Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis of FeTi from mixed oxide precursors

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ARTICLE INFO

Article history: Received 14 April 2008 Received in revised form 3 July 2008 Accepted 7 July 2008 Available online 15 August 2008

Keywords: Electrodeoxidation FeTi Molten calcium chloride Fe₂TiO₅

ABSTRACT

A study was carried out on the synthesis of FeTi intermetallics from mixed oxide precursors using the method of electro-deoxidation. Fe_2O_3 and TiO_2 mixed in molar proportions of 1:2 were sintered at temperatures ranging from 900 °C to 1300 °C. The sintered pellet of mixed oxides, connected as cathode, was then electrolyzed in a molten $CaCl_2$ at 900 °C using a graphite anode at a potential of 3.2 V. The electrolysis yielded the target composition FeTi in substantial amounts only when the sintering temperature was close to or above 1100 °C. The process of deoxidation was followed with the use of interrupted experiments. This has shown that the two-phase structure of Fe₂TiO₅ and TiO₂ in the oxide pellet reacts with the molten salt even before the electrolysis forming CaTiO₃, transforming the rest into a mixture of ilmenite (FeTiO₃) and a spinel phase (Fe₂TiO₄). During electrolysis these complex oxides were converted into simpler ones. Fe is the first element to be produced followed by the intermetallic Fe₂Ti. FeTi evolves quite late in the electrolysis which seemed to have followed the reduction of CaTiO₃. It is shown that interrupted experiments and examination of partially reduced pellets yield considerable information with regard to the sequence of changes that occur during the deoxidation process.

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ALLOYS AND COMPOUNDS

1. Introduction

There has been considerable interest in recent years in the solid-state deoxidation of oxides which would yield alloys and compounds at targeted compositions, e.g. [1,2]. It is an electrolysis process in molten salt, first developed in the 1990s by Fray et al. [3], for extraction of Ti from TiO₂. The process makes use of sintered oxide pellet as a starting material, connected to a current collector as the cathode and electrolyzed in a molten salt using a graphite anode. During electrolysis, oxygen in the cathode is ionized, dissolved in the electrolyte and discharged at the anode in the form of CO or CO₂. Thus unlike conventional electrolysis where the metal is deposited onto the cathode, here the cathode is gradually de-oxidized leaving the metallic elements behind.

Due to this special nature of the cathode, the preparation of oxide pellet as a cathode material has attracted considerable attention. In the case where the target is pure metal, e.g. Nb [4], Ta [5], efforts are mainly concentrated on controlling the porosity of the pellets. Normally pellets of high porosity are preferred since this is believed to improve the kinetics of deoxidation. In this context, especially in Ti, the formation of a perovskite phase, i.e. CaTiO₃, which occurs as a result of reaction of TiO₂ with the molten salt has received considerable attention [6]. In the case of compounds, an

added consideration is the stoichiometry of the product itself. As has been shown by Qiu et al. [7], oxides of the same mixture could lead to different products depending on the sintering conditions. In this study, the target compound, TbFe₂, can be obtained when the pellet was sintered at an elevated temperature, i.e. $1200 \,^{\circ}$ C.

The current work deals with the deoxidation of mixed oxides; Fe_2O_3 and TiO_2 and concentrates on the choice of sintering conditions which would yield FeTi intermetallics. Here, the target composition FeTi, is a well known compound that reversibly stores hydrogen at room temperature [8].

2. Materials and methods

Starting materials, Fe_2O_3 and TiO_2 (rutile), were of technical grades. Fe_2O_3 powders were needle-like and TiO_2 were rounded as given in Fig. 1. Both were roughly 1 μ m in size but in an agglomerated state. A mixture of Fe_2O_3 and TiO_2 in molar proportions of 1:2 was prepared, i.e. Fe:Ti ratio of 1:1, using a Spex mill at ball-topowder ratio (B/P) of 1. After 30 min of mixing, the mixture was further hand mixed adding some PVA solution and allowed to air dry for 24 h. The powder mixture was then cold compacted into a cylindrical pellet at a pressure of 110 MPa. The pellets were 18-mm in diameter and 2–3 mm in thickness weighing approximately 2 g.

Pellets were sintered at elevated temperatures. For this purpose they were heated up in a tube furnace in air atmosphere to the predetermined temperatures with a heating rate of 5 °C/min. The pellets were held at that temperature for 2 h.

Electro-deoxidation experiments were conducted in an electrolytic cell, shown schematically in Fig. 2. It comprises a stainless steel crucible for holding molten electrolyte and electrodes mounted on a top cover (not shown in the figure) immersible into the electrolyte. There were two pairs of electrodes; one pair was the auxiliary and the other was the working electrodes. The reactor was gas tight, allowing electrolysis in an argon atmosphere (99.995% purity) maintained at a flow rate of 150–250 ml/min. 1 kg of CaCl₂ was used as electrolyte. This was heated to 900 °C, i.e.



