



## The mechanism of periodic layer formation during solid-state reaction between Mg and SiO<sub>2</sub>

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### ABSTRACT

The as yet unresolved microstructure of the periodic layers formed in the reactive diffusion system Mg/SiO<sub>2</sub> was clarified by using high-resolution field-emission SEM. The periodic layered structure actually consists of the single-phase layer of Mg<sub>2</sub>Si and the two-phase layer of (Mg<sub>2</sub>Si + MgO) alternated within the reaction zone. According to the experimental observations and in line with the diffusion-induced stresses model, the mechanism controlling this phenomenon could be attributed to the stresses induced by the difference in interface growth rates of Mg<sub>2</sub>Si and MgO phases within the layer. When the elastic deformation of the slow-growing aggregated-MgO phase reaches its elastic maximum, it will be split off from the reaction front by the neighboring Mg<sub>2</sub>Si phase and a new periodic layer forms. The computer simulation results are coinciding well with the experimental data.

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### 1. Introduction

The periodic layer formation during solid-state reactions is one of the most fascinating reactive diffusion phenomena. Since its discovery by Osinski et al. in 1982, a number of systems have been reported that display regularly spaced layers of reaction products including systems such as Zn/Fe<sub>3</sub>Si, Zn/Co<sub>2</sub>Si, Zn/Ni<sub>3</sub>Si<sub>2</sub>, Mg/Ni<sub>50</sub>Co<sub>20</sub>Fe<sub>30</sub>, Ni/SiC, Pt/SiC, Co/SiC, Mg/SiO<sub>2</sub>, Zn/Ni<sub>3</sub>Si and Al/U<sub>10</sub>Mo [1–11]. The research work focusing on this phenomenon is not only a matter of curiosity, but it is also relevant to fundamental studies of reactive diffusion [12–19] and it might even find applications in areas such as in situ compositional modulation of Mg<sub>2</sub>Si-based thermoelectric materials intended for either cooling or harvesting of waste industrial heat.

Although several different models have been put forward to explain the formation of periodic layered structures in the reactive diffusion process [1–9], the exact nature of the reaction mechanism remains a controversial topic. In 2003, Chen et al. [20] proposed the

diffusion-induced stresses model to explain the formation mechanism and gave the general quantitative description applicable to periodic layered structures. The model attributed the layer formation to the accumulated stresses within the two-phase layer at the reaction front. If the interface growth rates of the two phases are not equal, the slow-growing phase  $\beta$  will be under tension by the fast growing phase  $\alpha$  and, eventually, it will split off from the reaction interface resulting in the formation of a new periodic layer (Table 1). Although the model explained successfully the important experimental features observed in several reaction systems such as Zn/Fe<sub>3</sub>Si, Zn/Co<sub>2</sub>Si and Pt/SiC [20–22], it could not address the formation mechanism in the interesting Mg/SiO<sub>2</sub> system because of the acute scarcity of experimental details concerning the layers' microstructure [9]. The periodic layer formation during the reaction between Mg and SiO<sub>2</sub> was first reported in 2001 by Gutman et al. [7] and, subsequently, a switch-over model and its modifications were proposed in 2001 and 2006 to explain the formation mechanism for this reaction system [8,9]. In this paper, we provide a detailed account of the periodic layer formation in the Mg/SiO<sub>2</sub> system based on our high-resolution field-emission SEM investigations and based on these observations we offer clarification of the controversial pattern formation mechanisms.

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**Table 1**

The representations of phase  $\alpha$  and  $\beta$  for the diffusion-induced stresses model proposed by Chen et al. [20] to explain the formation mechanism of the typical periodic layered structures.

Reaction system	Zn/Co <sub>2</sub> Si [1,3,6]	Zn/Fe <sub>3</sub> Si [1,2]	Pt/SiC [5,6]	Zn/Ni <sub>3</sub> Si [11]
Phase $\alpha$	CoZn <sub>13</sub>	FeZn <sub>10</sub> or <sup>a</sup> FeZn <sub>13</sub>	Pt <sub>7</sub> Si <sub>3</sub>	NiZn <sub>3</sub>
Phase $\beta$	CoSi	FeSi	C	Ni <sub>2</sub> Zn <sub>3</sub> Si or <sup>b</sup> NiSi

<sup>a</sup> There is a phase-transformation from the FeZn<sub>13</sub> phase to the FeZn<sub>10</sub> phase near the reaction front.

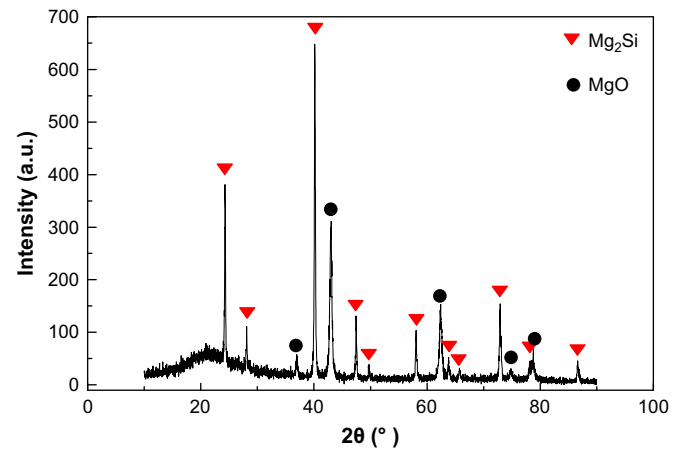
<sup>b</sup> It is not definite whether phase  $\beta$  is Ni<sub>2</sub>Zn<sub>3</sub>Si or NiSi, more measurements are needed for clarification.

