

Role of Mn and Co additives on the carbothermal nitridation of fly ash

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The effects of Mn and Co additives on the carbothermal nitridation of fly ash were examined at 1330, 1425 and 1475 °C in a N₂ atmosphere under normal pressure. Above 1425 °C, the nitridation of fly ash occurred and oxy-nitride phases, such as β-type sialon, α-type sialon and X₂N₂O (X=C or Si) type oxy-nitride phases were formed. The phase ratio among these phases was changed with the amount of additives. In the case of a Mn additive, the α to β phase transformation of sialon was accelerated with the amount of the additive. On the other hand, in the case of a Co additive, no effective role on the transformation was observed. At 1475 °C, the ash completely changed to β-type sialon.

Key words: fly-ash, sialon, nitridation, phase transformation.

Introduction

A large quantity of fly ash as a by-product from coal fired power plants is used efficiently in cement materials [1, 2]. The fly ash powder formed in the combustion field by the combustion of fine coal, has a spherical shape. Thus, it is convenient to use in concrete mixtures due to its fluidity. Recently, in Japan, for the efficient use of fly ash, the ash has been classified in some Japanese Industrial Standards (JIS) according to its chemical composition and particle size. By this classification, the composition of the ash is well controlled in terms of quality. High quality, low cost performance and fluidity have led new higher efficient use of fly ash in industry. For example, in the preparation of zeolite as a catalyst, in the use as a raw material for pottery and synthesis of sialon ceramics have been investigated for the more efficient use of fly ash [3-6].

The fly ash consists of mullite and quartz phases are dominantly, and a carbothermal nitridation process is needed for the preparation of silicon nitride and/or sialons from the ash [5-7]. Commonly, fly ash contains a small amount of iron oxide. It is known that iron oxide acts as catalyst in the carbothermal nitridation and in the α to β phase transformation [6, 7]. Hence, sialon powder can be obtained by the carbothermal nitridation of fly ash. However, the formation of sialon without additives requires long time sintering [3]. The fly ash also contains a large amount of a calcium component. Hence, the sialon that is generated from fly

ash by carbothermal nitridation contains calcium-stabilized α sialon [3]. The mechanical properties of sialon ceramics strongly depend on the volume fraction of the α phase/β phase. Hence, controlling the volume fraction, namely, controlling the α to β transformation of the sialon is needed for the application of the sialon that is produced from fly ash.

In this study, the carbothermal nitridation of fly ash with some additives were performed at normal pressure. Also the effect of the additives on the nitridation and α to β phase transformation of sialon phase were examined.

Experimental Procedures

Yonden-I fly ash that satisfied Japanese Industrial Standards (JIS-A-6201) was used in this experiment. The warranted composition of this fly ash was SiO₂ : Al₂O₃ : CaO : Fe₂O₃ = 73.30 : 14.39 : 10.47 : 1.83 in molar ratios. The specific surface area of this ash was higher than 0.5 m²/g.

High purity carbon powder (99.99% purity, High Purity Chemicals Co. Ltd.) was used as a reducing agent. Also high purity CoO (99.9% purity, High Purity Chemicals Co. Ltd.) and Mn₂O₃ (99.9% purity, High Purity Chemicals Co. Ltd.) were used as additives. CoO and Mn₂O₃ powders were added to the fly-ash powder at 0, 0.06, 0.12, 0.24, 0.6, 1.2, 2.4, 4.8 wt%. Carbon powder was added at 47.9 wt% for all samples. These powders were mixed in ethanol for 24 hours and then dried at 70 °C in an oven for 24 hours. The mixed powders were pressed into pellets.

The sinterings were performed at 1330, 1425 and 1475 °C in a N₂ atmosphere at normal pressure for 4 hours. The phase identification was performed by a powder X-ray diffraction method, where the step width

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increment and counting time were 0.03° and 3 seconds, respectively.

Results and Discussion

Figures 1(a) and (b) show an SEM image and a powder X-ray diffraction pattern from the raw fly ash. The ash exhibits a spherical shape with diameters below 10 μm. This ash consisted of quartz, mullite and a small amount of Fe₂O₃ phases as shown in Fig. 1(b). A large broad peak can be observed in (b), and thus a large amount of silica-based amorphous phase is also included in the ash. Hence, these four phases can be considered as the starting materials in this experiment.

