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Short communication

Effect of Mg^{2+}-and Fe^{3+}-ions on formation mechanism of aluminium titanate

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Abstract

The presence of Mg^{2+}- and Fe^{3+}-ions has an effect on the formation of Al_2TiO_5. Crystalline phases produced under the influence of the heat treatment have been identified in a heated X-ray diffraction chamber in the temperature range of 20–1500 °C. In the presence of Mg^{2+}- and Fe^{3+}-ions transitional phases are formed in the temperature range of 1000–1350 °C during Al_2TiO_5 formation. The XRD technique was used to identify the crystalline phases formed. On addition of MgO, chemical composition of the transitional phase formed is $Mg_{0.3}Al_{1.4}Ti_{1.3}O_5$, whereas on addition of Fe_2O_3 we have calculated a Powder Diffraction File card data for the transitional phase. Determination of the lattice parameters of the Al_2TiO_5 ceramics produced enabled verification of incorporation of Mg^{2+}- or Fe^{3+}-ions into the crystal lattice of Al_2TiO_5, i.e. the formation of Mg^{2+}- and Fe^{3+}-containing solid solutions.

Keywords: A. Powders: solid state reaction; B. X-ray methods; D. Al_2TiO_5; Formation mechanism

1. Introduction

Aluminium titanate based ceramic materials can be considered as structural materials of the future. Their unusual macroscopic properties, such as low thermal expansion coefficient (in this way excellent thermal shock resistance), low Young's modulus and low strength were related to micro cracks [1,2]. Their widespread industrial application is, however, restricted by several factors. Its applicability, is limited by the rapid decomposition of Al_2TiO_5 above 1280 °C as well as by its low mechanical strength. It is known that several additives (e.g. MgO, Fe_2O_3) may help reduce the rate of decomposition and increase the strength and conversion of Al_2TiO_5 [3–7]. Of course the amount of Al_2TiO_5 formed is influenced by the preparatory techniques, such as solid state reaction (reaction sintering or sintering of presynthesised Al_2TiO_5), sol–gel processing, combusting or hot pressing [8–12].

Present work intends to investigate the formation mechanism of Al_2TiO_5 in the presence of MgO and Fe_2O_3 additives.

The formation mechanism of the Al_2TiO_5 remains obscure up to now. The role of the transitional phases, produced (or not produced...) during the process of synthesis is discussed by several authors, but a unified view has not been declared. As reported – detailed in different ways – by Buscaglia [2,13] and Huang et al. [14] observations show that a transitional phase plays an important role in the course of formation of Al_2TiO_5, when it proceeds with the presence of the MgO. The authors agree about the fact that spinel ($MgAl_2O_4$) is formed in the first step when the substitute parameter is $x < 0.5$ (according to $Mg_xAl_{2(1-x)}Ti_{1+x}O_5$ relationship), although their opinions differ in the description of the processes, which result in the formation of the Al_2TiO_5. The production of the proper stoichiometric titanate phase results from this crystalline transitional phase and additional reactions of it.

The spinel is mentioned by Ohaya [15] and Djambazov et al. [16], as an identifiable crystalline phase in the system. On the other hand the spinel does not play a role in the formation of the titanate solid solutions from their publications.

An $MgTi_2O_5$ transitional phase is supposed to exist by Buscaglia if the substitute parameter is higher than 0.5, but the existence of it is controversial. According to Huang et al, in this case, beside the spinel, a solid solution of undetermined composition can exist too, as a transitional phase.

The forming of a transitional phase is mentioned by Tilloca [17] and Buscaglia et al. [18], also in the presence of Fe_2O_3, as

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Table 1
Designation of mixtures used for production of Al_2TiO_5.

Sample code	Al_2O_3:TiO_2 molar ratio	MgO content % by mass	Fe_2O_3 content % by mass
AT	1:1	–	–
ATMg3	1:1	3	–
ATMg5	1:1	5	–
ATFe3	1:1	–	3
ATFe5	1:1	–	5

additive material, during the formation of the Al_2TiO_5. The composition of the transitional phase is Fe_2TiO_5 in both references.

By this means the question of the being of the transitional phases during the formation of the Al_2TiO_5, is still open.

