Secondary phases in natural magnesite sintered with addition of titania, ilmenite and zirconia

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The detail microstructures of sintered natural magnesite with addition of titania, zirconia and ilmenite mineralisers were studied using scanning electron microscopy (SEM) with special emphasis on energy dispersive X-ray analyses (EDXA). The study was directed towards the determination of secondary phase composition in sintered magnesite with different mineraliser addition. In order to evaluate the secondary phases with addition of transition metal oxides, keeping titania (TiO_2) as a reference mineraliser, a natural analog of titania containing iron i.e., Ilmenite ($Fe_2O_3 \cdot TiO_2$) and pure Zirconia (ZrO_2) were added to magnesite which was then sintered up to 1700 °C. The relative behaviour of these pure and mixed oxide mineralisers during the sintering of magnesite has been evaluated with respect to their microstructure and secondary phase composition. The present paper showed that titania addition to natural magnesites resulted in the formation of calcium titanate in the secondary phase upon sintering. Zirconia, on the other hand, did not show any reaction product in the secondary phase. The addition of titania in the form of mixed oxide, ilmenite, also gave rise to calcium titanate formation, providing a similar microstructure, specially with reference to spatial distribution of phases in the secondary phase. © *1999 Kluwer Academic Publishers*

1. Introduction
In a previous paper [1], the microstructural characteristics of sintered natural Indian magnesites with titania as a mineraliser was reported. The study elucidated that the addition of titania altered the secondary phase distribution. That titania forms a crystalline reaction product with calcia impurity present in natural magnesite was based on coexistence of Ca and Ti in the intergranular region. This paper presents results that provide confirmation of formation of calcium titanate in sintered natural magnesite with addition of titania is in direct contrast to the earlier studies on magnesia sintering [2, 3].

The evidence of calcium titanate as a reaction product in titania added sintered magnesite also led to studies with two other transition metal oxides which are known to influence the sintering of magnesia. The addition of iron and zirconia to magnesite promotes low temperature densification that appears to be proportional to the extent of solid solution and resulting vacancies [4–8]. In order to study the secondary phase due to transition metal oxides keeping titania as a reference mineraliser, a natural analog of titania containing iron, viz., ilmenite $Fe_2O_3 \cdot TiO_2$ and pure zirconia were added to magnesite which was then sintered. The relative behaviour of these pure and mixed oxide mineralisers during the sintering of magnesite has been evaluated, and the microstructure and secondary phase compositions with reference to that containing titania is reported.

2. Experimental procedure
2.1. Raw materials
A cryptocrystalline natural Indian magnesite from Salem (Tamil Nadu region, India) was used as the base material. Physical, chemical, petrographical and sintering characteristics of this magnesite were reported earlier [1, 9]. The three mineralisers used are listed below: Titania in anatase form, 99.9% pure, 0.4 μm mean particle size Zirconia, in monoclinic form, 99.5% pure, 5 μm mean particle size Ilmenite, in tetragonal form, 95% pure, 9 μm mean particle size after vibro-grinding (natural mineral from Kishenganj, Bihar, India).

2.2. Sample preparation
The ilmenite was ground in a vibro-energy mill to the required fineness. The parent magnesite was mixed with 0.2 and 0.5% mineraliser with respect to the raw magnesite and pressed into pellets form (25 mm dia) at a

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specific pressure of 120 MPa. These pellets were fired in electrically heated furnace up to 1700 °C and soaked for one as well as two hours followed by natural cooling in the furnace itself. Details of the sample are provided elsewhere [9].

Thin and polished sections were characterised with the help of an optical microscope in reflected and transmitted modes. Back scattered electron images and elemental mapping were used for microstructure analysis. In addition, an X-ray powder diffractometer utilising a copper target with nickel filter was used for secondary phase identification of the sintered magnesites. Considering such phase analysis of the sinter to be insufficient, a method was developed to leach out a major portion of the magnesia (periclase) phase to reveal the secondary phases with greater clarity. Details of the developed method are presented elsewhere [10]. The leach residue was subjected to powder X-ray diffraction for phase identification.

