio in equilibrium with MnO/Mn is about 1/3 x 10⁴ at this temperature and thus the change in CO₂ partial pressure in the gas phase between an oxide particle and a carbon particle is only about 3 x 10⁻⁴ atmos, and hence very little oxygen can be transported as CO₂ in the gas phase.

These considerations suggest that expectations of successful plasma heating applications to the reduction of stable metal oxides to metals at high temperatures which are not otherwise capable of reduction will not be significant when this gas phase mechanism of reduction is predominant.

The fact that many elements which form stable oxides such as chromium,

titanium and silicon also form stable carbides plays a significant role in the discussion of the reduction of these oxides by carbon. Thus, as an example Worrel (6) has shown that chromium oxide can only be reduced to carbide at temperatures below 1800 K. The reduction of titanium oxides to metal is not possible because of the high stability of the carbide TiC at temperatures up to the limit considered here. On the other hand, silicon can be obtained by reaction between liquid silica and silicon carbide at temperatures above about 2100 K although the pressure of silicon monoxide gas above this mixture of phases is high under these circumstances.

Experimental studies of the reduction of chromite with carbon in the EAFR provide a useful comparison with the conventional submerged arc process. In this latter process the slag phase serves not only to contain the molten chromium oxide during the interfacial reduction



but as an electrical resistance heater in circuit with the graphite electrodes. The presence of these electrodes within the condensed system tends to bring the metal phase to saturation with carbon.

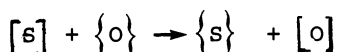
In the EAFR treatment the graphite electrodes are not in contact with the condensed phases, and thus the metal phase can be retained at any carbon content which is judged appropriate. Secondly the slag phase is heated by radiation from the plasma zone, and hence its chemistry can be adjusted to optimize the slag-metal reactions and to maintain the viscosity at a suitable level for the transit of liquid metal drops through the slag phase.

Naturally occurring mineral chromite always contains some silica (1 - 10 wt.%) as well as sulfur, and in the submerged arc furnace reduction of natural chromites Kadarmetov et al (7) suggested that sulphur recycling occurs by the formation of volatile SiS(g) at the slag surface which condenses on the descending fresh charge and returns to the slag. In the more open structure of the EAFR, it has been found that sulfur is indeed removed by volatilization, but since there is very little recycling, the sulfur content of the resulting ferrochromium is responsible for less than 10% of the sulfur recovery the majority being found in the exit dust of the preheater,

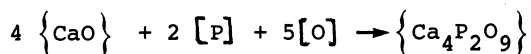
Similarly in submerged furnace practice, Robiette (8) suggests that

about 80% of the mineral phosphorus content is recovered in the ferro-chromium alloy. This is somewhat higher than the fraction found in EAFR reduction the range usually being between 10 and 50%.

The advantages that may be expected from heating a slag-metal system by means of a high temperature radiant source placed above the system are related to the physical chemistry of the slag-metal system, and to the necessity to contain the reactants. When the slag is heated by resistance heating then the metal phase will have the major opportunity to come to equilibrium during passage as droplets through the slag. However, when the slag is heated by radiation, it is quite possible that the major site of energy absorption would be at the slag-metal interface since the metal is opaque to the radiation to which the slag will be to some extent transparent. It is thus conceivable that the temperature at the slag-metal interface will be the highest in the condensed phase section of the furnace, and, of course it is here where slag-metal reactions can occur under optimum conditions. Typical reactions involved in metal refining such as sulfur-oxygen exchange between the metal and slag



and the dephosphorization reaction

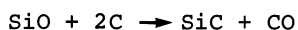


could be carried out at temperatures around 2000 K which is well above the present temperature capabilities of industrial systems. As an example of this, in recent studies of the preparation of ferro-manganese using the 25 Kw EAFR it has been possible to make alloys with less than 0.005% phosphorus even when deliberate additions of calcium phosphate were made to the slag. A further comment on refining reactions is that the efficient slag heating capabilities of the extended arc permits the use of slags with a basicity considerably higher than that normally used since the higher temperatures needed to melt highly basic compositions are readily achieved. This reduces the dissolution of the MgO lining to the furnace which has been the most useful container material.

