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# Novel process for enhanced lunar oxygen recovery

N. J. WELHAM
*Departments of Applied Mathematics and Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 0200, Australia*
*E-mail: nicholas.welham@anu.edu.au*

The generally accepted method for recovering oxygen on an extraterrestrial body is by thermal reduction of indigenous minerals, the most amenable of which is ilmenite, $FeTiO_3$. Thermodynamic modelling shows that carbon is a more effective reductant than hydrogen. In this paper the effect of extended ball milling on the carbothermic reduction of a terrestrial beach sand derived ilmenite is examined. The rate of oxygen recovery into the gas phase is substantially faster for powders milled together and a concomitent lowering of onset temperature is also noted. XRD examination of the final powders indicate that reduction of ilmenite proceeds *via* elemental iron and rutile which is then further reduced to sub-oxides. The presence of nitrogen, or excess carbon, leads to vastly greater oxygen recovery due to the formation of titanium nitride or carbide with complete release of oxygen from the mineral achieved in 1 h at 1200°C. *© 2001 Kluwer Academic Publishers*

## 1. Introduction

For the success of any future lunar base the most critical supply will be that of oxygen. It is generally accepted that oxygen is too costly to transport to the base [1] and therefore it will need to be extracted from the minerals which comprise the lunar surface. Of the numerous processes that can extract oxygen only two are considered viable, reduction of ilmenite and reduction of ferrous iron in glass [2]. There are two reductants considered for their potential use, hydrogen and carbon. Carbon was the initial choice in early studies [3, 4], but hydrogen has been the predominant reductant studied recently [5–12]. Much work on the carbothermic reduction of ilmenite has been reported over the past thirty years [13–30], but with the aim of producing synthetic rutile as a feedstuff for pigment titanium dioxide production. However, these processes have all involved relatively long processing times at high temperatures, with a typical commercial ilmenite reduction process having a residence time of 24 h at 1150°C. A higher temperature process has been proposed [17, 31] in which temperatures of 1425°C for up to 21 h were used. The resultant product showed incomplete reduction with $Ti_2O_3$ present along with elemental iron and a Ti(C,O) phase of undefined composition.

Hydrogen reduction of lunar ilmenite has been shown to be rapid with little reduction at 1000°C beyond 10 min [12], synthetic ilmenite is reportedly slower with the reaction complete in 20 min [5]. A maximum oxygen yield of 4.6% was reported for a lunar sample heated at 1000°C under 10 atm of hydrogen, the solid products consisted of iron and the reduced titanium oxides $Ti_7O_{13}$, $Ti_6O_{11}$ and $Ti_4O_7$ [12]. Other work has indicated that there is an initially fast reaction which is followed by a slower mass loss process [10]. It has been shown that partly reduced ilmenite consists of a core of unreduced ilmenite surrounded by elemental iron and titanium oxides which contain an increasing fraction of Ti(III) towards the surface [21]. The typical particle size for beach sand ilmenite is $\sim$150 $\mu$m and slow solid-state diffusion of oxygen within the grains is the primary cause for the slow reduction after the initial rapid reaction which forms a product layer on the surface. Even using ultrafine ($\sim$20–25 nm) $TiO_2$ particles coated with carbon as a starting material the presence of $Ti_nO_{2n-1}$ phases was evident [32–34].

The chemistry involved in the reduction is somewhat simpler for hydrogen than for carbon since the ultimate aim is to form water, which can be electrolysed to form oxygen and hydrogen. Carbon reduction also requires hydrogen to effect the production of water by further reaction between carbon oxides and hydrogen [35]. However, the carbon based reduction process does not involve using a gas handling system to recycle hydrogen into the reduction zone and can therefore be run under reduced pressure. These advantages over hydrogen indicate that the carbothermic production of oxygen warrants further investigation. It has been shown in a number of systems that reduction reactions involving carbon can be induced during extended milling [36–41], although only a few reactions have been reported with carbon as the main reductant [40, 41]. In systems involving carbon as the reductant it has also been demonstrated that significant decreases in the onset temperature and the rate of reaction can also be achieved in solid-solid systems [42, 43].

