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# Influence of MnO and $TiO_2$ additives on density, microstructure and mechanical properties of $Al_2O_3$

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**Abstract**

Effect of manganese oxide and titanium oxide as additives on sintering of alumina is described. Sintered density, average grain size and microstructural features have been investigated along with the mechanical properties. The addition of manganese oxide produced a relatively uniform, dense microstructure at high temperature. Titania up to 0.2 wt.% is found to be the most effective additive in promoting grain growth. Titania doping leads to achieving theoretical density at 1400 °C. The secondary phase, $Al_2TiO_5$ mostly precipitates at triple junctions and occasionally along the grain boundaries. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

*Keywords:* B. Microstructure; C. Mechanical properties; D. Alumina; Secondary phase; Additive

## 1. Introduction

Polycrystalline alumina microstructures and their related properties often depend critically on both the presence of dopants and of residual impurities, such as magnesium, calcium and silicon [1,2]. The usefulness of dopants in promoting sintering and controlling grain growth in alumina is recognised. The role of magnesia in sintering of alumina has been very effective for controlling abnormal grain growth through a solid-solution pinning mechanism and thus, achieving theoretical densities in alumina. Major consequences are a reduced tendency for pore-boundary separation to occur and related protection against abnormal grain growth. The microstructure of such materials generally consists of uniform sized and equiaxed grains of alumina.

Additives forming liquid silicates (e.g. in the alumina–calcia–silica system) has achieved considerable importance, because it contains many eutectics with temperatures in the range of 1200–1400 °C. The lowest eutectic is at 1170 °C in the wollastonite–silica–anorthite system and other eutectics with temperatures less than 1400 °C are close to the wollastonite–alumina line. Additions at the percentage level of wollastonite or an appropriate silica-oxide or carbonate mixture to alumina, generate several volume percentage of wetting liquid as the temperature approaches 1400 °C and sintering of the alumina to theoretical density is achieved readily through a process assumed to involve the solution and recrystallisation of alumina particles in the liquid. The characteristic of such sintered materials consists of large, platelike or rodlike grains of $\alpha$-$Al_2O_3$ [2–4]. The origin of platelike grains, microstructure features and their growth kinetics are reported elsewhere [5,6]. Cook and Schrott [7] found that Ca was present as a segregate at grain boundaries of $Al_2O_3$. The grain boundary mobility of $Al_2O_3$ is considered to be hindered by the CaO and $SiO_2$ rich grain boundary phase. The shape of the CaO and $SiO_2$ condensed phase is thin, plate-like with 10–20 Å thickness [8]. Consequently, the pinning effect of CaO and $SiO_2$ is categorised as the facial pinning effects. For this reason, preferably a small amount of the sintering additives should be incorporated into alumina to gain the desired effect without compromising the properties.

In this work, the microstructures and mechanical properties of alumina doped with various amounts of manganese oxide and titanium oxide and their sintering behaviour have been studied.

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There are only a few investigations on the influence of manganese oxide addition on the sintering behaviour of alumina [9,10]. The examination of the microstructural features during sintering and detailed analysis on the densification regime has not yet been reported in detail [11,12]. According to the results of early studies based on shrinkage data, the sintering rates accelerated until the additive concentration exceeded a certain level, typically up to 0.3 wt.% manganese oxide. It was proposed that the favourable addition is in the range of 0.1–1.0 wt.%, which caused a change in the diffusion mechanism from grain-boundary diffusion to bulk diffusion. It was also suggested that a change in mechanism from volume diffusion to grain-boundary diffusion occurred beyond 0.3 wt.% manganese oxide. With $TiO_2$ as the sintering agent, the sintering rate increases to a maximum, then levels off and starts decreasing as the additive concentration exceeds 0.3 wt.% presumably due to the formation of a secondary phase. However, in these studies the formation of the second phase particles was not experimentally verified [9,10].