In the present study we investigated the various transitional phases of Al_2TiO_5 ceramics generated in the course of heat treatment and on addition of different auxiliary additives.

2. Experimental

The starting materials used were as follows: TiO_2 (anatase) of 8.9 m^2/g specific surface and 99.99% pure (Merck); α-Al_2O_3 of 5.4 m^2/g specific surface and 99.99% pure (Research and Development for Silicates and Ceramics Ltd., Hungary). The additives used were analytically pure MgO and Fe_2O_3 (Merck).

For the mixtures investigated, the Al_2O_3: TiO_2 molar ratio was stoichiometric, whereas the quantity of both additive materials varied between 0% and 5% by mass. Determination of phase composition was performed by using a Philips PW 3710 type XRD instrument. The phase-formation mechanism was investigated by Anton Paar HTK 06 type High Temperature Camera, determination of lattice parameters was done by a Philips Appleman Refinement Program, and calculation of *d*-spacing values was achieved by Dicvol 91 Program.

Mixtures indicated in Table 1 were used for the heated chamber X-ray investigations after wet homogenisation of the starting materials in a porcelain ball mill for 2 h. In order to determine the transitional phases and investigate the lattice parameters, the starting material mixtures were dried until constant weight at 105 °C and rods of 1 cm^2 cross section and 6 cm length were pressed at 150 MPa pressure using cold isostatic press (National Forge Europe).

In the course of the heated chamber X-ray investigation, diffractograms were taken at 20, 1000, 1100, 1200, 1250, 1300, 1350, 1400, 1450, 1500 and again at 20 °C between the 24° and 45° angle range at 0.025 $°2\Theta$/s scanning speed, the dwell time was 1 h.

Quantitative evaluations of the individual crystalline phases were done on the bases of the following Miller index X-ray diffraction peaks:

Anatase (A)	101	*d* = 0.352 nm
Rutile (R)	110	*d* = 0.324 nm
Corundum (K)	113	*d* = 0.208 nm
Aluminium titanate (AT)	101	*d* = 0.335 nm

In order to determine the lattice parameters, the cold isostatic pressed rods were placed in KO II. type German made supercanthal heated furnace and heat treated at 1500 °C for 4 h. The samples were then cooled to room temperature and investigated by XRD.

3. Results

Fig. 1 depicts the heated chamber XRD diffractograms for different temperatures of the AT sample not containing any additives. Fig. 2 shows the counts of characteristic reflections of the various phases as a function of temperature. Based on Figs. 1 and 2, it is obvious that only a small amount of Al-titanate is produced under the given investigation conditions. Formation of Al-titanate starts at 1250 °C and increases steadily up to 1500 °C. The dominant process is the change of modification of TiO_2 from anatase to rutile. Formation of Al_2TiO_5 commences when the ratio of rutile:anatase modifications exceeds the value of 3.

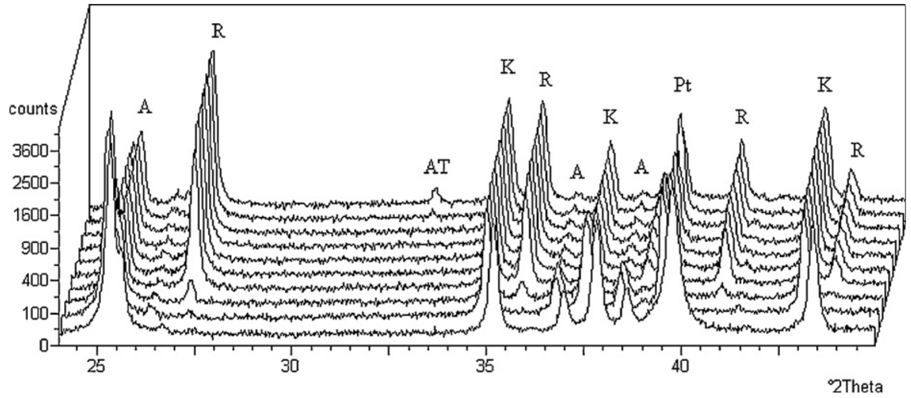

Fig. 1. Heated chamber X-ray diffractogram of the starting mixture AT.

