JOURNAL OF MATERIALS SCIENCE **24** (1989) 1337–1342

Thermal processing of ilmenite and titania-doped haematite using microwave energy

R. A. WRIGHT
Department of Engineering Mechanics, USAF Columbia University, New York, New York 10027, USA

F. H. COCKS
Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27706, USA

D. T. VANIMAN*, R. D. BLAKE‡, T. T. MEEK‡
**Earth and Space Division and ‡Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

To test the potential for microwave processing of lunar materials the heating of ilmenite-rock mixtures, and TiO_2-doped haematite were investigated using microwave radiation. Ilmenite-rich rocks will couple, without a coupling agent, to microwave radiation. The microwave experiments are repeatable. Attempts to couple TiO_2-doped haematite to microwave radiation were very successful, with susceptibility increasing with TiO_2 content. Scanning electron microscopy (SEM) showed increased grain size and particle size with increased TiO_2 content in the microwave-heated products of the haematite-TiO_2 system. The differences between microwave and furnace melts of ilmenite-rich rocks were also investigated. Petrographic analysis revealed a large amount of titanomagetite in microwave melts while furnace melts contained a large amount of haematite, but the cause of this difference is not fully understood.

1. Introduction

The experiments described in this paper are based on the proposed use of microwave radiation for thermal processing, particularly in the microwave melting of lunar materials [1].

The primary objectives of these experiments were to determine if an ilmenite-rich terrestrial rock would couple to microwave radiation and melt without the use of a coupling agent (i.e. glycerol), and to determine if microstructural differences occurred in microwave and furnace melts of this sample. The ilmenite-rich sample (a "Norwegian Ilmenite" obtained from Wards Natural Science) contains about 75% ilmenite and 20% plagioclase, a rough analogue of two common lunar soil constituents, plus other distinctly terrestial minerals [1]. Secondary objectives included determining if ilmenite could itself be used as a coupling agent, and if TiO_2-doped haematite would couple to microwave radiation.

Data were obtained by heating the ilmenite-rich sample; by heating mixtures of this ilmenite-rich sample with basalt; by heating TiO_2-doped haematite using microwaves, and by thermally processing the ilmenite-rich sample in a conventional furnace. Analysis was done using time-temperature data along with X-ray diffraction, metallurgical, and petrographic techniques.

Experimental results indicate that ilmenite-enriched mixtures do couple to microwave radiation without a coupling agent, and that ilmenite itself can be used as a coupling agent. Microstructural differences between microwave and furnace melts were observed. Attempts to couple TiO_2-doped haematite to microwave radiation were also successful.

The experiments described in this paper represent initial inquiries into the viability of microwave processing [1]. The results of these experiments provide greater impetus for further research in this area.

2. Experimental procedure and materials

2.1. Microwave melting

Thermal processing by microwaves was done using a Litton model 1521 microwave oven with the cavity insulated on three sides with zircar A-15 insulation board. The oven operates at 2.45 GHz and has a power output of 700 W. The rock sample containing 75% ilmenite and 20% plagioclase was crushed to −70 mesh, and two tests were conducted using 17 g samples in alumina crucibles. The samples were insulated with zircar A-15 insulation board as shown in Figs 1 and 2. Total processing time was 1 h 50 min, and time-temperature data were taken with the use of a 0.635 cm i.d. alumina tube that extended from the base of the crucible to the glass door of the oven (to obtain black body conditions) so that a Leeds and Northrop optical pyrometer could be used to sight down the tube onto the outside wall of the reaction

0022–2461/89 $03.00 + .12

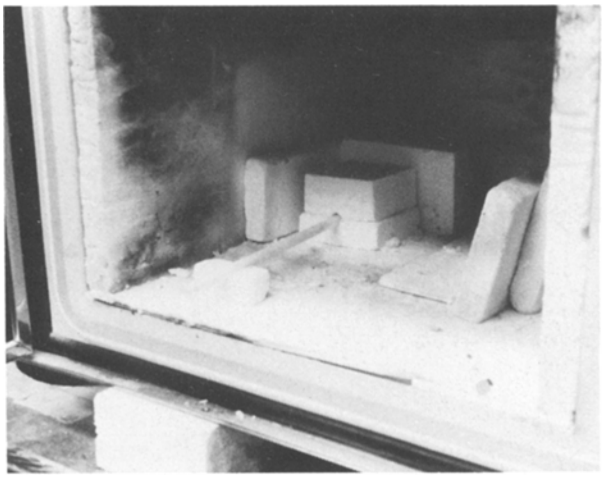

Figure 1 5.08 cm thick zircar cavity built around the sample.

crucible. The microwave-heated samples were analysed using X-ray diffraction and petrographic techniques.