3. Results and discussion

The secondary phase microstructure in sintered natural Indian magnesite with and without titania addition has been discussed previously [1, 9]. The grain growth and phase distribution was noted to be dependent on the thermal history and mineraliser content; however, the secondary phases present were not totally evaluated. The typical powder pattern of a magnesite sample sintered at 1650 °C for 1 h is shown in Fig. 1 as S061. The major phase evident is periclase with small quantities of monticellite ($CaMgSiO_4$) and much lesser amount forsterite (Mg_2SiO_4). Clear identification of the secondary phase is difficult. The diffraction pattern of the residue obtained upon extraction of a major portion of MgO phase shown as S061E in Fig. 1, positively iden-
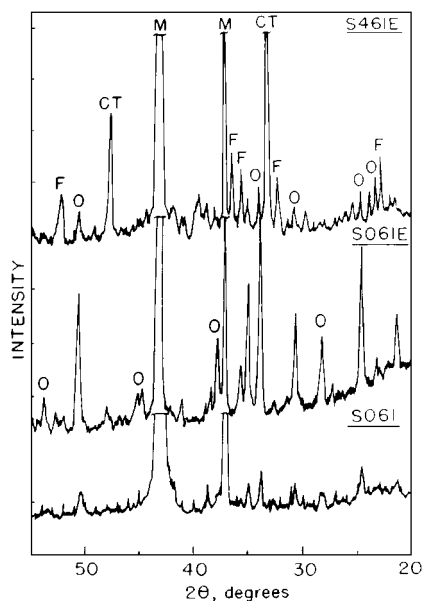

Figure 2 Backscattered electron image of S472 indicates 0.5 wt % titania added Salem magnesite fired at 1700 °C. It shows unique neck growth and the isolated pockets of bright liquid phase confirming the presence of calcium titanate phase.

tifies monticellite to be the major crystalline secondary phase with minor amount of forsterite. The presence of a hump in the diffraction pattern around $20°2\theta$ for Cu-K_α radiation indicates the presence of amorphous phase (not shown in Fig. 1).

Fig. 2 depicts a backscattered image of titania added magnesite showing typical neck growth nature of magnesia refractory within the liquid phase. The liquid phase consists of two phases; one is grey phase and another is bright phase indicating coexistence of two types of secondary phases. Titania addition to this magnesite prior to sintering leads to the formation of calcium titanate as one of the secondary phases. This was confirmed through powder XRD of the extract of a magnesite sample with 0.5% titania with respect to the original magnesite, sintered to 1650 °C with 1 h soak, marked as S461E in Fig. 1. In addition, an interesting sequence of crystalline secondary phases was observed compared to the parent S061 with no titania. The monticellite content reduced with direct formation of calcium titanate and forsterite as evident in Fig. 1.

A digitised elemental map of the triple grain junction in a 0.5 wt % titania sample sintered at 1700 °C with 2 h soak is shown in Fig. 3. The map shows a portion of the junction to be composed of Ca and Ti, while another to be Mg and Si. The later combination is also supported from the XRD pattern of the leached residue (Fig. 1) which shows the presence of crystalline magnesium silicate. Magnesium and Ti are mutually exclusive. Thus, there are two typical regions within the same triple grain junction. These results and the finding of XRD leads to the conclusion that the presence of titania causes the formation of a reactive liquid that operates during the sintering process in titania aided sintering of natural magnesite. The possible reaction in progress is as follows:

$$2CaMgSiO_4 + TiO_2 \rightarrow 2MgO{\cdot}SiO_2 + CaTiO_3$$
$$+ CaSiO_3 \qquad (1)$$

The magnesium silicate and calcium titanate reaction products are evident in the XRD, with amorphous