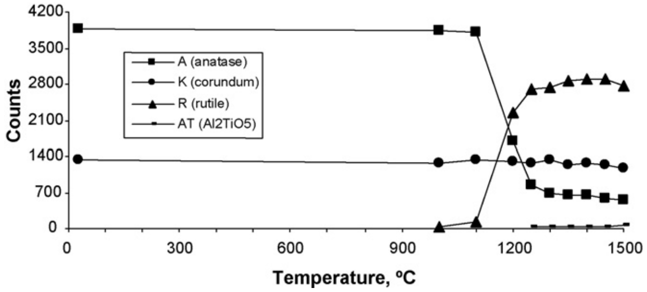

Fig. 2. Change of quantity of significant phases as a function of temperature for the starting mixture AT.

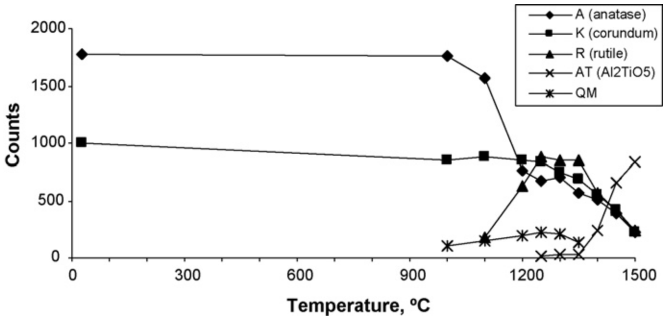

Fig. 4. Change of quantity of significant phases as a function of temperature for the starting mixture ATMg5.

It can be observed on the heated chamber X-ray diffractogram of the sample containing 5% by mass MgO (Fig. 3) as well as on the diagram exhibiting the quantitative distribution of significant phases present as a function of temperature (Fig. 4) that the rutile to anatase transformation starts at 1000 °C also for this sample, simultaneously with which appears a phase different from any crystalline phases typical to the given system; this phase is designated as Q_M. The highest formation rate for the Q_M crystalline phase is about 1300 °C. It is clearly seen that the appearance of Al_2TiO_5 is at about 1250 °C, similarly to the sample without additive, but the rate of formation of Al_2TiO_5 is much accelerated when the amount of the transitional phase (Q_M) starts to decrease above 1350 °C. This implies that the greatest part of Al-titanate is produced from this transitional Q_M phase.

It can be concluded after investigation of the ATF starting material mixtures that the trends observed are similar for those experienced in the case of the ATM samples. Figs. 5 and 6 depict the heated chamber X-ray diffractogram and the rate of formation of the significant phase as a function of temperature within the ATFe5 sample, respectively.

The anatase to rutile transformation starts at 1000 °C. The highest quantity of the transitional (Q_F) phase is reached at 1350 °C which is the starting temperature of Al-titanate formation. On elevating the temperature to 1500 °C, the quantity of Al-titanate rapidly increases with the transitional phase disappearing from the system only at 1500 °C.

Due to the fact that Q_M and Q_F are transitional phases in the given systems, determination of their composition was performed using a special heat treatment technique. The ATM specimens were heat treated at 1300 °C for 30 min, whereas the ATF specimens were heat treated at 1100 °C for 30 min.

Then the samples were taken out of the furnace so as to freeze the characteristic state evolved on heating. Designations of the samples obtained are ATMQ and ATFQ. Figs. 7 and 8 show the XRD diffractograms taken on ATMQ and ATFQ samples.

It is deducted from the investigation of *d*-values of the Q_M transitional phase that it corresponds to a compound with the overall composition of $Mg_{0.3}Al_{1.4}Ti_{1.3}O_5$.

During investigation of the *d*-values of the Q_F compound, this phase could not be successfully identified on the basis of PDF cards.

After collection of the *d*-values belonging to this unknown phase and assuming it has an orthorhombic structure, the *d*-values corresponding to relevant Miller indices were calculated (Table 2). On the basis of satisfactory matching found for the measured and calculated data it is assumed that the Q_F phase is of orthorhombic structure. Clarification of its chemical composition is to be done by subsequent analyses.