2.2. Conventional melting

Two identical samples of the ilmenite–plagioclase rock were prepared for thermal processing by conventional furnaces. Two tests were conducted using two different furnaces. One sample was placed in a cam-driven, Barber–Coleman furnace equipped with a Honeywell strip chart for the time–temperature readings. The sample was heated at an average rate of 82° C h^{-1} to 1400° C. It was soaked at that temperature for 1 h and then furnace cooled at an average rate of 38.3° C h^{-1}. The second sample was placed in a Deltech high temperature annealing oven, model DT22B2-6, that was already at 1400° C. The sample was soaked for 1 h, removed, and air cooled. Only the air-cooled sample, which approximated more closely the microwave tests, was analysed using X-ray diffraction and petrographic techniques.

2.3. Microwave sintering of TiO_2-doped haematite

Haematite (alpha Fe_2O_3) doped with TiO_2 was thermally processed using microwave radiation. Doped samples of 0.1, 0.3, and 0.9 wt % TiO_2 were prepared by ball milling with distilled water for 72 h and then air drying. Each sample was powdered, and approximately 20 g was heated in an alumina crucible. Zircar A-15 insulation board was used in the same manner as for the tests with the ilmenite–plagioclase rock. Time–temperature readings were not recorded, but the total processing time was 90 min. Each sample was qualitatively analysed using scanning electron photomicrographs.

Figure 2 7.62 × 7.62 cm zircar cavity shaped to fit sample. Alumina tube extends to make optical temperature readings.

2.4. Microwave melting of basalt–ilmenite mixtures

Samples of a terrestrial basalt [1] were mixed with 0.0, 5.0, 7.5, 9.0, and 10.0 wt % of the ilmenite–plagioclase rock, crushed to −70 mesh, and thermally processed using microwave radiation in batches of approximately 30 g in alumina crucibles. In another test, 1.0 wt % of the ilmenite–plagioclase rock was not randomly mixed with the basalt, rather it was placed between two layers of basalt. All of the basalt–ilmenite tests were also insulated with zircar A-15 insulation board. Time–temperature data were taken for the mixture with 10% ilmenite rock only; the mixtures using less ilmenite percentage did not melt. All samples were processed for approximately 90 min.

2.5. Temperature measurements

It is important to note the inherent error in temperature measurements. As mentioned previously, a pyrometer was used to take optical temperature readings through the tinted glass door of the microwave oven. The optical transmission losses through the door caused the readings to be lower than the actual temperature. Using a tungsten filament placed inside the reaction cavity to calibrate the temperature readings, it was estimated that there was a 150° C loss in recorded temperature data. However since the same two individuals took all readings, they were still used as a relative measure of temperature.

3. Results and discussion

3.1. Microwave and conventional melting of the ilmenite–plagioclase rock

Before discussing the differences observed between the two thermal processing methods, it is important to point out that the ilmenite–plagioclase rock did couple to microwave radiation without a coupling agent. Other experiments using a pure ilmenite mixed with synthesis glasses showed that ilmenite alone does act as a coupling agent [3]. The coupling may have occurred by the electric field coupling to vacancies and impurities in the ilmenite structure which sharply decrease the energy gap between valence and conduction bands and increase electrical conductivity [2]. Coupling may also have occurred due to the magnetic properties of ilmenite. Ilmenite is paramagnetic under normal temperatures [4] and antiferromagnetic at low (−217° C) temperatures [5]. It is reported that ilmenite continues to be paramagnetic up to approximately 570° C, but curie temperature data show significant scatter [4]. These magnetic properties may cause inductive coupling with the magnetic field.

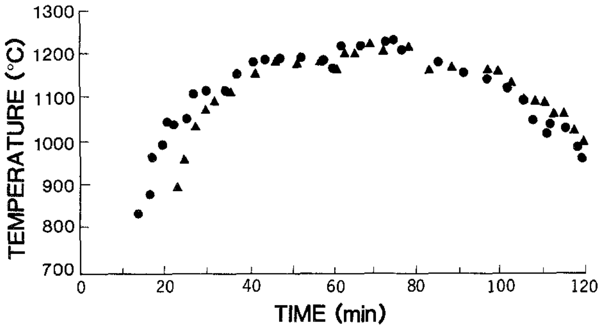

Figure 3 Time–temperature curve microwave heated samples of ilmenite. (●) RF1, (▲) RF2.