Titania is known as an effective additive to densify alumina below the normal densification temperature [13,14]. This is because it is very sensitive to oxygen partial pressure, forming $Ti_{Al}^{\bullet}$ and $V_{Al}'''$ which promote the sintering of $Al_2O_3$. Titania is dissolved in $Al_2O_3$ up to 0.27 wt.% in the temperature range from 1300 to 1700 °C in air [15]. When the amount of $TiO_2$ is above the solubility limit, the excess $TiO_2$ co-existed with $Al_2O_3$ as rutile below 1350 °C. Above 1450 °C, $TiO_2$ and $Al_2O_3$ form a compound $Al_2TiO_5$. When $TiO_2$ is excessively present beyond the dissolvable level, it greatly affects the microstructure and mechanical strength. However, only a few researchers have discussed the sintering process of titania-doped alumina powder at low oxygen pressure. The relation between the solid solutions and the initial stage sintering of alumina has been reported by measuring the shrinkage of powder compacts under thermal and isothermal condition [16].

## 2. Experimental procedure

### 2.1. Manganese oxide

The sol-gel derived alumina powder and reagent grade manganese acetate, tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$) were used as the starting materials. The manganese acetate was dissolved in water to yield 0.1, 0.3, 0.5, 1.0, 1.5 and 3.0 wt.% manganese oxide and to this solution, alumina powder was added gradually and its pH was maintained at 3.0 with the addition of HCl and formic acid. The formic acid was found a suitable pH stabilizer for the present system. Continuous stirring was applied to the suspension during mixing to prevent sedimentation and the slurry was continuously stir/dried and hand ground. On calcining the powder at 400 °C for 1.0 h in air, the acetate decomposed into oxide.

### 2.2. Titanium oxide

The starting materials were sol-gel derived $Al_2O_3$ and $Ti(OC_3H_7)_4$. Alumina compacts containing various amounts of titanium oxide were prepared by adding titanium-isopropoxide (TIP) into alumina. The TIP was hydrolyzed by the addition of water to yield $TiO_2$ at 0–4.0 wt.%. The mixture was dried at 100 °C and it was decomposed into oxide at 400 °C.

The prepared alumina powders with the above additives were uniaxially pressed into pellets of size 10 mm dia and rectangular bars (60×5×5 mm). A mixture of PVA and PEG was added as a binding agent. Compacts were sintered at various sintering temperatures.

## 3. Results and discussion

### 3.1. Sintering studies

#### 3.1.1. Manganese oxide

The sol-gel derived alumina powder compact without addition was sintered to 98.5% of T.D. at 1550 °C for 3.0 h. The doped samples reached 98–99% of T.D at the same sintering temperature of 1550 °C for 3.0 h.

#### 3.1.2. Titanium oxide

Fig. 1 illustrates the effect of $TiO_2$ content on the sintered density of titania doped alumina sintered at 1400–1600 °C for 3.0 h. The green density of the alumina decreases with increasing titania content from 58 to 53% of T.D. However, when the material is sintered to 1400 °C, the density increases from 81 to 98% of T.D

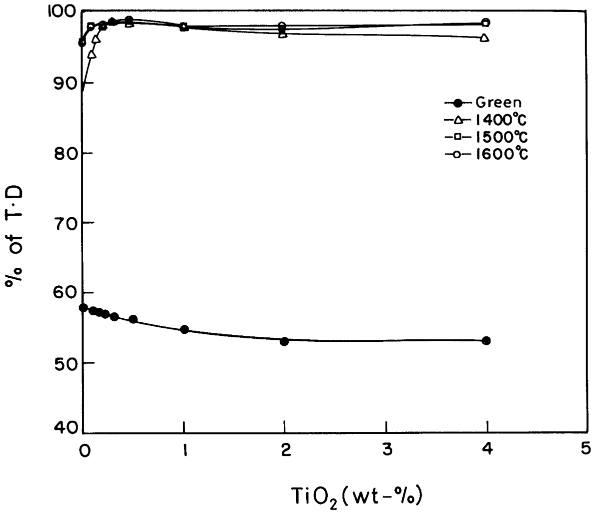

Fig. 1. The effect of sintering temperature on sintered density of $TiO_2$ doped $Al_2O_3$.

for the concentration of 0.2 wt.%. At 1500 °C, 96% of T.D is obtained for pure and 98% of T.D for 0.1 wt.% of $TiO_2$. At higher temperatures, the addition of titania does not elevate the sintered density.