Investigations of solid solution formation for samples with and without additives were performed by comparison of the lattice parameters determined for the samples. The values of the lattice parameters for Al-titanate solid solutions prepared with additive materials were compared to the lattice constants of aluminium titanate produced under similar conditions but without any additives. Lattice parameters of the different samples are tabulated:

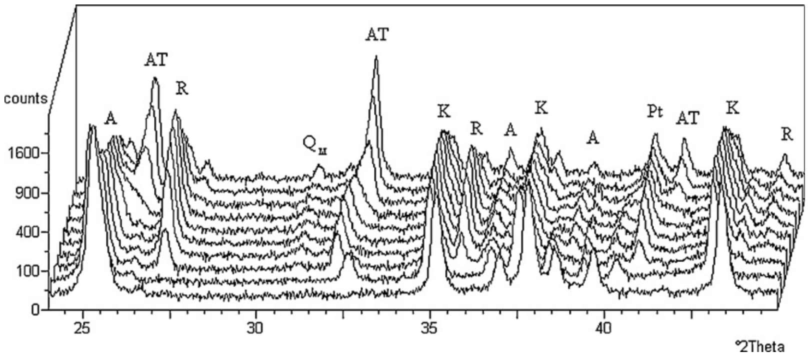

Fig. 3. Heated chamber X-ray diffractogram of the starting mixture ATMg5.

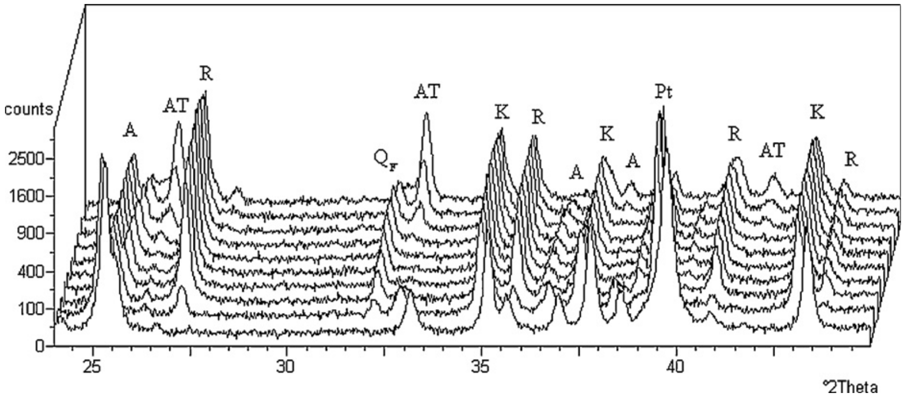

Fig. 5. Heated chamber X-ray diffractogram of the starting mixture ATFe5.

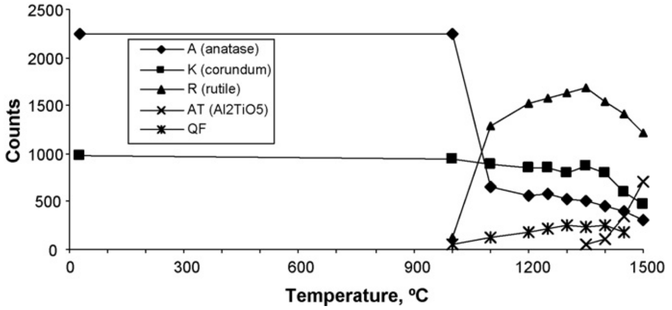

Fig. 6. Change of quantity of significant phases as a function of temperature for the starting mixture ATFe5.

AT	ATMg5	ATFe5	
a [nm]	0.942483	0.945557	0.943899
b [nm]	0.963841	0.966724	0.965071
c [nm]	0.359067	0.359189	0.359502

It can be seen that in the case of both the MgO and the Fe_2O_3 additive, the '*a*' and '*b*' lattice parameter values of the Al-titanate formed are increased, whereas the '*c*' value hardly changes.

It can be observed that the structure prepared with MgO additive shows greater changes that with Fe_2O_3 additive. Reason for this is to be found in the size of the ions forming the Al-titanate lattice as well as in those of the substituting ions.