Decoupling also occurs as indicated by downward trends in temperature. This may be due to reactions coming to completion and forming phases with altered dielectric properties and less favourable coupling to the UHF field [1].

The question of experimental repeatability was of primary concern. Field strength data and indications of field strength fluctuations were not available, but time–temperature curves indicate that the experiments are repeatable. Both samples of the ilmenite–plagioclase rock followed very similar heating and cooling patterns as shown in Fig. 3.

Analysis of X-ray diffraction data from microwave melted and conventionally melted ilmenite revealed no significant difference in mineral composition. However, the patterns did show major differences in peak intensity. The difference in mineralogy between the melts is primarily of a quantitative nature.

The quantitative differences are more clearly seen in petrographic results. The original ilmenite-rich rock had exsolution lamellae of haematite within ilmenite (Fig. 4). Both microwave melts were still mostly ilmenite, without haematite ex-solution lamellae, but contained significant amounts of titanomagnetite which is high in Ti^{4+} and very low in Fe^{3+}. Only small amounts of haematite were observed (Fig. 5). The microwave melts were different in texture, in that one contained

Figure 5 Microwave melted ilmenite rock. Crystals of haematite, ilmenite, and titanomagnetite (cruciform) in glassy silicate matrix.

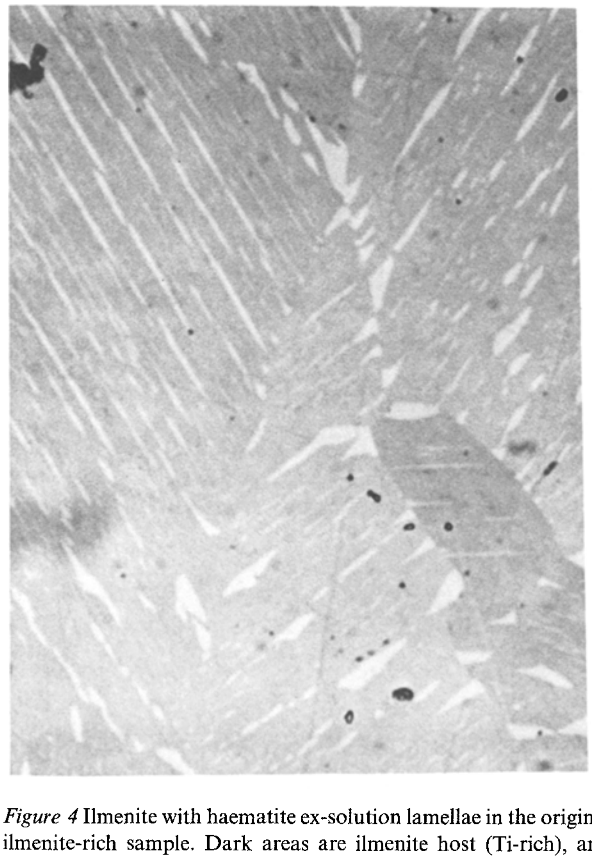

Figure 4 Ilmenite with haematite ex-solution lamellae in the original ilmenite-rich sample. Dark areas are ilmenite host (Ti-rich), and light areas are haematite (Fe-rich).

