Preparation of Glass Ceramics by Reactive Crystallization with Waste Glass and Spinel

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ABSTRACT

Magnesium silicate glass ceramics were prepared by reactive crystallization with mixed powder of waste glass and spinel. The effects of spinel content and sintering temperature and holding time on the crystal phase and morphology of magnesium silicate glass ceramics were investigated. The reactive crystallizing behavior between waste glass powder and spinel was studied using energy dispersive spectrometer during the holding process. The result show that the optimum preparation conditions were as follows: the addition of 30 wt% spinel used as crystallization promoting agent, sintering temperature of 900 ºC and holding time of 2 h. The magnesium silicate and alumina crystals were formed via an interaction between glass powder and spinel instead of direct precipitation from the parent glass. With increasing of the holding time, the Al and Mg element contents of the glass were increased, on the contrary, that Si element content was decreased in the glass phase. It shows that the Si element is diffused from glass into spinel phase and subsequently magnesium silicate crystals are formed.

INTRODUCTION

Magnesium silicate (MgSiO$_3$) owing to their low thermal expansion mismatch with metals are promising materials for bioactive coating of implants [1-2]. Carbonation of abundantly available magnesium silicates such as serpentinites could be an attractive route to capture and store CO$_2$ [3].

Usually, in the conventional sinter-crystallization process, a particularly formulated parent glass must be used to ensure that the magnesium silicate precipitates from the glass during sintering [4]. The reactive crystallization mechanism was quite different between reactive crystallization method and the traditional method of preparing glass ceramics. It is known that fluoramphibole glass-ceramics may be fabricated through a direct reaction between fluornica and...
soda-lime glass powders, so that the processing can be simplified and the cost can be reduced greatly because recycled window glass can be utilized [5]. The reactive crystallization method is a new way of fabricating glass ceramics [6].

In this study, magnesium silicate glass ceramics was prepared by reactive crystallization with mixed powder of waste glass and spinel. The reactive crystallizing behavior was also characterized.

EXPERIMENTAL

Preparation of magnesium silicate glass ceramics. The waste glass powder mixed with 10%, 20%, 30%, 40% and 50% spinel powder by weight, respectively. Then a 6 wt% PVA water solution as a binder was added to the powders, and finally were uniaxially pressed into cylindrical compacts at 7.5 Mpa. The compacts were sintered at 800-1000 ºC for 2 h and holding time at 900 ºC for 0.5-4 h.

Preparation of sandwich sample. A thin spinel powder layer was embedded within the two layers glass powders and tabletted and tested under the same process as mentioned above.

Characterization. The crystallization reaction temperature of the glass and spinel powders was identified by differential thermal analysis (DTA, STA449F3) at a heating rate of 20 K/min. The crystalline phase was identified by XRD using an Empyrean X-ray diffractometer with Cu Kα radiation. SEM images were observed by JSM-6360LV scanning electron microscopy. The changes of element content of the glass in the sandwich sample were characterized by energy dispersive spectrometer (EDS) (Oxford-INCA).

RESULTS AND DISCUSSION

The DTA curve of mixed powder of waste glass and spinel is shown in Fig.1. The exothermic peak was observed at 532.0 ºC, 627.2 ºC and 890.8 ºC, which was attributed to the reaction crystallization between the glass and the spinel.

Fig.2 shows the XRD patterns of glass ceramics with different content of spinel. As clearly seen in Fig.2, four crystalline phases, i.e., magnesium silicate (MgSiO₃, JCPDS No.19-0768) as the major phase and alumina (Al₂O₃, JCPDS No.88-0107) as the minor phase and silica (SiO₂, JCPDS No.16-0380) as the minor phase, were
developed. Obviously, a reaction between spinel (MgAl$_2$O$_4$, JCPDS No. 21-1152) and glass occurred during the firing process to form the magnesium silicate and alumina. The reaction path may be as following:

$$\text{MgAl}_2\text{O}_4 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{Al}_2\text{O}_3$$

![XRD patterns of glass ceramics with different content of spinel.](image)

Fig.2 shows that the intensity of X-rays diffraction pattern of magnesium silicate is improved with increasing spinel amount when the content of spinel is less than 30%, but the peak intensities of the magnesium silicate maintained at the same level while the content of spinel was increased continuously. The morphologies of magnesium silicate glass ceramics are shown in Fig.3, they were pillarlike and embedded in the glass matrix.

![SEM images of glass ceramics with spinel content.](image)

Fig. 3. SEM images of glass ceramics with spinel content (a) 10% (b) 20% (c) 30% (d) 40% (e) 50%.

After sintering, the magnesium silicate and alumina were formed in the glass ceramics because of a reaction between spinel crystals and glass powder, as shown in Fig. 4. Heating up to the temperatures of 800~900 °C the content of magnesium silicate increased. However, the peaks corresponding to magnesium silicate changed little when heating temperature increased further.
The morphologies of the glass ceramics sintered at various temperatures are shown in Fig. 5. The microstructures consisted of pillarlike crystals and glassy phase when sintered at 900 ºC.

![XRD patterns of glass ceramics sintered at different temperatures.](image1)

**Figure 4.** XRD patterns of glass ceramics sintered at different temperatures.

![SEM images of glass ceramics sintered at different temperatures.](image2)

**Figure 5.** SEM images of glass ceramics sintered at (a) 800 ºC, (b) 850 ºC, (c) 900 ºC, (d) 950 ºC, (e) 1000 ºC.

Fig. 6 shows the evolution of crystallization in the glass ceramic during isothermal treatment at 900 ºC. All magnesium silicate, alumina, silica and spinel coexisted in the glass ceramics with different holding time. The morphologies of the glass ceramics with different holding time are shown in Fig. 7. When the holding time was 2 h, a large amount of pillarlike magnesium silicate crystal can be precipitated.
Figure 6. XRD patterns of glass ceramics with different holding time.

Figure 7. SEM images of glass ceramics with holding time (a) 0.5h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h.

The content change of Si, Al and Mg elements in glass phase during different holding time are shown in Fig.8. With the increasing of the holding time, the Al and Mg element contents of the glass were increased, on the contrary, that Si element content was decreased in the glass phase. It shows that the Si element is diffused from glass into spinel phase; subsequently, magnesium silicate crystals are formed.

Figure 8. Content change of element in glass phase during different holding time.
SUMMARY

The magnesium silicate glass ceramics can be prepared by reactive crystallization with mixed powder of waste glass and spinel. The optimum preparation conditions are as follows: the addition of 30 wt% spinel used as crystallization promoting agent, sintering temperature of 900 °C and holding time of 2 h. In the reactive crystallization process the Si element is diffused from glass to spinel phase; subsequently, magnesium silicate crystals are formed.

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