## 2. Methods

Pure amorphous SiO<sub>2</sub> plates were cut into 0.8 × 7 × 7 mm pieces. The slices were encapsulated with Mg bulk (99.8% pure) in the evacuated quartz tubes (18 mm in dia) and annealed at 700 °C or 800 °C for varying times. The quartz tubes also reacted with Mg because the annealing temperatures were higher than the melting point of Mg. The microstructures of the reaction zone were characterized by scanning electron microscopy (SEM, KYKY 2800B, JSM-5600LV), high-resolution field-emission SEM (FE-SEM, Hitachi S-5500) and X-ray diffraction (XRD, MultiFlex).

## 3. Experimental results

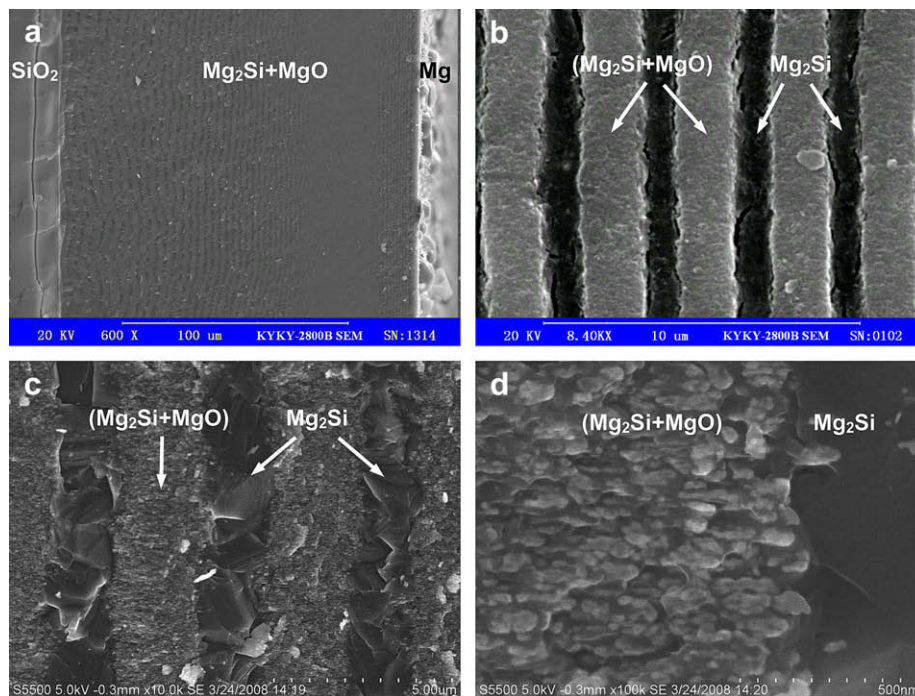
The periodic layered structure with the dark and bright layers alternating in the reaction zone was observed for the reaction system Mg/SiO<sub>2</sub> annealed at 700 °C in vacuum for various times (Fig. 1). X-ray diffraction analysis of the ground powders of the solid-state reaction products revealed that the reaction zone is composed mainly of Mg<sub>2</sub>Si and MgO phases (Fig. 2). Using high-resolution field-emission SEM (Hitachi S-5500), it was clarified that the dark layer is the Mg<sub>2</sub>Si phase and the bright layer is composed of two phases, MgO and Mg<sub>2</sub>Si (Fig. 1c and d).



**Fig. 2.** X-ray diffraction (XRD) of the ground powders of the solid-state reaction product of the diffusion couple Mg/SiO<sub>2</sub> annealed at 700 °C for 8 h.

During the reaction process, the MgO phase within the bright layers slowly transforms from the continuous aggregation near the reaction front to the form of discontinuous nano-particles far from the reaction front (Fig. 3, d → c → b → a). This transformation is likely due to the Rayleigh instability [23,24] or Ostwald ripening [25] caused by the residual diffusion-induced stresses within the periodic layers. It is reminiscent of the water column being transformed to a cluster of droplets by the surface stress and the pull of gravity.

At the reaction front close to the SiO<sub>2</sub> substrate, we found a narrow transition zone that has not been reported in the previous studies [7–9]. The transition zone is more prominent on the polished sample inlaid in the resin than on the sample left unpolished prior to SEM investigations (Fig. 4). According to the calculated phase diagram of Si–O–Mg (Fig. 5 [26]), the bright line within the transition zone is considered to be composed of Mg<sub>2</sub>SiO<sub>4</sub> and Si,



**Fig. 1.** Scanning electron microscopy (SEM) of the periodic layered structure formed in the reaction system Mg/SiO<sub>2</sub> annealed at 700 °C for 2 h. (a) unpolished, observed by KYKY 2800B; (b) polished, observed by KYKY 2800B; (c), (d) unpolished, observed by Field-emission SEM, Hitachi S-5500.

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