Therefore an examination of the recovery of oxygen from ilmenite after milling with carbon was undertaken to assess the scientific practicalities of the process.

## 2. Thermodynamic assessment

A thermodynamic assessment of the previously reported reductants, carbon [3, 4] and hydrogen [5–12] was performed to determine which had the greater potential to remove oxygen from the mineral ilmenite. The assessment was made using the Outokumpu HSC package [44] which uses a free energy minimisation technique to determine the equilibrium condition for a suite of phases. The starting phases were ilmenite and either carbon or hydrogen, both of which were added at twice the stoichiometric requirement for removal of all of the oxygen (as either CO or water). The temperature in the system was raised and a new equilibrium calculated using the previous equilibrium as a starting point. This method simulates isothermal processing for infinite time thereby allowing reactions to go to equilibrium, in all cases the system is closed and the gaseous products are assumed to remain within the system—unlike a practical application of this process where gas removal would occur.

It should be noted that there is a series of titanium oxides containing both Ti(III) and Ti(IV) which have the general formula $Ti_nO_{2n-1}$. Specific phases with $n \leq 10$ have been crystallographically characterised [45, 46] but the higher values of $n$ have not been examined in similar detail. It has been shown that slightly reduced rutile (with $n > 700$) can be formed that is crystallographically distinguishable from rutile [47]. There is very little thermodynamic data for these phases with only data for $n \leq 4$ present within the database used for these calculations. The undoubted presence of phases with higher values of $n$ during ilmenite reduction [13–30] (and also mixed iron(III)-titanium(III/IV) oxides analogous to the $Ti_nO_{2n-1}$ phases) make these calculations presented a first approximation. It should be noted that there calculations do not account for activation energy requirements of the reaction(s) and although feasible there may be no reaction in practice.

The results from the calculations shown in Fig. 1, clearly indicate that hydrogen is predicted to extract more oxygen than carbon only below 710°C, indeed, hydrogen is even predicted to cause some reduction at 25°C (∼0.02% oxygen extracted). Experimental evidence indicates that for a lunar sample heated at 1000°C under 10 atm of hydrogen there was a maximum oxygen yield of 4.6%, somewhat less than the 12.2% predicted. Hydrogen reduction of lunar ilmenite has been shown to be rapid for 10 min with a further slow reaction occurring [10, 12]. This slow reaction may well be the reason for the apparently low yield compared with thermodynamic prediction (which assumes equilibrium) whereas the experimental work was limited by the slow kinetics of the second stage. Examination of the distribution of the titanium in the system (Fig. 1) shows clearly that little reduction beyond $TiO_2$ occurs even at 1500°C, although 0.2% of $Ti_nO_{2n-1}$ phases are predicted to be present at equilibrium. Previous experimental work [12] has indicated that the solid products of reduction at 1000°C consisted of iron and the reduced titanium oxides $Ti_7O_{13}$, $Ti_6O_{11}$ and $Ti_4O_7$, clearly somewhat different to the prediction here, partly due to the absence of data for the higher $Ti_nO_{2n-1}$ phases.