Figure 2 shows an SEM image for the sample sintered at 1425 °C without additives. No densification occurred and the pellets were easily destroyed into powder after the sintering. It was confirmed that the grain size and its morphology was changed by the sintering. The grain size of the sintered sample was at least 5 times larger than that of before sintering.

Figures 3(a), (b) and (c) show the powder X-ray diffraction patterns of the samples without additives after sinterings at 1330, 1425 and 1475 °C, respectively. The amount of mullite and amorphous phases drastically decreased at 1330 °C as shown in Fig. 3(a), where, quartz was the dominant phase. The quartz phase completely disappeared at 1425 °C and only oxy-

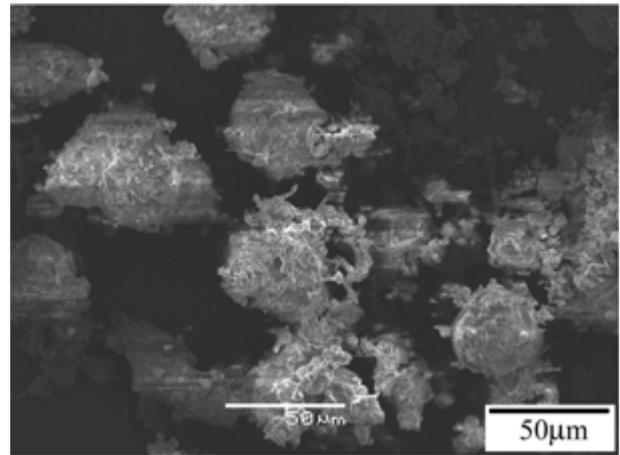


Fig. 2. SEM image of the sample sintered at 1425 °C without additives.

nitride phases, namely, β-type sialon, α-type sialon and X₂N₂O (X=C, Si) type oxy-nitride phases, can be recognized as shown in Fig. 3(b), where, the β phase and X₂N₂O phase were dominant. At 1475 °C, the X₂N₂O phase completely disappeared as shown in Fig. 3(c), where β-type sialon was the dominant phase. The

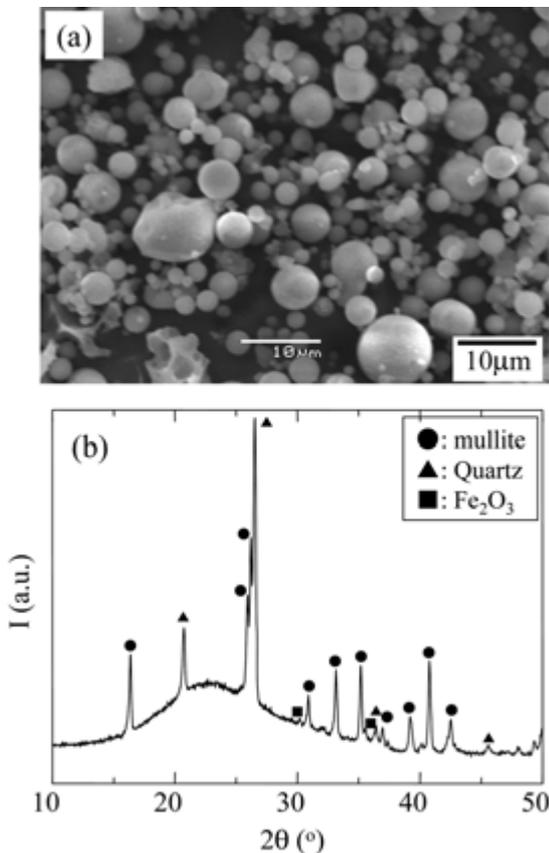


Fig. 1. SEM image (a) and X-ray diffraction pattern of fly-ash.