### 3.2. Microstructure analysis

#### 3.2.1. Manganese oxide

Fig. 2a shows the microstructure of pure alumina sintered to 98.5% of T.D at 1550 °C. There appears to be a homogeneous grain growth with a few isolated pores.

However, 0.1 wt.% manganese oxide addition leads to inhomogeneous grain growth at a sintering temperature of 1550 °C. The resultant microstructure shows localized regions of finer grains surrounded by larger sized grains (Fig. 2b). A further increase of the additive concentration to 0.3 wt.% causes a dramatic change in the microstructure at the same sintering temperature. An exaggerated grain growth with grains as large as 20–100 μm is observed (Fig. 2c). A considerable amount of both intergranular and intragranular pores are also seen in the microstructure. The average grain size for the samples is 10 μm. Fine pores of less than 1.0 μm in size trapped inside the grains become more evident after a soaking time of 3.0 h at 1550 °C.

According to the phase diagram given in Fig. 3, a eutectic composition is present on the MnO-rich side of the binary $MnO–Al_2O_3$ system at 1520 °C [17]. The micrographs shown for the samples with 0.1–0.5 wt.% manganese oxide addition sintered at 1550–1600 °C do not indicate the presence of any secondary phase formation between the grains. Based on these observations it is concluded that the volume or grain boundary diffusion mechanism acts as the controlling process according to the composition and the sintering conditions during the later stages of densification rather than the formation of an intergranular liquid-phase.

In fact, manganese displays a variable valency, so that a complex series of oxides may exist. The valency change of manganese also leads to many defect structures and formation of non-stoichiometric compounds. Therefore, it may be suggested that different manganese

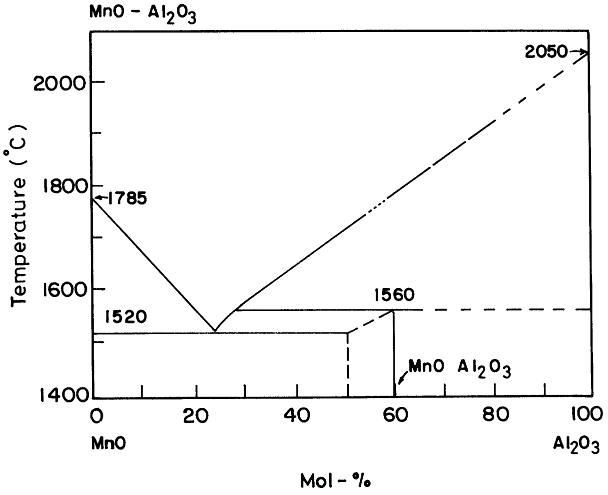

Fig. 3. The phase diagram of the $MnO–Al_2O_3$ system.