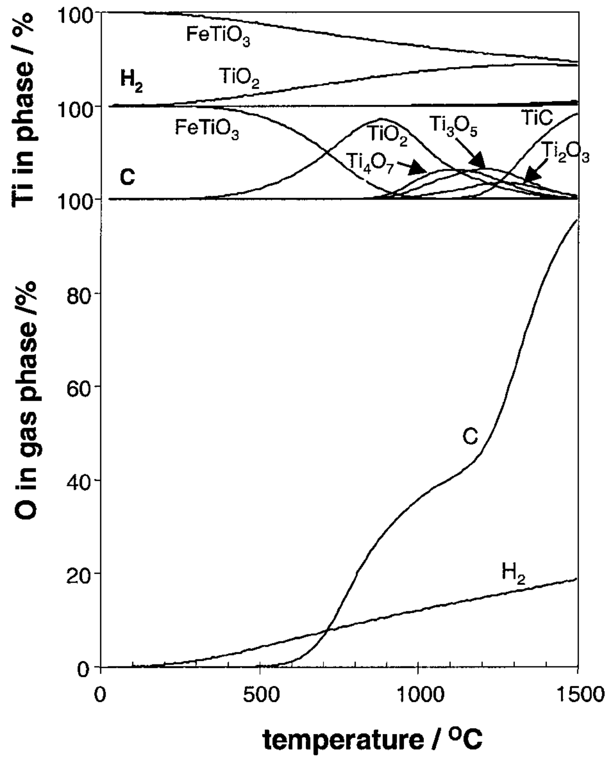

*Figure 1* Fraction of oxygen extracted into the gas phase (as CO, $CO_2$ or $H_2O$) during reduction of ilmenite by carbon or hydrogen. Also shown is the fraction of titnaium in the phases formed during the reduction.

Carbon shows more effectiveness as a reductant with increasing oxygen recovery into the gas phase until TiC is formed. Examination of the solid products indicates the products have decreasing $n$ with increasing temperature, as observed experimentally [30], until TiC forms.

From these data it is clear that carbon is a much more effective reductant than hydrogen with substantially more oxygen removed into the gas phase at most practical processing temperatures.

## 3. Experimental

The ilmenite used was examined microscopically and found to be very pure with only traces (<1 number %) of other minerals, particle sizing showed $d_{10} = 130\ \mu$m and $d_{90} = 270\ \mu$m. Carbon was added to enable complete reduction of ilmenite i.e. to Fe and Ti with a molar ratio of 1 : 3 for reaction (1).

$$FeTiO_3 + 3C = Fe + Ti + 3CO \qquad (1)$$

The samples were milled under vacuum ($\sim 10^{-2}$ Pa) at room temperature in a stainless steel ball mill [48] with five 1″ Ø (25.4 mm) stainless steel balls confined in the vertical plane. A constant mass of 7.00 g was used for each milling experiment.

Samples were prepared by physically mixing as-received powders and mixing powders milled separately for 20 h, these powders will be termed “unmilled” and “milled then mixed” in the subsequent discussions.

Mixing was performed by rotating a vial containing the powders end-over-end for 24 h to ensure consistent composition. Powders of the required stoichiometry were also milled together for 2, 20 and 200 h.

A Shimadzu TGA-50 thermogravimetric analyser (TGA) with an alumina crucible containing approximately 50 mg of powder was heated at 20°C min$^{-1}$, in dry argon flowing at 80 ml min$^{-1}$ to 1100°C then held for 15 minutes. The mass loss curves were normalised to the mass of powder at 200°C to account for any variation in mass loss due to moisture within the sample. Samples were also isothermally annealed for 0.5 h at 1000°C in argon.

Further samples were prepared using a 4 : 1 ratio of carbon : ilmenite, this was predicted to allow formation of TiC as it is reportedly [49] difficult to separate oxygen from titanium. These samples were milled for 100 h, then processed by TGA and isothermal annealing at up to 1400°C in argon or nitrogen atmosphere.

The powder products were qualitatively analysed by X-ray diffraction (XRD) using monochromatic Co $k_\alpha$ radiation ($\lambda = 0.178896$ nm), samples were run over the range 20–60° $2\theta$ using a count time of 1 s per 0.02° step.

## 4. Results

The mass loss with time curves for the variously prepared powders are shown in Fig. 2, also presented is data for the carbon used, trace (f). Below 800°C there is little difference between the powders with all showing a mass loss that is mainly associated with the carbon and not with the ilmenite, similar mass loss profiles have been observed in other forms of carbon milled for various times [50]. XRD of samples of unmilled powder and 200 h milled powder heated up to 800°C and then cooled, showed no evidence for any phases other than ilmenite. Clearly, no reduction occurred in any sample below 800°C.