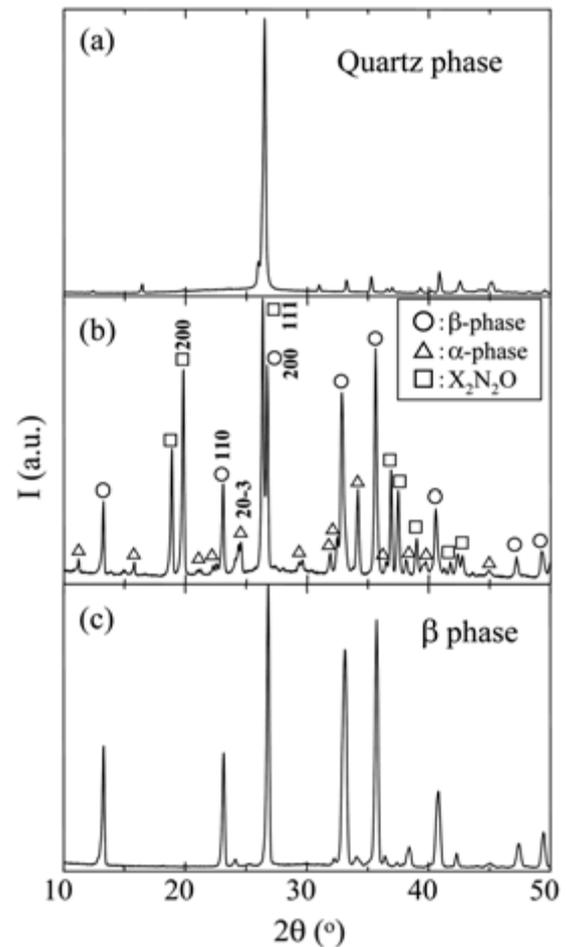


Fig. 3. X-ray diffraction patterns of the samples without additives after heat treatment at 1330 (a), 1425 (b) and 1475 °C (c).

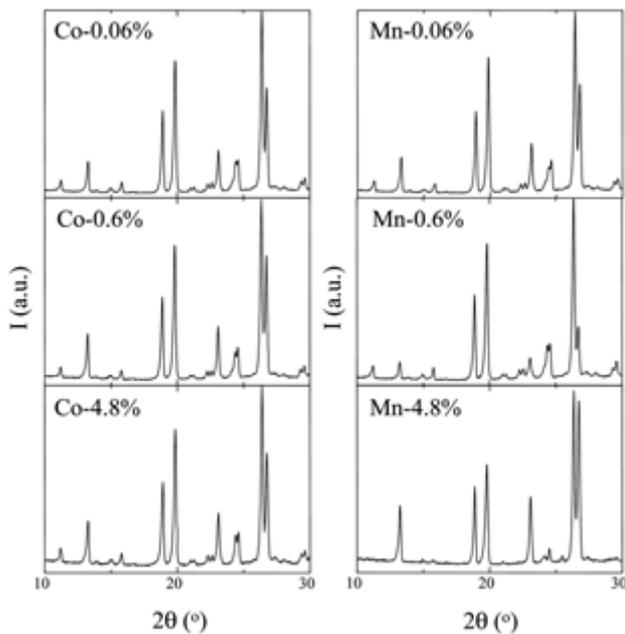


Fig. 4. X-ray diffraction patterns of the samples sintered at 1425 °C with CoO and Mn₂O₃ additives.

same tendency could be recognized in the samples with Mn₂O₃ and CoO additives.

Figures 4 show the X-ray diffraction patterns of the samples with CoO and Mn₂O₃ additives at 1425 °C, where, β -type sialon, α -type sialon and X₂N₂O (X=C, Si) type oxy-nitride phases could be recognized. The phase ratio among these phases changed with the amount of the additives, especially, drastic changes could be observed in the case of Mn₂O₃ additive. The relative intensities for the peaks of the α phase, indicated by arrows in the figure, decreased with increasing Mn additive content. On the other hand, in the case of the Co additive, no changes of the relative intensities among α and β phases could be observed.