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^{0925-8388/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2008.07.018



Fig. 1. SEM images of oxide powders: (a) Fe_2O_3 and (b) TiO_2 used in the experiments. Note that Fe_2O_3 powders are needle-like whereas TiO_2 are in the form of rounded particles.

the electrolysis temperature, slowly so as to reduce its moisture content. The electrolyte was further purified by pre-electrolysis using a graphite anode and stainless steel cathode, at a potential of 3.0 V for 6 h. The current, during the pre-electrolysis following an initial transient rise, decreases gradually over a period of typically 4 h, finally settling down to a constant value. After pre-electrolysis, these auxiliary electrodes were removed and the electrolysis was initiated by immersing the working electrodes, i.e. oxide pellet (cathode) and a fresh graphite rod (anode) into the molten salt. The electrolysis was carried out at a constant potential of 3.2 V for 24 h. Current vs. time data were collected by a computer. The temperature of the system was controlled $\pm 10\,^\circ$ C of the selected temperature.

Following electrolysis, the pellet and the graphite rod were removed from the electrolyte by positioning them above the melt. After cooling it down to room tem-



Fig. 2. Schematic drawing of an electrolytic cell used in the deoxidation experiments.

perature, the reactor lid was opened and the sample with its stainless steel connector was removed. The sample which was in the form of sponge-like agglomerate was washed in hot water and all undissolved material was collected for XRD and SEM analysis.

3. Results and discussion

SEM images of pellets sintered at 900 °C and 1300 °C are given in Fig. 3. It is seen that the structure which was highly porous at 900 °C (and also at 1100 °C), was quite dense at 1300 °C. The porosity values were \approx 47% and 45.1% with sintering at 900 °C and 1100 °C



Fig. 3. Micrographs of the oxide pellets sintered for 2 h at (a) 900 °C and (b) 1300 °C. The graphs refer to broken pellets as viewed in the through thickness section, (c) is the same as (b) but the section is polished and viewed in back-scattered mode to reveal the two-phase structure.



Fig. 4. X-ray diffractograms of the oxide pellets Fe_2O_3 and TiO_2 mixed in molar proportions of 1:2 and sintered at (a) 900 °C, (b) 1100 °C. Note the presence of Fe_2TiO_5 along with Fe_2O_3 and TiO_2 at 900 °C. Also note that at 1100 °C the sintered pellet has a two-phase structure: Fe_2TiO_5 and TiO_2 .

respectively, whereas that arising from sintering at 1300 $^\circ\text{C}$ had a value of 17.3%.

X-ray diffractograms of the sintered pellets are given in Fig. 4. The diffractogram of the sample sintered at 900 °C comprises the initial phases, i.e. Fe_2O_3 and TiO_2 , as well as a new phase; pseudobrookite (Fe_2TiO_5). The formation of this phase via the reaction of TiO_2 with Fe_2O_3 is expected since the associated Gibbs energy change is negative at the current sintering temperatures [9]. In pellets sintered at 1100 °C, Fe_2O_3 is consumed totally by the reaction with the result that the structure is made up of two phases; Fe_2TiO_5 and TiO_2 , see Fig. 4(b). The same was also the case for the pellet sintered at 1300 °C. The two-phase structure is clearly visible in this latter sample, brought out by the back scattered image given in Fig. 3(c).

X-ray diffractograms of the pellets after deoxidation are given in Fig. 5. It was observed that deoxidation was successful in varying degrees. The greater portion of the pellet sintered at 900 °C after deoxidation was Fe and a Ti bearing compound. The compound was TiC, most probably formed, at the end of electrolysis, following the reaction:

$$Ti + 2CO = TiC + CO_2 \tag{1}$$

Here CO is the anode product (see below) which can accumulate in the cell vessel and could react with Ti reduced from TiO_2 at the cathode. The minor constituents of the sample were Fe₂Ti and



Fig. 5. X-ray diffractograms of the pellets deoxidized at 900 °C for 24 h at 3.2 V. The diffractograms refer to pellets sintered at (a) 900 °C, and (b) 1100 °C.



Fig. 6. SEM image of metallic agglomerate, FeTi, obtained from deoxidation of mixed oxide pellet sintered at 1300 °C.

FeTi. Sintering at 900°C, however, was not successful in yielding the target composition in substantial amounts.