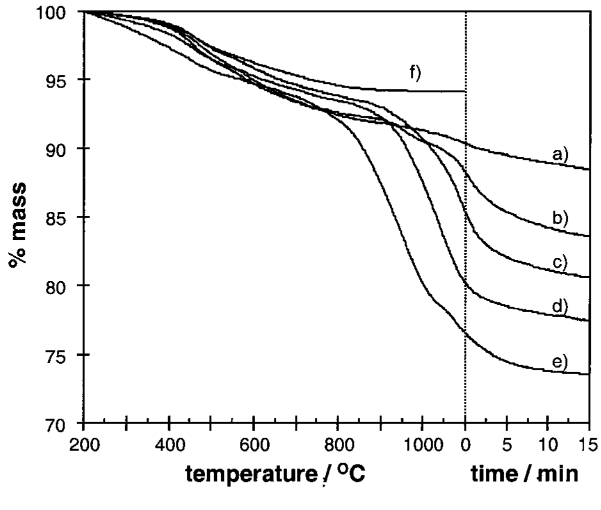

*Figure 2* Thermogravimetric traces for a 1 : 3 molar ratio of ilmenite : carbon heated to 1100°C at 20°C min$^{-1}$ and then held at 1100°C for 15 min in an argon atmosphere. a) unmilled ilmenite +20 h milled carbon; b) 20 h milled ilmenite +20 h milled carbon; c) ilmenite and carbon milled together for 2 h; d) ilmenite and carbon milled together for 20 h; e) ilmenite and carbon milled together for 200 h; f) pure carbon (adjusted to the correct stoichiometric ratio).

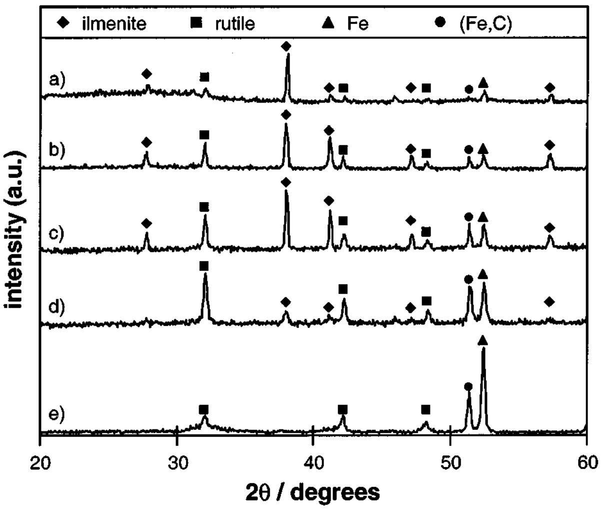

*Figure 3* XRD traces of 1 : 3 ilmenite : carbon powders heated for 0.5 h at 1000°C, the letters correspond to those used in Fig. 1.

Above 800°C there are substantial differences between the various samples. The unmilled sample (a) shows very little mass loss even after 15 min at 1100°C, the trace of the "milled then mixed" sample (b) shows the onset of reduction at 1050°C. The samples milled for 2, 20 and 200 h, (c), (d) and (e) respectively, show decreasing onset temperatures and increased mass losses with increasing milling time. All samples show a similar rate of mass loss after annealing for 10 min at 1100°C, this would imply that the rate determining step is the same for all samples.

XRD traces of samples of powders annealed at 1000°C under argon for 0.5 h are shown in Fig. 3. From these traces, it is clear that the peaks for rutile and iron increase as the ilmenite peaks decrease. Almost complete reduction to rutile is evident after heating the 20 h milled powder, trace (d), to 1000°C for 0.5 h. It is interesting to note that the iron is present in two forms, elemental and in solid-solution with carbon (Fe, C). These phases emerge together indicating that there is an equilibrium between the two and the remaining free carbon. For the 200 h sample the rutile peaks are extremely weak and there is some broadening around the main peak at 31°. Clearly, rutile is also being reduced, probably to one, or more, of the Magneli phases with the general formula $Ti_nO_{2n-1}$ which have peaks around the main rutile peak. The absence of sufficiently well defined peaks means that the specific phase(s) cannot be identified. The ratio of the peaks for iron and (Fe, C) has changed with elemental iron predominating, it would seem that some of the carbon being consumed in the reduction of rutile is from the (Fe, C) phase, although there is probably also some free carbon in the system.