To clarify these phase relations, the relative intensity ratios of β -type (110)/ β -type(200), β -type(110)/X₂N₂O (111) and α -type(20-3)/ β -type(110) were plotted against the amount of additives. Figures 5(a), (b) and (c) show the peak intensity ratio changes of β -type(110)/ β -type(200), β -type(110)/X₂N₂O(111) and α -type(20-3)/ β -type(110), respectively. The intensity ratio of β -type(110)/ β -type(200) shows a constant value regardless of the amount of additive and the type of the additive. Thus, it is considered that no anisotropical crystal growth of this phase occurred for all cases. On the other hand, the intensity ratio of β -type(110)/X₂N₂O(111) changes with the amount of additives (Fig. 5(b)), especially, drastic changes can be observed in the case of the Mn₂O₃ additive. The ratio decreased with the Mn content up to 0.06 wt% and then increased with Mn content. In the case of Co, no changes were observed. These facts mean that the relative amount of the β phase decreased by adding small amounts of Mn

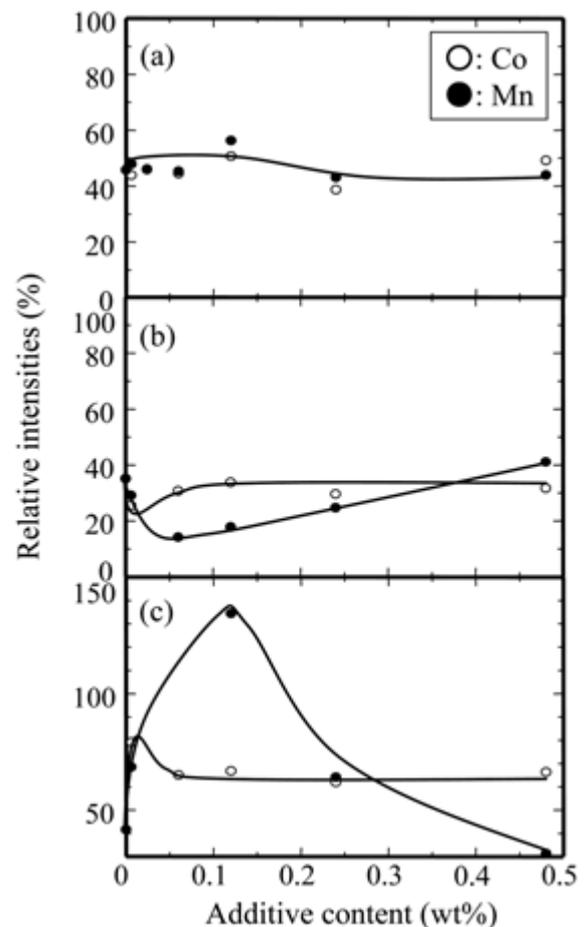


Fig. 5. Peak intensity ratio changes of (a): β -type(110)/ β -type(200), (b): β -type(110)/X₂N₂O(111) and (c): α -type(20-3)/ β -type(110).

additive. However, the formation of the β phase which accelerated by the Mn additive when the amount of the additive was higher than 0.06 wt%.

The intensity ratios of α -type(20-3)/ β -type(110) drastically change with additive content as shown in Fig. 5(c). In the case of Co, firstly, the ratio slightly increased with Co content up to 0.06 wt% and then, shows a constant value. The volume fraction of α phase decreased by the Co addition. This fact means that the stabilization of the α phase by the calcium component was achieved by a small Co addition.

On the other hand, in the case of Mn, the intensity ratio drastically increased up to 0.12 wt% and then, drastically decreased. The α phase disappeared in the sample at Mn = 0.48 wt%. These facts suggest that the α to β transformation of the sialon phase is blocked for the Mn content up to 0.12 wt% and then, was accelerated above Mn = 0.12 wt%. In other words, the stabilization of the α phase by calcium component was accelerated by the addition of a small amount of Mn. Later, the stabilization was blocked by further additions of Mn. The effect of Co additions on the phase relations between the α and β phases is smaller than

that of Mn additions. Hence, in the nitridation of fly ash, it is convenient to control the phase relations between the α and β phases by Mn additions.

Summary

By addition of a small amount of Mn and Co additives, the stabilization of the α phase was accelerated. The effect of Mn additions on the stabilization of the α phase was larger than that of Co additions. Furthermore, in the case of Mn additions, the stabilization of the α phase was blocked above 0.12 wt% Mn additions. The phase relations between α and β phases are well controlled by Mn additions.

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