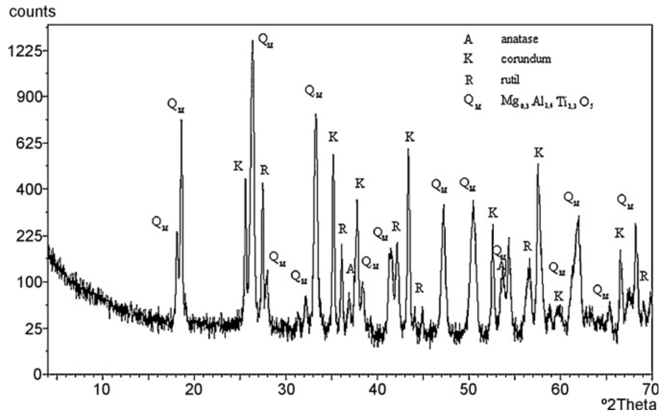

Fig. 7. X-ray diffractogram of the sample ATMQ fired at 1300 °C.

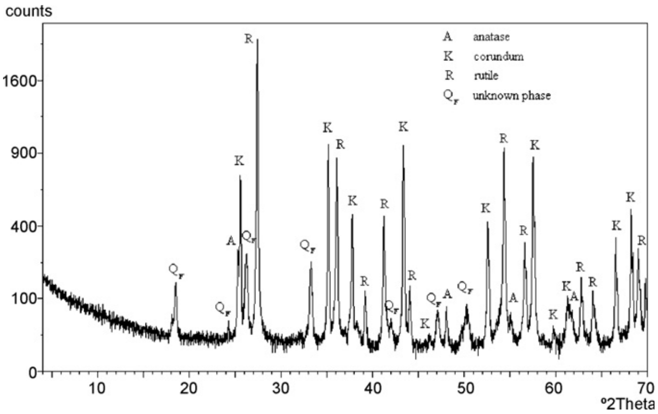

Fig. 8. X-ray diffractogram of the sample ATFQ fired at 1100 °C.

The replacement of Al^{3+} for Fe^{3+} causes only a slight alteration within the lattice structure of the Al_2TiO_5 due to the nearly identical size of the two ions (Al^{3+}: 0.068 nm, Fe^{3+}: 0.069 nm).

In the case of replacement of Al^{3+} for Mg^{2+}, the need to ensure charge neutrality results in the assumption that possibly two Al^{3+} is replaced by one Mg^{2+} and one Ti^{4+}-ions together. The sizes of the two latter ions (Mg^{2+}: 0.086 nm, Ti^{4+}:

Table 2
Identification card for Q_F transitional phase.

d_{input} (nm)	Relative intensity (%)	d_{calc} (nm)	*h*	*k*	*l*
0.47741	46	0.477844	1	1	0
0.36628	9	0.366358	0	0	1
0.33973	100	0.339686	1	0	1
0.26911	87	0.268507	1	2	0
–	–	0.216569	1	2	1
0.21514	13	0.215378	3	1	1
0.19308	21	0.192788	4	0	1
0.18125	21	0.179553	1	0	2
–	–	0.183530	1	3	0
–	–	0.182365	4	1	1
–	–	0.183179	0	0	2
–	–	0.179465	3	2	1
–	–	0.181375	5	0	0
0.15301	6	0.153471	0	2	2
–		0.151320	1	2	2
–		0.152406	5	2	0

0.075 nm) however are greater than that of the Al^{3+}, therefore a greater deformation of the crystal lattice is expected, which is supported also by the experimental results.

4. Conclusions

1. It was determined that formation of AT for both MgO-doped and Fe_2O_3-doped systems (up to 5%(n/n) substitution limit) involves a transition phase and these crystalline phases remain stable between 1000 and 1400 °C.
2. Composition of the transitional phase is $Mg_{0.3}Al_{1.4}Ti_{1.3}O_5$ for the system with MgO additive.
3. In the case of the system with Fe_2O_3 additive, composition of the transitional phase is unknown, but the measured and calculated typical plane *d*-spacing values are indicated.
4. It was confirmed by X-ray diffraction and lattice parameter investigations that both Mg^{2+} and Fe^{3+} ions build in the crystal lattice of Al_2TiO_5 forming solid solution series.

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