Increasing the carbon content to that required for the thermodynamically more favourable formation of TiC by reaction (2) gave the traces in Fig. 4 which are plotted in terms of oxygen recovery into the gas phase.

$$FeTiO_3 + 4C = Fe + TiC + 3CO(g) \qquad (2)$$

It is clear from these traces there are substantial gains to be made, in terms of mass loss, by slightly increasing the carbon fraction in the system. The lines on the left hand side of the diagram represent the theoretical

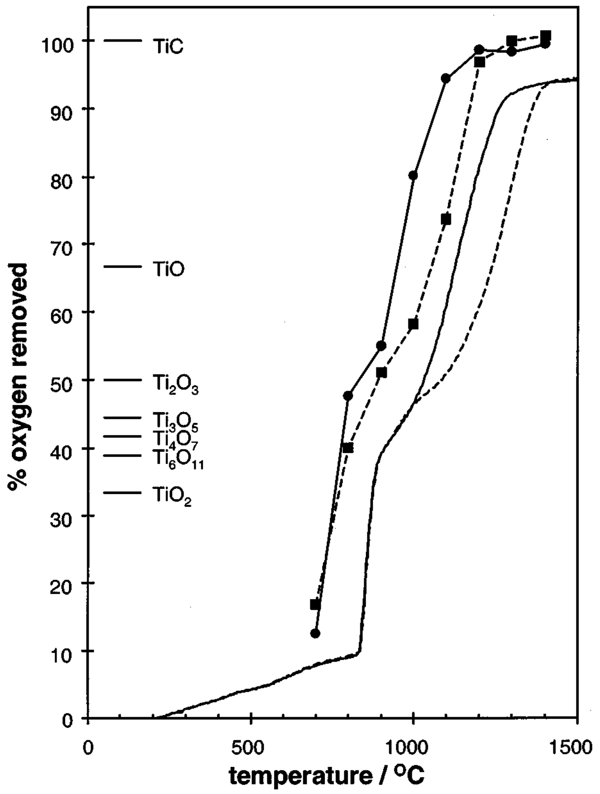

*Figure 4* Thermogravimetric traces for a 1 : 4 molar ratio of ilmenite : carbon milled for 100 h, heated to 1500°C at 20°C $min^{-1}$ (lines) or annealed for 1 h at temperature (symbols) in either argon (dashed lines) or nitrogen (solid lines) atmosphere.

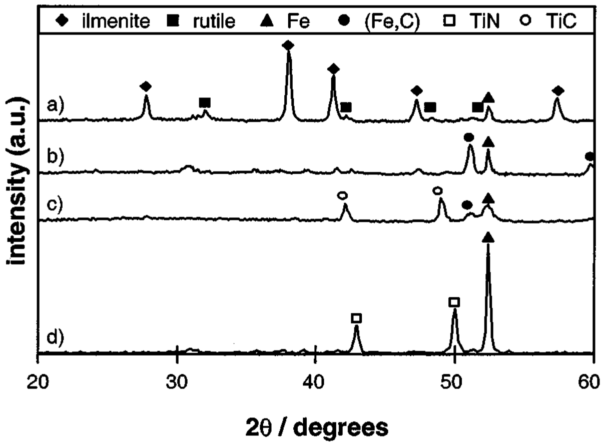

*Figure 5* XRD traces of 1 : 4 ilmenite : carbon powders heated for 1 h. a) at 700°C; b) at 900°C; and c) 1200°C under argon; d) at 1000°C in nitrogen.

oxygen recovery for the formation of elemental iron and various titanium oxides from a 4 : 1 molar ratio of carbon : ilmenite. The shape of the traces are similar to those for the lower ratio, although the onset of the first major reduction stage (to iron and $TiO_2$) at ~800°C is somewhat more abrupt. The onset temperature is similar to that for the 200 h milled sample which had a lower carbon fraction suggesting that a higher carbon content may offset the milling time to some extent, as has been noted elsewhere [29].