VAPORIZATION IN OXIDE SYSTEMS

One of the major industrial problems in the large production of silicon is the evaporation of silicon monoxide from the molten charge. This

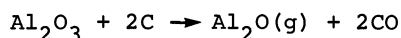
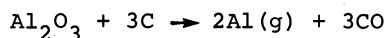
causes the closing of the pores in the colder parts of the furnace burden, and hence prevents the escape of carbon monoxide which can have dangerous consequences. The use of the separate particle furnace charge which is available in a fluidized bed system or in the falling charge of the EAFR avoids the difficulties of SiO condensation, and there is good evidence that the silicon is returned to the furnace as silicon carbide. This probably occurs because the gaseous SiO molecules can reach very high temperatures during the ascent through the plasma, and hence the surface temperature of the reaction between the molecules and the descending carbon particles can be high enough to allow silicon carbide formation at the gas-solid interface. It was observed during experiments to prepare silicon in the EAFR that the silicon fume leaving the top of the furnace was very much more dense when carbon was absent from the descending charge than when it was present. The recirculation of silicon by means of the reaction



seems a very reasonable explanation of this occurrence.

The condensate of silicon monoxide disproportionates to give silicon metal and silica. This reaction which is common amongst lower valency high temperature species, suggests that future routes to the extraction of metals could be via such disproportionation reactions.

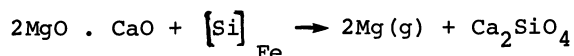
The carbothermic reduction of alumina would seem to be possible if temperatures in excess of 2000 K can be readily achieved. The reduction reaction is very complex, producing a number of gaseous species at high temperatures, depending upon the state of reduction. Reactions which must be considered are



as well as the reactions producing condensed phases which include the oxycarbide $\text{Al}_4\text{O}_4\text{C}$ as well as the carbide Al_4C_3 . At temperatures around 2500 K where the vapour pressure of aluminium is about 0.22 atmos, the condensed phases in equilibrium with graphite are an aluminium-carbon alloy and an alumina slag containing carbon (9). The vapour phase will contain $\text{Al}(\text{g})$ and $\text{Al}_2\text{O}(\text{g})$ in approximately equal proportions. These gases may undergo further reaction with the descending, cooler, carbon particles of the burden, as in the case

of silicon production, to recycle the metal to the hearth of the furnace. It should be noted that such a reaction scheme for the production of aluminium is somewhat speculative at present due to the paucity of our quantitative knowledge of the Al-O-C ternary system above 2000°K.

Finally, the very stable oxides MgO and CaO can be reduced by carbon at high enough temperatures and, in principle, it should be possible to produce magnesium and calcium vapour by direct reduction with carbon at temperatures around 2000 K. Unfortunately the major difficulty surrounding such an application as this in plasma technology is the very real possibility of back-reaction before the system can be quenched. A useful reaction which can be employed to avoid this problem is that used in the Pidgeon process where ferrosilicon is used as the reductant in place of carbon, and some calcium oxide is added to lower the activity of the product silica



Since there is only one gaseous product, the possibility of back-reaction does not arise. This reaction would seem to be particularly well suited to plasma technology in view of the excellent slag-heating capabilities of plasma flames.

REFERENCES

1. C.A. Pickles, A. McLean, C.B. Alcock and R.S. Segsworth. *Advances in extractive metallurgy*, I.M.M., London (1977).
2. C. Bonet, G. Vallabona and M. Foex. *Bull. Soc. Fr. Céram.* 94, 27 (1972).
3. C.B. Alcock and M. Peleg. *Trans. Brit. Ceram. Soc.*, 66, 217 (1967).
4. C.A. Pickles, S.S. Wang, A. McLean, C.B. Alcock and R.S. Segsworth. *Trans. I.S.I. Japan* 18, 369 (1978).
5. F.D. Richardson and J.H.E. Jeffes. *J.I.S.I.* 160, 261 (1948).
6. W.L. Worrell, *Met. Trans.* 233, 1173 (1965).
7. Kh.N. Kadarmetov, L.N. Rukasov and V.L. Koloyatsev. *Stal.* (Eng. Ed.) 622 (1964).
8. A.G.E. Robiette. *Electric Smelting Processes*. J. Wiley & Son, N.Y. (1973).
9. G. Gittlesen, O. Herstad and K. Motzfeld in *Selected Topics in High Temp. Chem.* Universitetsforlaget, Oslo 1966.