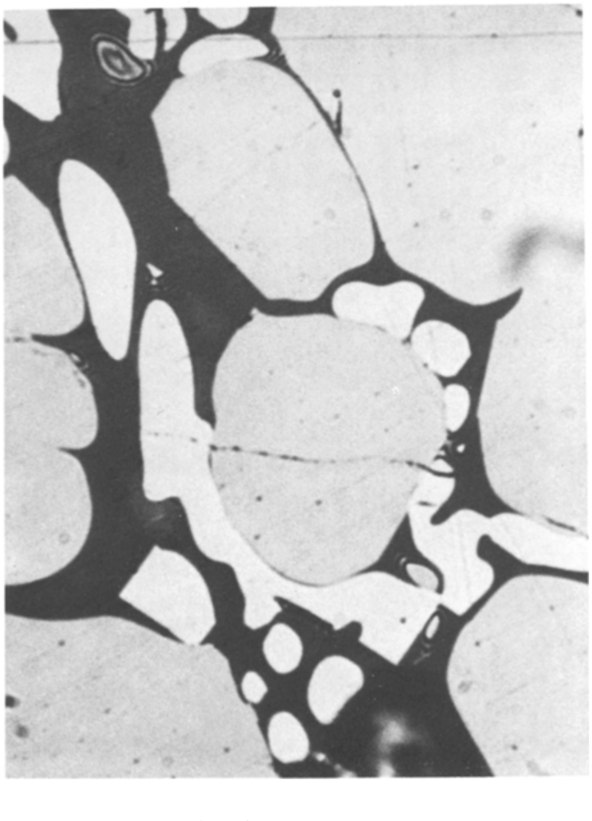

Figure 6 Furnace-melted ilmenite rock. White crystals are haematite, grey crystals are titanomagnetite, in dark glassy silicate matrix.

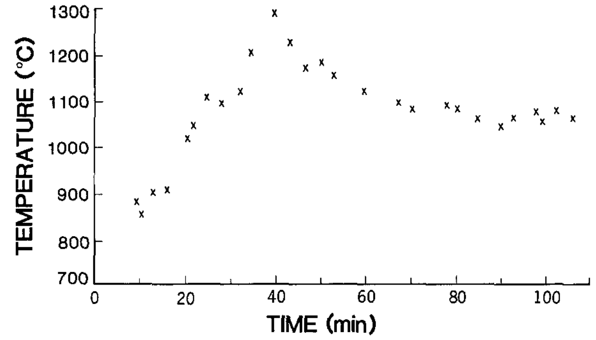

Figure 7 Time–temperature curve for basalt–10% ilmenite sample.

cruciform and dendritic titanomagnetite crystals, while the other contained large titanomagnetite crystals. On the other hand, the furnace melt remained mostly ilmenite, although without haematite exsolution lamellae, and haematite. Only a small amount of titanomagnetite, in small cruciform crystals, was formed (Fig. 6). In a conventional furnace the air heats first, while, in a microwave oven the sample heats first. It is known [5] that magnetite forms a haematite when heated to 550° C. However, microwave processing may also be suppressing the Fe^{2+} to Fe^{3+} transition, leading to more titanomagnetite and less haematite formation. Initial experiments in heating $Cu-Cu_2O$ in microwave environment, using an argon gas atmosphere, revealed oxygen-depletion after 45 min of heating up to 700° C. The P_{O_2} of oxygen in Cu_2O is 10^{-15} atm at 700° C; oxygen loss was verified using ESCA and occurred uniformly throughout the sample. Similar oxygen loss may occur in microwave-heated Fe–O systems.

One other point to note is that there appeared to be more glass in the microwave melts than in the furnace melts. The complexity of the ilmenite-rich rock, which contains approximately 25% silicate component, may have permitted complex silicate–oxide mineral interactions. Transport mechanisms in a microwave field are poorly understood; however, there is evidence for enhanced diffusion [1].

3.2. Microwave melting of basalt–ilmenite rock mixtures

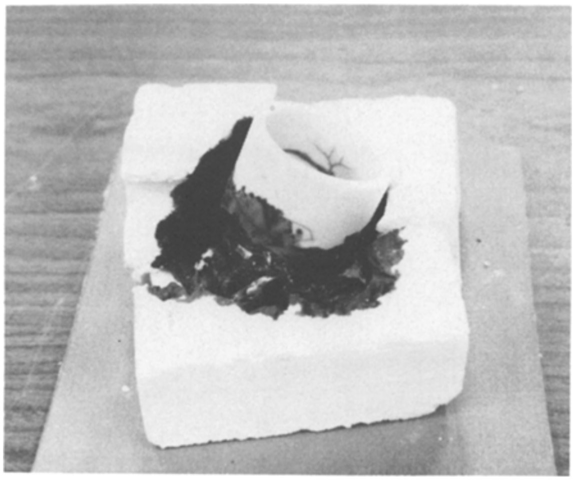

Figure 8 Melted combination of basalt–10% ilmenite rock, alumina crucible, and zircar insulation.