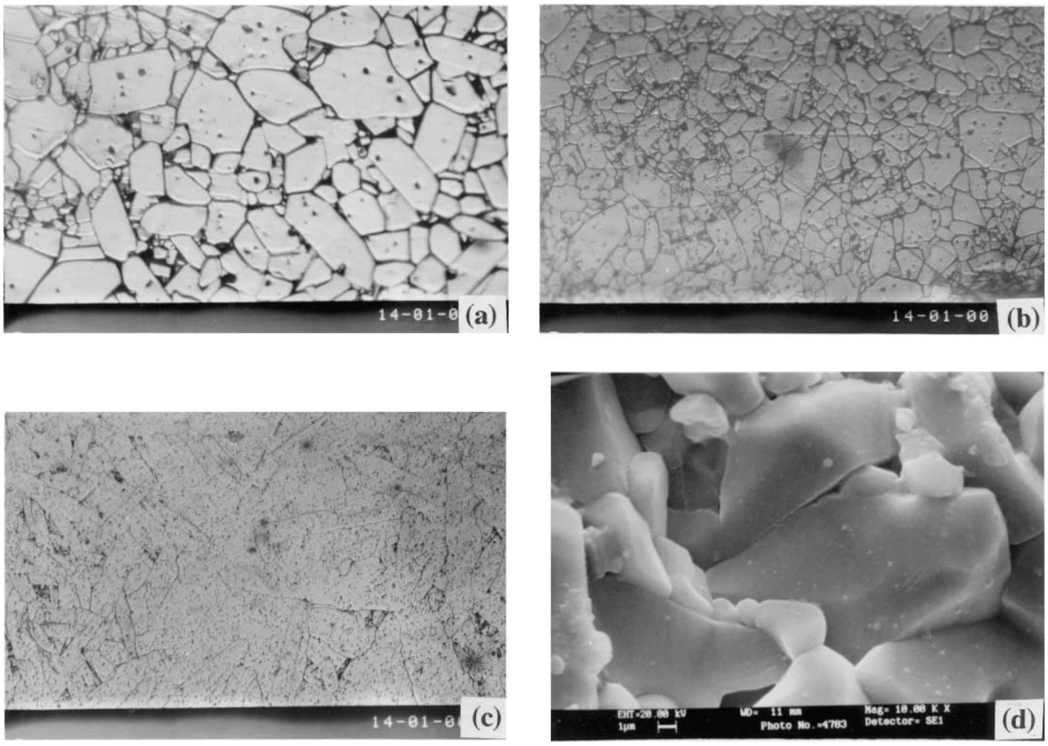

Fig. 2. Micrograph of alumina sintered at 1500 °C, (a) pure, (b) 0.1 wt.%, (c) 0.5 wt.% and (d) 1.5 wt.% manganese oxide.

cations with different valency states substitute the aluminum cation sites within the crystalline structure, resulting in either a vacancy formation or an extra electron. This type of phenomenon is observed during the sintering of $TiO_2$ doped alumina powder by the activation of the volume diffusion rate of species [18]. The micrograph shows that the manganese is well distributed throughout the grains and no segregation of manganese is detected at the grain boundaries. Therefore, it may be elaborated that the manganese cations substitute the Al sites, resulting in fast diffusion within the single grains during the sintering process. As a result of the fast diffusion paths formed, the process of excessive grain growth is enhanced when the amount of manganese oxide addition is increased from 0.1 to 0.5%.

On the other hand, when the compacts containing 1.5 wt.% manganese oxide are sintered at 1550 °C, the presence of a secondary intergranular phase both in the form of continuous layer and irregular shapes indicate that the controlling mechanism is due to the grain boundary diffusion process (Fig. 2d).

### 3.2.2. Titanium oxide

Fig. 4 shows the fracture surface of alumina with $TiO_2$ as the dopant, sintered at 1400 °C. The grain size increases as the $TiO_2$ content is increased from 0 to 0.2 wt.% and then decreases with the titania content up to 4.0 wt.% (Fig. 4). The number of the fine grains increases as the titania content is increased. The finer grains may contain high proportions of titanium. This suggests that they are titanium compounds, primarily $Al_2TiO_5$. The secondary phase is almost spherical or corn shaped. The secondary phase precipitates, mostly at triple junctions and occasionally along grain boundaries. The existence of this secondary phase reduces the driving force for grain growth by pinning effect. The shape of the secondary phase depends upon the particle orientation with respect to those of the grains and grain boundary miss orientation. Krivanek et al. [19] using a 100 Å diameter probe, have reported that $TiO_2$ doped $Al_2O_3$ had no platelike secondary phase along grain boundaries. The secondary phase, small round grains, is probably $Al_2TiO_5$ because the phase diagram [20] gives $Al_2TiO_5$ as the only stoichiometric compound known in the $Al_2O_3$–$TiO_2$ binary system. The grain size of the secondary phase is in the range of 0.5–3.0 μm (Fig. 4b). It is noted that the largest grain size are observed for a $TiO_2$ content close to the solubility limit (Fig. 4a) because the $TiO_2$ content accelerates grain growth. However, the grain growth decreases as the $TiO_2$ content increases beyond the solubility limit because the presence of a secondary phase between the α-$Al_2O_3$ grains inhibits their growth.