The sample sintered at 1100 °C and 1300 °C yielded mainly FeTi, which is the target composition plus Fe₂Ti as a minor phase. Fe which was quite dominant at 900 °C was insignificant in these samples. The same was true for Ti, implying that this element, upon reduction, reacted with the existing phases yielding the target composition FeTi. The SEM image of one such sample is given in Fig. 6.

The conditions of sintering reported above for the successful synthesis of FeTi are consistent with that reported in a similar study conducted by Ma et al. [10]. The sintering in this study was carried out at 1050 °C, which after electrolysis, yielded a product with X-ray diffractogram very similar to the one reported in Fig. 5(b).

To follow the details of electro-deoxidation, samples sintered at 1300 °C were selected for further study. A current–time plot for this sample covering the first 6 h of electro-deoxidation is given in Fig. 7. It is seen that the current, following a rapid rise to a peak value, drops down to a smaller value which then decreases gradually with time. Three positions were selected on this curve for structural examinations and accordingly three samples were prepared. The samples which were maintained above the salt bath during pre-electrolysis were then processed sequentially. One sample was immersed into the salt bath, maintained there for 30 min and then lifted out. The others were electrolyzed as soon as they were immersed; one for 30 min and the other for 6 h.



Fig. 7. Current–time data collected during deoxidation of the oxide pellet sintered at 1300 °C.



Fig. 8. X-ray diffractograms of the oxide pellets sintered at 1300 °C and deoxidized in CaCl₂ at 900 °C (3.2 V). The diffractograms refer to pellets; (a) in the sintered condition, (b) sintered and immersed into the salt bath for 30 min, (c), (d) and (e) refer to sintered pellets electrolyzed for 30 min, 6 h and 24 h respectively.

The sequence of changes that occurred in the samples during electrolysis can be seen in Fig. 8. The X-ray diffractogram shows a systematic change from the sintered condition to that after the 24 h electrolysis. In the immersed sample, Fe₂TiO₅ and TiO₂, i.e. the phases in the sintered sample, continue to be the major constituents, but there are also other phases. These are ilmenite (FeTiO₃), a spinel phase (Fe_2TiO_4), and a perovskite phase (CaTiO₃). After 30 min of electrolysis, the phases did not change much, though CaTiO₃ is much stronger and a metallic phase Fe is already present in the sample. After 6 h, the Fe₂TiO₅ and TiO₂ are all consumed. Fe is now the dominant phase accompanied by the intermetallic Fe₂Ti. The target composition FeTi can be identified in this sample, but it is far from being a major phase. It is interesting to note that CaTiO₃ continues to be the major phase in this sample. It appears that beyond this, the electrolysis mainly consumes CaTiO₃ and with the production of Ti as a result, the greater portion of the sample is converted into FeTi, see Fig. 8(e).

The observations reported above imply that, from the oxide state to the final composition FeTi, electroreduction follows quite a systematic route. It appears that the oxides are already modified upon immersion into the salt bath even before the electrolysis. Thus a two-phase structure, i.e. Fe_2TiO_5 and TiO_2 , is in part converted into a mixture of phases comprising CaTiO₃, FeTiO₃ and Fe₂TiO₄.

With the progress of electrolysis, as the oxygen is discharged, these complex oxides are consumed and instead the remaining oxygen is tied up in simpler oxides such as FeO and CaO. It appears that Fe is reduced quickly from the iron bearing oxides. In contrast, the reduction of Ti is quite sluggish. After 6 h of electrolysis, the greater portion of Ti is still tied up in CaTiO₃.

Using the thermodynamic data, the decomposition voltages of various oxides have been calculated and are listed below with descending order. The values here were determined for the reactions taking place at 900 °C, the anode product being CO(g).

$$Fe_2TiO_4 + 2C = 2Fe + TiO_2 + 2CO, \quad \Delta E = 0.051$$
 (3)

$$FeTiO_3 + C = Fe + TiO_2 + CO, \quad \Delta E = 0.036$$
(4)

$$TiO_2 + 2C = Ti + 2CO, \quad \Delta E = -0.784$$
 (5)

$$CaTiO_3 + 2C = Ti + CaO + 2CO, \quad \Delta E = -1.015$$
 (6)

It should be noted that with the reactions (2)-(4) which give rise to Fe have reduction potentials more positive than those which give rise to Ti, i.e. the reactions (5) and (6). The early formation of Fe and the persistence of Ti bearing oxides until the very end of electrolysis are consistent with the above values. It is also worth noting that CaTiO₃ has a higher decomposition potential than pure TiO₂ which implies that the reduction process is made difficult by CaTiO₃ formation.