TABLE I Time to red heat for various mixtures of Fe_2O_3 doped with TiO_2 in a 2.45 GHz electromagnetic field

Atom % TiO_2	Time to red heat (min)
0.0	no coupling
0.9	8
0.3	17
0.1	20

Basalt alone only coupled weakly to 2.45 GHz microwave radiation. Compared to the ilmenite–plagioclase rock, it is not a defect-filled system and is not as magnetic. Higher field strengths may allow basalt to couple. Also, basalt mixed with 5.0, 7.5 and 9.0 wt % of the ilmenite–plagioclase rock would not couple. However, in two tests, adding 10.0 wt % of ilmenite–plagioclase rock as a coupling agent allowed the mixture to couple. It was shown that the ilmenite–plagioclase rock is susceptible to direct heating by microwave radiation. An amount of 10 wt % of this rock, randomly mixed in basalt, may be sufficient to initiate the conductive heating of the basalt, raising the temperature to that necessary for the basalt to begin coupling. When the ilmenite–plagioclase rock was not randomly mixed but placed between two layers of basalt, only 1% of the ilmenite–plagioclase rock was required.

The time–temperature data for the test using 10 wt % of the ilmenite–plagioclase rock are shown in Fig. 7. The temperature dropped approximately 200° C from peak temperature, and stayed constant for approximately 90 min. It was observed that the sample, alumina crucible, and zircar insulation were melting together as shown in Fig. 8. Pyrometer readings on the crucible surface indicated that the temperature was approximately 1300° C; however the melting temperature of alumina is in the order of 2050° C. A sufficiently high temperature was reached to initiate reaction between the alumina crucible and the basalt and ilmenite–plagioclase rock mixture.

3.3. Microwave sintering of TiO_2 doped haematite

The results for this series of tests are summarized in Table I. Pure α-Fe_2O_3 did not couple to microwave radiation, but by adding just 0.1 at % TiO_2, the sample reached red heat in 20 min. It was observed that the time to red heat decreased with increased TiO_2 content.

The coupling of TiO_2-doped haematite to microwave radiation may be due to the defect (vacancy) structure

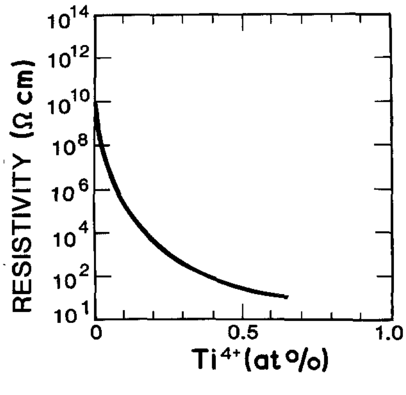

Figure 9 Effect of added TiO_2 on the conductivity of Fe_2O_3.