## 3.3. Mechanical properties

### 3.3.1. Manganese oxide

Table 1 shows the hardness measurements as a function of sintering temperature and additive concentration. It is observed that there is an increase in hardness value with sintering temperature. Initially there is a slight decrease in the hardness value with the manganese oxide addition up to 0.5 wt.%. Then the hardness increases with increasing concentration of the additive and reaches a maximum value of 23 GPa for 3.0 wt.% manganese oxide addition at a sintering temperature of

Table 1
Vickers' hardness and flexural strength for manganese oxide doped alumina

| Additive concentration (wt.%) | Hardness (GPa) (for 2.0 kg) | | Flexural strength (MPa) | |
|---|---|---|---|---|
| | 1550 °C | 1600 °C | 1550 °C | 1600 °C |
| 0 | 18.13 | 19.83 | 306.0 | 330.0 |
| 0.1 | 17.93 | 19.28 | 261.7 | 285.8 |
| 0.3 | 17.13 | 18.28 | 258.7 | 175.1 |
| 0.5 | 16.99 | 17.33 | 365.9 | 162.0 |
| 1.0 | 21.82 | – | – | – |
| 1.5 | 21.50 | – | – | – |
| 3.0 | 23.20 | – | – | – |

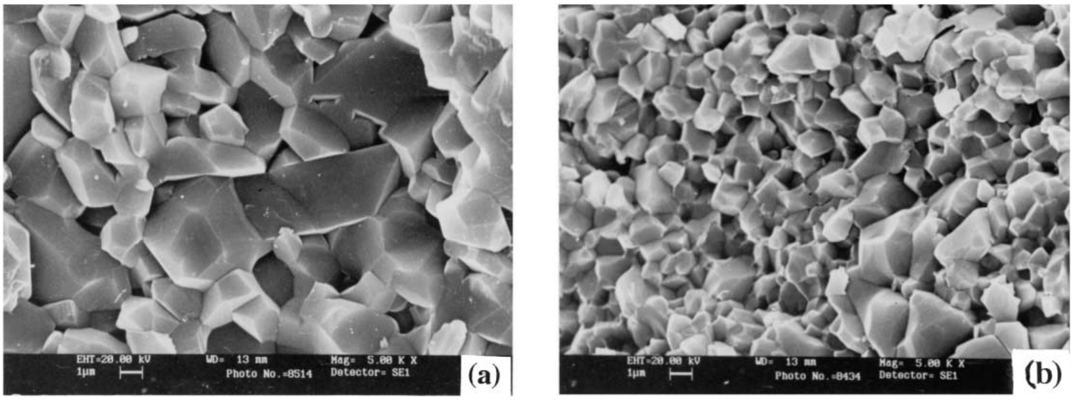

Fig. 4. Fracture surface of alumina with (a) 0.2 wt.% and (b) 4.0 wt.% $TiO_2$ sintered at 1400 °C.