Figure 1 XRD pattern of sintered Salem magnesite. S061 represents the original; S061E is the pattern after a portion of MgO has been extracted from the original; S461E is the 0.5 wt % titania added magnesite after MgO extraction. MgO extraction reveals crystalline secondary phases and presence of calcium titanate. O = monticellite, CT = Calcium titanate, F = forsterite, M = magnesia.
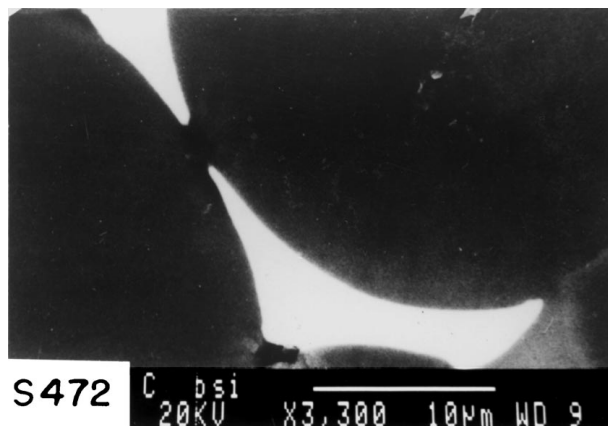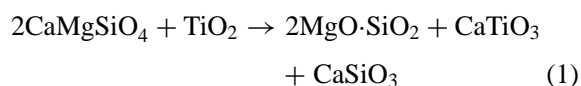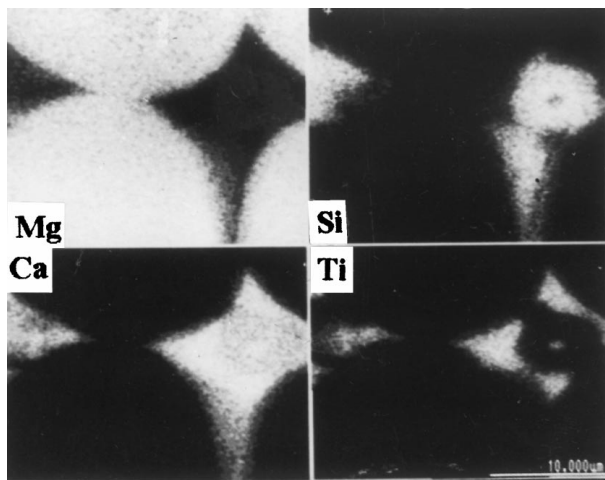
Figure 3 EDXA digital elemental image in 0.5% titania added sintered Salem magnesite showing the existence of calcium and titanium at the grain boundary.
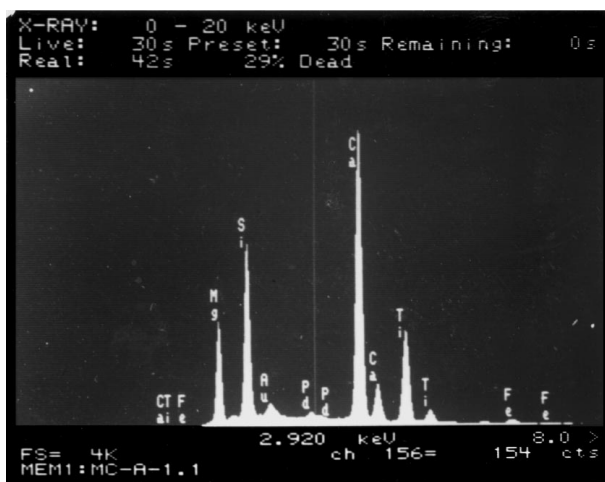

Figure 4 Elemental distribution of titania added sintered magnesite.

glassy phase. The elemental distribution in the titania added sintered magnesite is depicted in Fig. 4. The authors postulate that the addition of titania to magnesite results in the formation of reactive liquid that promotes sintering and grain growth in natural Indian magnesite. It is possible that the monticellite reaction given in Equation 1 in the grain boundary provides a fast diffusion path for Mg, thus enhancing densification and grain growth. No evidence of a precursor Mg-Ti phase was observed as in the case of studies by Cosic *et al.* [11]. The additive ion Ti^{+3} and Ti^{+4} in the magnesite grain interfaces can substitute Mg^{+2} ions and form cation vacancies resulting in solid solution at the grain boundaries. Titanium is generally strongly attracted to the oxide interface and concentrates there because of its high chemical reactivity with oxygen [4]. It is suggested that the presence of titania in the interstitial matrix increases the flux, giving rise to a transport mechanism of Flux Growth [12] represented by dissolution from one grain, diffusion through the liquid secondary phase and epitaxial growth on the other grain. In this case the sintering and grain growth may have been intensified due to the presence of a liquid phase in the system $MgO-TiO_2$.

MgO and TiO_2 react [11] to form $MgTiO_3$ which, in the presence of calcia, forms stable $CaTiO_3$ and MgO. The effect of this mechanism depends largely on the amount of the liquid phase. When the amount of liquid is small in relation to the grain boundary and the porosity is still preferentially situated at the multiple grain junction, it may control the grain growth behaviour by influencing the impeding factors. However, when the amount of liquid secondary phase is relatively large so that all the grains are completely enveloped, Ostwald Ripening would govern the grain growth behaviour. Besides, if there is a size difference between particles, grain growth occurs by Ostwald Ripening during liquid phase sintering by decreasing the solid-liquid interface area [9]. Then pore-drag or precipitate drag would no longer play a role in grain growth. Only impurity drag being governed by diffusion within the crystal lattice can remain in a modified state [13].