It is interesting to note that there is little or no effect of atmosphere until 1100°C where the sample heated in nitrogen started to lose mass much more rapidly than that heated in argon. The same mass loss in nitrogen occurred ~150°C lower than in argon indicating the beneficial presence of nitrogen, although by 1400°C the mass loss in both samples was essentially identical. Even at 1500°C there is a slight mass loss continuing to occur in both samples, clearly the reaction is incomplete.

For the samples annealed for 1 h, the same general shape of the mass loss curve was evident, but around 200°C lower than during TGA. This is typical as TGA is a dynamic process where reactions tend not to attain equilibrium and mass losses occur more rapidly at higher temperatures. The effect of atmosphere is now clear at 1000°C where a ~20% difference in oxygen recovery is indicated.

XRD of selected powders are shown in Fig. 5, trace (a) shows that at 700°C there is little reaction with ilmenite the predominant phase present, both elemental iron and rutile have small peaks indicating that even at 700°C a slow reduction was occurring. Increasing the annealing temperature to 900°C, trace (b), shows that ilmenite reduction was complete and that rutile reduction had also occurred with no distinct titanium phase identifiable, although the peaks present were due to one, or more, of the $Ti_nO_{2n-1}$ phases. After 1 h at 1200°C in argon the titanium product is primarily carbide, although the peaks are shifted towards higher $2\theta$ which indicates that either the carbide is carbon deficient [49] or oxygen remains in the lattice as an oxycarbide, $TiC_xO_{1-x}$. This phase has been observed during the carbothermic reduction of both rutile [51–53] and ilmenite [17, 31]. XRD of the sample annealed at 1400°C showed that the peaks were closer to those of TiC, the increased mass loss with temperature would seem to confirm the presence of oxycarbide, from which the removal of small amounts of oxygen is reportedly difficult [17, 31, 49], but can be achieved by increasing the annealing temperature [17, 49], as shown here.

The more rapid loss in nitrogen can be attributed to the formation of titanium nitride, which was detected by XRD at 1000°C, as shown by trace (d). The sample heated in nitrogen provided little further oxygen above 1200°C whereas the sample in argon continued to evolve oxygen up to 1400°C. Clearly, the presence of nitrogen aids the removal of oxygen from the ilmenite with a somewhat slower reaction occurring in the argon sample at high temperatures. The more rapid removal of oxygen in the presence of nitrogen is probably due to a larger gas-solid interface allowing ready nitrogen incorporation, unlike the slower diffusion of carbon into the lattice from point contacts where reaction with oxygen is also occurring.

## 5. Discussion

It is clear that premilling a mixture of carbon and ilmenite substantially increases the kinetics of oxygen removal from the mineral. The increased kinetics at low temperature indicate that less thermal energy needs to be input into the system for the same oxygen recovery. Alternatively, increasing the carbon content to that necessary for carbide formation leads to essentially complete oxygen recovery in 1 h at1200°C, although other work [28] has indicated that a shorter annealing time leads to formation of a sub-stoichiometric carbide,

$TiC_{0.5-1}$ giving a potential carbon saving. It has been shown that little is to be gained during hydrogen reduction beyond 10 min at 1000°C [12], synthetic ilmenite is reportedly slower with the reaction complete in 20 min [5]. The presence of nitrogen is also a major advantage with the formation of titanium nitride occurring at a lower temperature than for the carbide.

It should be noted that in lunar ilmenite there is no oxidation of the ferrous iron in the mineral, unlike the terrestrial mineral [54]. However, although beach sand ilmenite was used in these experiments, the results are significant in that it is not the reduction of ilmenite where the improved oxygen yield is obtained but the subsequent reduction of $TiO_2$. The phases reported as products of ilmenite reduction by hydrogen, $Ti_7O_{13}$, $Ti_6O_{11}$ and $Ti_4O_7$ [12], do not show a much greater mass loss than the initial reaction to $TiO_2$. Even the most oxygen deficient phase reported, $Ti_4O_7$ represents a relatively small improvement over $TiO_2$ (33.3% of the oxygen is removed from ilmenite when $TiO_2$ is formed, 41.7% when $Ti_4O_7$ is formed). For substantially greater oxygen recovery the ratio of titanium to oxygen in the product phase needs to be maximised. It has been noted that reductants as powerful as magnesium are incapable of removing oxygen to below 2.5 wt% during titanium production at 1000°C [55].