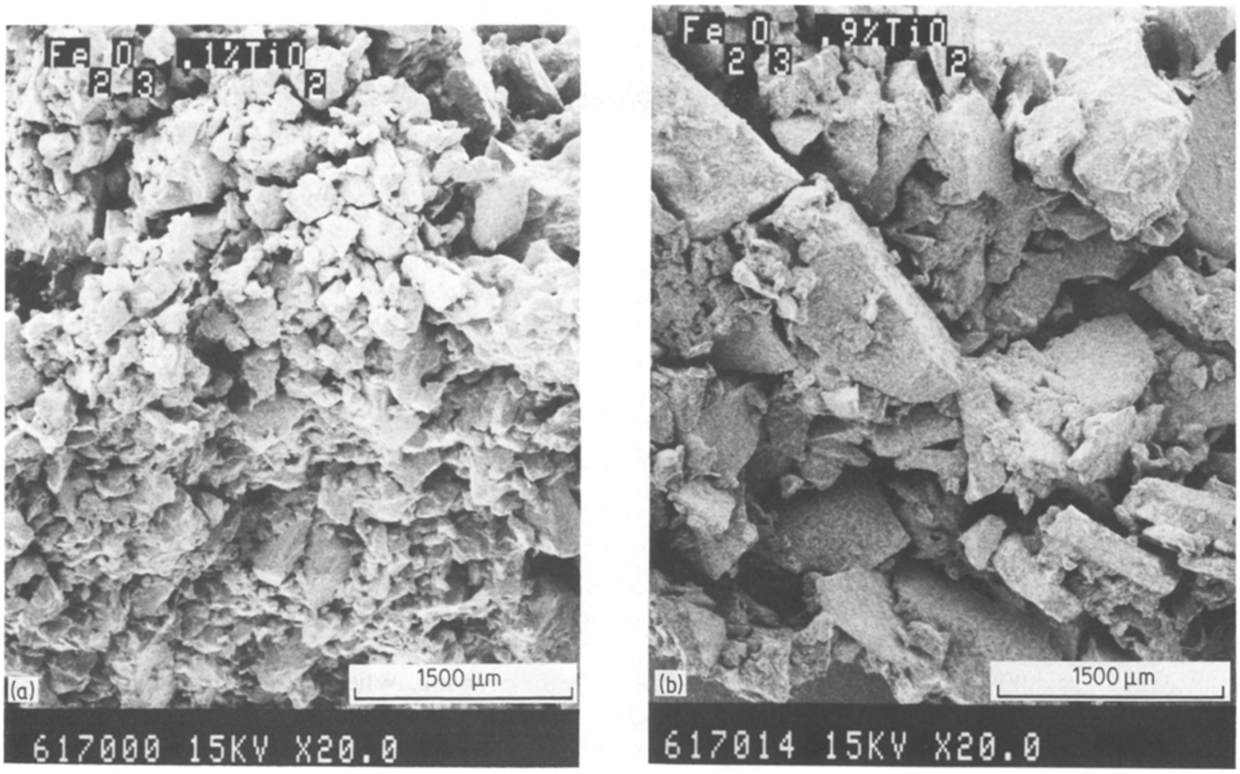

Figure 10 Comparative size distribution of particles for (a) 0.1% and (b) 0.9% TiO_2-doped haematite. (× 9)

that results by introducing TiO_2 into α-Fe_2O_3. Lark-Horovitz [6] suggest that if Ti^{4+} is added to α-Fe_2O_3, an increased fraction of Fe^{3+} are forced into the Fe^{2+} state. Alpha Fe_2O_3 is an n-type semiconductor in which a certain amount of Fe^{2+} already exists. Therefore, the conductivity is substantially increased as shown in Fig. 9. According to this rationale the number of newly created Fe^{2+} is equal to the amount of Ti^{4+} introduced, so the increase in conductivity is determined by the concentration of TiO_2. This assumes that a two-phase haematite-rutile of haematite-pseudo brookite system is not formed, but the strong response seen in Fig. 9 would be difficult to explain if a defect structure were not formed.

Scanning electron photomicrographs reveal qualitative differences in the microwave heated samples with increased TiO_2 content. The size distribution of agglomerating particles tends to become much wider (Fig. 10), and grain size becomes much larger (Fig. 11) as doped TiO_2 content increases.