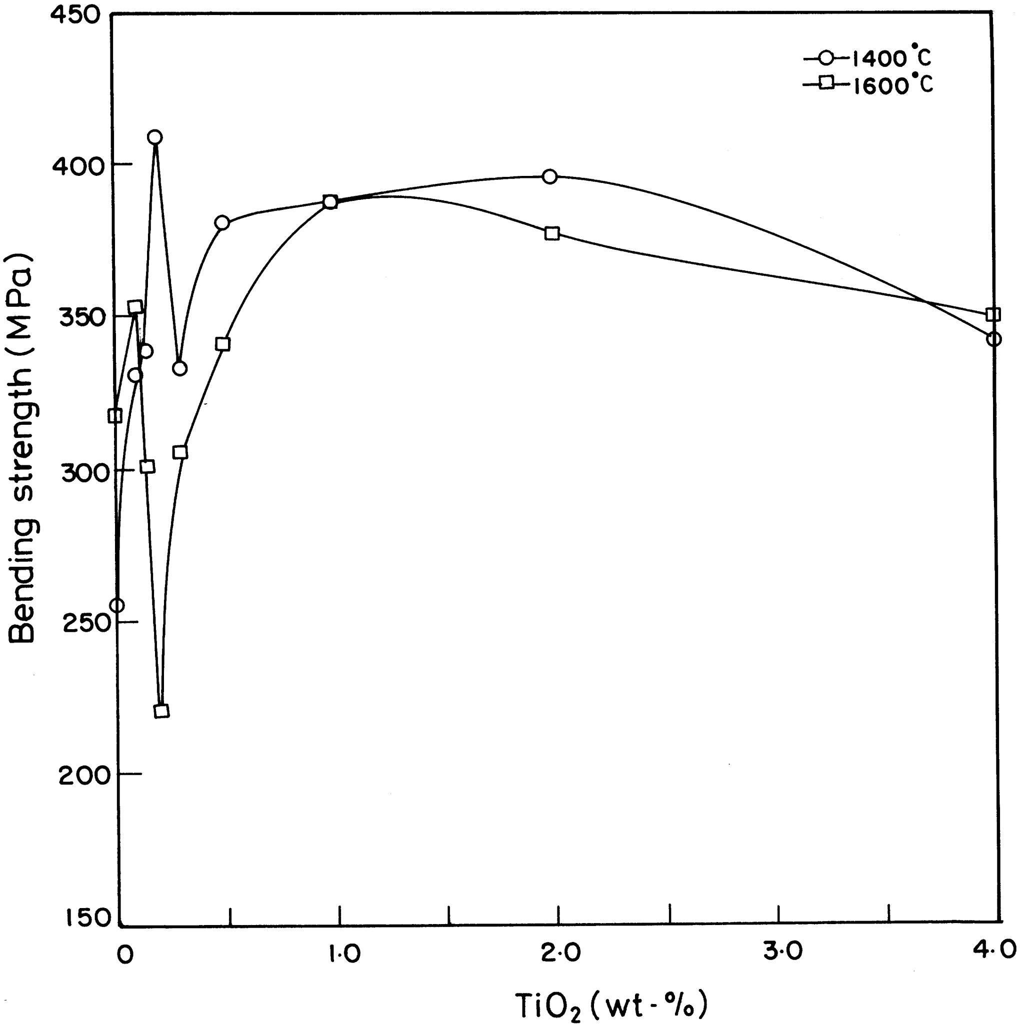

Fig. 5. Flexural strength of $TiO_2$ doped $Al_2O_3$.

1550 °C. This may be attributed to the formation of a secondary phase in the intergranular phase, in the form of continuous layers. A similar behaviour is also observed for the flexural strength for the same wt.% additions of manganese oxide. Here the flexural strength value of 366 MPa is obtained for 0.5 wt.% manganese oxide addition sintered at 1550 °C (Table 1). The data show higher strength values above 0.5 wt.% manganese oxide addition. It is hard to suggest any correlation with respect to the function of manganese oxide addition on materials strength. However, it can be proposed that manganese addition to pure alumina yields a structurally more reliable product.

### 3.3.2. *Titanium oxide*

Fig. 5 shows the variation of flexural strength of $Al_2O_3$ with $TiO_2$ as sintering additive sintered at 1400 and 1600 °C. It can be seen that a maximum value of 409 MPa is observed for the samples sintered at 1400 °C for a $TiO_2$ content of 0.2 wt.%. The effects of $TiO_2$ content on the flexural strength are complex. At 1600 °C, the flexural strength increases from 315 to 353 MPa as the $TiO_2$ content increases from 0 to 0.1 wt.%. As the $TiO_2$ is increased a sudden decrease in strength value to 220 MPa is observed. Again the strength increases as the $TiO_2$ content increases. At 4.0 wt.% of $TiO_2$, a flexural strength of 347 MPa is observed. It is found to be higher than the flexural strength of pure alumina.

## 4. Conclusion

The colloidal approach is an effective method to obtain a homogeneous distribution of additives. There is always a small amount of pores is present when manganese oxide is used as additive. As higher the amount of manganese, as higher is the amount of pores for the same sintering temperature and a large number of closed pores are trapped within the grains. Grain growth has been promoted with manganese oxide addition and exaggerated grain growth behaviour is observed in some cases due to an extended sintering time. A slight decrease in hardness has been observed as the amount of manganese is increased. Higher hardness and strength values are observed for manganese oxide additions above 0.5 wt.%.

The $Al_2O_3$ sample doped with 0.2 wt.% of $TiO_2$ reaches 98% of T.D at 1400 °C. A further increase in titania concentration and increase in sintering temperature does not enhance the density. The flexural strength of materials sintered at 1400 °C increases with increasing amount of $TiO_2$ up to the solubility limit. After the solubility limit, there is a sudden decrease in strength. The flexural strength increases with further increase of the amount of $TiO_2$. Increasing the $TiO_2$ content results in the reduction of the grain size of $Al_2O_3$. The presence of large amount of secondary phase controls the grain growth and reduces the flexural strength.

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