When ilmenite, which is a mixed oxide of TiO_2 and Fe_2O_3 was added to natural magnesite, it was anticipated that both cations, viz. Fe and Ti, would contribute to the sintering of magnesite. A large amount of secondary liquid phase was found to be distributed uniformly forming a silicate coating throughout the matrix and periclase grains in the 0.2 wt % ilmenite added Salem magnesite compacts. It is interesting to note that the titanate phase extends from one grain to another. As in the case of pure titania mineraliser, a channel containing Mg was also formed within the triple junction region in case of ilmenite as seen in Fig. 5. Two types of secondary phases, one titania rich and the other silica rich were generally identified in the EDXA digitised maps of the sample shown in Fig. 6. The Ti was again associated with Ca indicating presence of $CaTiO_3$. Interestingly, Ti and Si were mutually exclusive though Ca was found to coexist with both.

The addition of ZrO_2 to natural magnesite indicated yet another type of behaviour. The back scattered electron image in Fig. 7a of a sample of 0.5 wt % zirconia bearing magnesite sintered at $1650\,°C$ with 4 h soak shows the angular grain shape and distribution of secondary phase in the triple grain junction region and in the grain boundary. A magnified image of triple grain
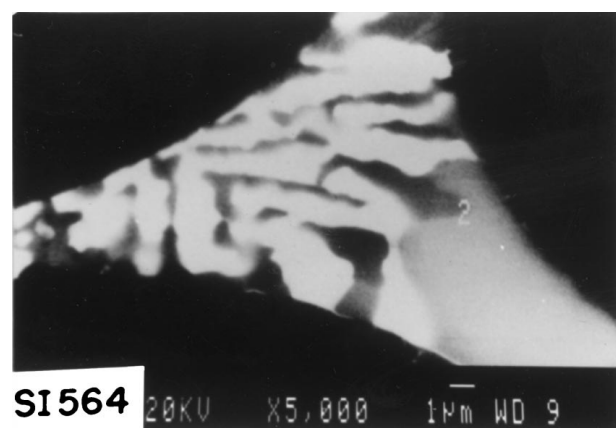

Figure 5 Backscattered electron image of SI564 indicates 0.5% ilmenite added Salem magnesite, fired at $1650\,°C$ for 4 h. Two secondary phases were found. Light phase (2) is secondary silicate (forsterite) phase and bright phase (1) is the calcium titanate phase.
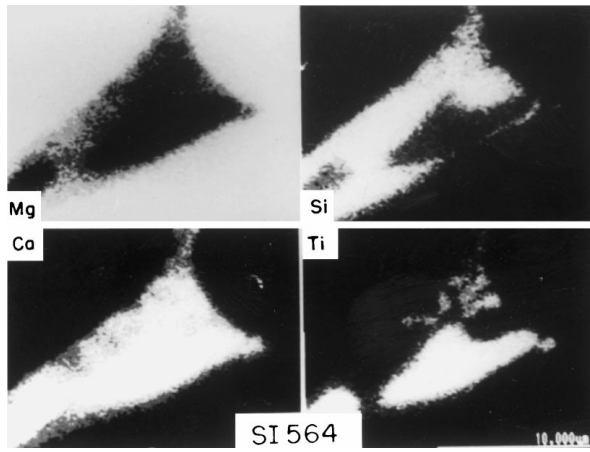
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Figure 6 Coexistence of calcium and titanium at the grain boundary of sintered Salem magnesite with 0.5% ilmenite; EDXA digitised image.

Figure 7 Secondary and backscattered electron images of SZ564 indicates 0.5% zirconia added Salem magnesite fired at 1650 °C for 4 h: (a) Showing the distribution of secondary phases in triple grain junctions; (b) an illustration of the dynamic state of ZrO_2 exsolution (1) in "suspended animation".
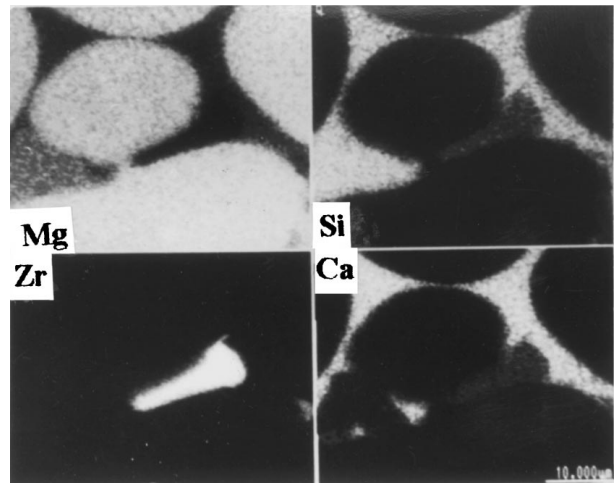

Figure 8 Digital image of zirconia added sintered magnesite showing isolation of zirconia phase in the grain boundary while other elements coexist with each other.