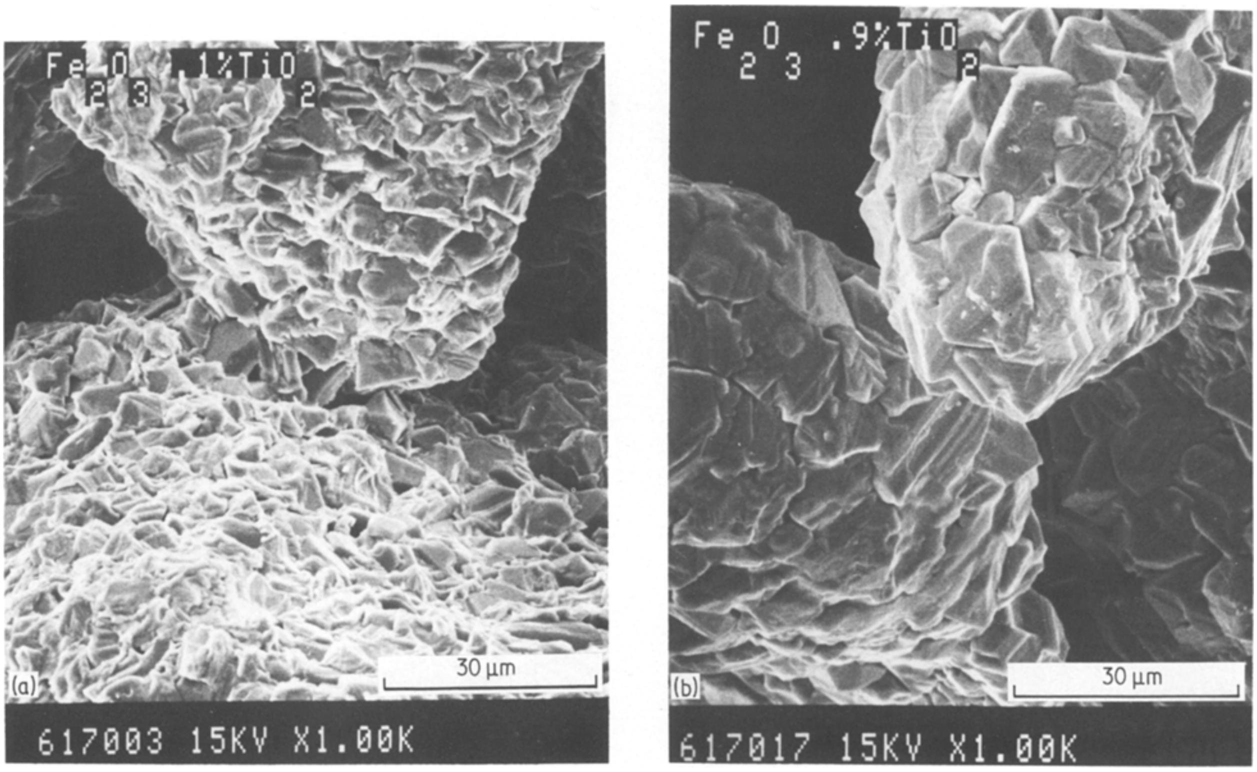

Figure 11 Comparative grain size for (a) 0.1% and (b) 0.9% TiO_2-doped haematite. (× 45).

4. Conclusions

Ilmenite-rich rocks not only couple directly to microwave radiation, but can also be used as coupling agents. With respect to lunar processing, this fact may be exploited commercially by not having to transport coupling agents into space. Ilmenite–plagioclase mixtures can be used as readily as pure ilmenite, suggesting that ilmenite-rich lunar soils need not be processed before use as coupling agents. The practicality of these proposals lies in the fact that lunar ilmente is almost identical to terrestrial ilmenite and may even be better suited due to radiation defects [1]. Also, ilmenite is the most common lunar opaque mineral sometimes making up 20% of the volume of rocks [7]. Questions do remain as to the reasons for the difference in microwave melt textures, but time–temperature data indicate repeatability of the experimental data obtained.

The possibility also exists of fabricating low efficiency solar cells (10%) using ilmenite found on the moon. Ilmenite has a measured band gap of 2.58 eV and a quantum efficiency of approximately 11% as determined using the information in [8]. Another encouraging characteristic of ilmenite is its insensitivity to solar radiation damage. As stated previously ilmenite is present in large quantity on the moon and thus could be a source of inexpensive and very durable photovolatic cells.

As for the TiO_2-doped haematite, TiO_2 made the combination susceptible to direct heating by microwave radiation. Increasing the TiO_2 content apparently increased the defect Fe^{2+} content which, in turn, increased the conductivity. Thus, its susceptibility to microwave heating increased.

References

1. T. T. MEEK, F. H. COCKS, D. T. VANAMIN and R. A. WRIGHT, in "Microwave Processing of Lunar Materials: Potential Applications", Lunar Bases and Space Activities in the 21st Century pp. 479–486 (Lunar and Planetary Institute, Houston, 1985).
2. A. J. BERTEAUD and J. C. BADOT, *J. Microwave Power* **11** (4) (1976) 317.
3. D. T. VANIMAN, T. T. MEEK and R. D. BLAKE, in "Fusing Lunar Materials with Microwave Energy. Part II: Melting of Simulated Glassy Apollo II Soil." Lunar and Planetary Science Vol. XVII (The Lunar and Planetary Institute, Houston 1986) pp. 911–2.
4. V. KROPACEK and M. KRS, *Studia Geoph. et Geod.* **15** (1971) 161.
5. C. A. LAWSON, G. L. NORD, E. DOWTY and R. B. HARGRAVES, *Science* **213** (1981) 1372.
6. K. LARK-HOROVITZ, *Elect. Engng.* **68** (1949) 1047.
7. J. W. FRONDEL, "A Glossary of Lunar Materials" (John Wiley, New York, 1973) p. 72.
8. J. J. LOFERSKI, *J. Appl. Phys.* **27** (1956) 777.

Received 24 June
and accepted 9 September 1986