It seems clear that the difficulty associated with the removal of oxygen from the titanium oxides [49, 55] can be overcome by forming stable compounds rather than trying to form the metal. However, this route necessitates the provision of more raw materials (i.e. more carbon or nitrogen) to the system than the conventional process where the titanium remains as an oxide. For a system where complete oxygen recovery is achieved the final solid material has the potential to be an important engineering material being a composite of elemental iron and titanium carbide or nitride. Indeed, it is feasible to control the carbon content of the iron phase so that its melting point is close to the eutectic (1148°C for 4.2 at% C) and the mixture could be cast directly from the melt.

It is improbable that any preconcentration of lunar soils will be performed prior to the reduction process as this adds complexity. Thus, other minerals, such as olivine and pyroxene are also potential sources of oxygen with up to 20% of mare basalt being olivine [54] (ilmenite is 0–12% [54]), although there has been much less work reported on these minerals than on ilmenite. Work on lunar soils [8–10] indicate that both minerals undergo slight reduction by hydrogen at 1000°C. The reaction between olivine and hydrogen was found to be controlled by diffusion of hydrogen through the surface layer of iron and vitreous silica [56]. Therefore, ultrafine grinding of the mineral prior to reduction would appear to be a prudent step since by increasing the surface area, more mineral could be reduced prior to diffusion control. The reduction rate was also observed to decrease as the fraction of Mg in the mineral increased [56]. Carbon is not a particularly suitable reductant for $Mg_2SiO_4$ with the minimum temperature at which the free energy for reduction to Mg and $SiO_2$ becomes negative is over 2000°C [44]. Indeed, it is predicted that the reduction is more likely to occur at the silicon - oxygen bond with reduction to MgO and Si expected to occur at $>1840$°C with carbon. These temperatures can be compared with those for $Fe_2SiO_4$ which should be reduced by carbon to Fe and silica at $>780$°C, partial reduction to $FeSiO_3$ and Fe is also predicted to occur at $>780$°C. Presumably, the properties of olivine are intermediate between the two end members and the reported slowing of reaction [56] was due to the fraction of reducible material at the surface decreasing with magnesium content.

It may well be that these minerals would also become more extensively reduced at lower temperature after premilling with carbon and further investigations are underway to determine whether this is the case. The formation of highly stable non-elemental compounds containing silicon and / or magnesium may also allow increased oxygen recovery at lower temperatures, but at the expense of supplying another feedstock which may not be recovered.

This general process, with the formation of a several useful compounds in addition to extracting oxygen, would seem to be a more sensible route than a route which only recovers oxygen. It is clear that the formation of compounds, such as nitrides or carbides, aids the reduction process enormously with a larger fraction of oxygen recovered than in systems where compound formation is not possible.

## 6. Conclusions

Premilling of a mixture of ilmenite and carbon increases the rate of reaction whilst lowering the onset temperature. The phases have to be milled together with separate milling having only a relatively small effect. This is due to the increased mixing of the two phases during milling shortening the diffusion paths, so that solid-state diffusion only plays a significant part in the latter stages of reduction. It is advantageous to anneal in nitrogen which gives almost complete oxygen release from the mineral within 1 h at 1100°C by the formation of titanium nitride. For annealing in an inert atmosphere, it is necessary to heat for 1 h at 1200°C to get most oxygen from the ilmenite, although a slow mass loss continues due to oxycarbide formation. The final product of heating was elemental iron containing a dispersion of either titanium nitride or titanium carbide, this may also prove to be a useful engineering material.

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