Figure 9 XRD powder patterns of sintered Salem magnesites with zirconia (marked SZ) and ilmenite addition (SI) showing zirconia phase in the former, and calcium titanate and magnesioferrite phases in the latter. O = monticellite, CT = Calcium titanate, F = forsterite, M = magnesia, Z = zirconia, MF = magnesioferrite. The sample (SO) does not contain any zirconia.

region is shown in Fig. 7b. the bright circular and oblate regions are zirconia. The rounded nature of these precipitates is typical of zirconia precipitation in composites such as alumina-zirconia ceramics [13]. The figure also describes the ZrO_2 regions in the process of coalescence. It is proposed that ZrO_2 precipitates not only intensified the secondary liquid formation, but also promoted diffusion through the limited liquid within the system. The circular and oblate precipitates of ZrO_2 suggests mass transportation during liquid phase sintering through solution precipitation route, possibly by forming solid solution with the parent material, and promoting sintering through vacancy creation. This figure illustrates the dynamic state of ZrO_2 exsolution in "suspended animation" and it remains as isolated ZrO_2 phase as shown in Fig. 8 digitised image. Segregation of the liquid may have given rise to more direct bonding observed in these magnesites after sintering, but segregation also led to the loosened texture observed.
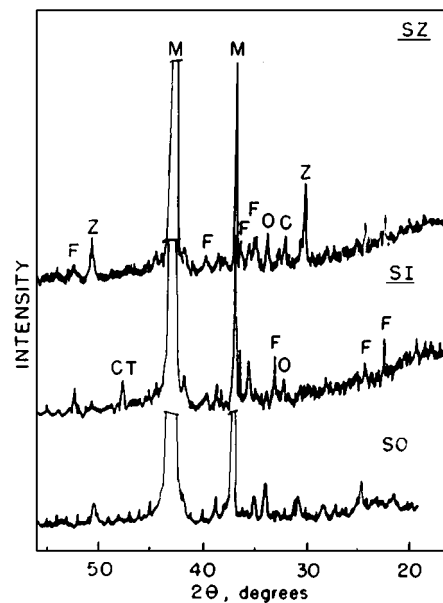
X-ray powder diffraction of ilmenite and zirconia added sintered magnesia sample is shown in Fig. 9 as SI and SZ. The powder XRD pattern of ilmenite bearing sintered magnesite reproduced as SI in Fig. 9 shows the presence of forsterite, monticellite, calcium titanate and magnesioferrite as the major crystalline secondary phases together with amorphous phase. Thus, the sintering mechanism in ilmenite bearing samples is similar to the titania based samples, with some enhanced surface diffusion due to the presence of Fe which reacts to form magnesioferrite. Similarly when zirconia added sample is compared with S0, which contains no ZrO_2, it is clear that ZrO_2 is present as cubic zirconia in the former sample. Under equilibrium condition the binary system $MgO-ZrO_2$ shows the co-existence of cubic zirconia up to 2070 °C [14]. The present sample was fired at 1700 °C for 2 h where c-ZrO_2 is seen to be present.

4. Conclusion

1. The study demonstrates that titania addition to natural magnesite results in the formation of calcium titanate in the secondary phase upon sintering. This formation can provide a reactive liquid during sintering that controls the grain growth and secondary phase distribution of the resultant sinter. The addition of titania in the form of mixed oxide, ilmenite, also gives rise to calcium titanate formation, providing a similar microstructure, specially with reference to spatial distribution of phases in the secondary phase. Magnesioferrite is also formed through reaction with Fe present in ilmenite.

2. Zirconia on the other hand, does not show any reaction product in the secondary phase. An exsolution precipitate of ZrO_2 is observed indicating that Zr interacts with the parent MgO as a solid solution and precipitates as a higher temperature in the liquid secondary phase. All these three mineralisers promote grain growth and matrix densification.

3. Three distinct behaviour were noted in these system: titania reacting with impurity calcia to form calcium titanate; iron oxide reacting with parent magnesia to form magnesioferrite; and zirconia exsolving to precipitate as zirconia itself. On the basis of this study, it is concluded that transition metal oxide aided sintering of magnesite follows specific reaction paths that enhance sintering and grain growth which is dependent on the transition metal cation used.

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