Electrolysis, with the sequence of changes described above, may be contrasted with the sintering process. While during sintering Fe₂O₃ and TiO₂ are combined into more complex oxides, i.e. Fe₂TiO₅, with electrolysis, the structure first attacked probably by CaO which is normally present in CaCl₂ as it forms during the drying process, is then gradually reduced into simpler oxides yielding first Fe and then Ti. Even though the structure formed by sintering is later disintegrated, it appears that the state, which had evolved during sintering, exercises a considerable effect on the nature of the reduction process. This effect of sintering is most probably related to the length scale of the chemical species in the oxide preforms. At 900 °C, the sintered pellet is grossly heterogeneous in that it contains unreacted Fe₂O₃ and TiO₂ phases as well as Fe₂TiO₅. With the porosity of 47%, elements that are obtained as a result of deoxidation, i.e. Fe and Ti, especially from the unreacted phases, are not close enough to react with one another. Accordingly deoxidation yields a range of phases, namely Fe, Ti (i.e. TiC see above) as pure elements, and Fe₂Ti and FeTi as intermetallics.

At higher sintering temperatures, the reaction goes to completion. Thus all Fe_2O_3 is consumed and the preform is made up of two phases Fe_2TiO_5 and TiO_2 . The structure, therefore, is more homogenous than that given above. Even though this structure is modified upon immersion into the salt bath, this modification probably occurs with a length scale that is comparable to the original structure. Thus upon reduction, elements are close to each other and with diffusion over small distances they react with each other yielding the intermetallics. The result, at the end of electrolysis, is that FeTi makes up the considerable portion of the product.

As a final remark, it should be pointed out that, with the current processing conditions, the phases Fe₂Ti and a small amount of Ti (i.e. TiC) do form in the final product. Since the target composition is FeTi, the formation of these other phases need to be minimized or should be prevented altogether. Following the approach given above, it may be suggested that one method of achieving this, would be to make use of mixed oxides with refined structures, i.e. to employ a processing route that would yield the mixed oxide pellet with as fine a structure as possible. The other route would be to produce a single-phase pellet, namely ilmenite (FeTiO₃). It appears that the ilmenite approach, with Fe:Ti in 1:1 proportion, would be particularly worthwhile since this would make the electrolysis possible in a variety of sintering conditions. For instance, pellets of increased porosity could be electrolyzed which might accelerate

the reduction process, an approach which would create difficulties in the mixed oxide approach.

4. Conclusion

In the current work, a study was carried out on the synthesis of FeTi intermetallics from mixed oxide precursors. Fe_2O_3 and TiO_2 mixed in molar proportions of 1:2 were sintered at elevated temperatures ranging from 900 °C to 1300 °C. The sintered oxide was electrolyzed in a molten CaCl₂ at 900 °C using a graphite anode at a potential of 3.2 V. The study has shown that the use of sintering temperatures close to or above 1100 °C leads to the formation of a two-phase structure Fe_2TiO_5 and TiO_2 which when electrolyzed successfully yields the target composition FeTi in substantial amounts. The study further shows that interrupted experiments during the electrolysis and the examination of partially reduced pellets yield considerable information with regard to the sequence of changes that occur during the deoxidation process.

Acknowledgements

We would like to thank Prof. Derek J. Fray for useful discussions. Support for this work was provided by DPT with project number BAP-03-08-DPT.200305K120920-20, which we gratefully acknowledge. The authors also thank Cara Keyman for reading the manuscript.

References

- [1] D.J. Fray, JOM 53 (2001) 26-31.
- [2] R.O. Suzuki, K. Tatemoto, H. Kitagawa, J. Alloys Compd. 385 (2004) 173-180.
- [3] G.Z. Chen, D.J. Fray, T.W. Farthing, Nature 407 (2000) 361-364.
- [4] X.Y. Yan, D.J. Fray, J. Electrochem. Soc. 152 (2005) E308–E318.
- [5] X.F. Hu, Q. Xu, Acta Metall. Sin. 42 (2006) 285-289.
- [6] K. Jiang, X.H. Hu, M. Ma, D.H. Wang, G.H. Qiu, X.B. Jin, G.Z. Chen, Angew. Chem. Int. Ed. 45 (2006) 428–432.
- [7] G. Qiu, D. Wang, M. Ma, X. Jin, G. Chen, J. Electroanal. Chem. 589 (2006) 139–147.
 [8] J. Reilly, R. Wiswall, Inorg. Chem. 13 (1974) 218–222.
- [9] I. Barin, O. Knacke, O. Kubaschewski, Thermochemical Properties of Inorganic Substances, 2nd ed., Springer-Verlag, Berlin, 1973.
- [10] M. Ma, D. Wang, X. Hu, X. Jin, G. Chen, Chem. Eur. J. 12 (2006) 5075-5081.