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Microstructure characterization on the formation of in situ Mg_2Si and MgO reinforcements in AZ91D/Flyash composites

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ABSTRACT

5 wt.% and 100 μm in size of fly ash cenosphere particles were incorporated in AZ91D Mg alloy to fabricate in situ Mg_2Si and MgO reinforced AZ91D/Flyash composites by means of compocasting method. The in situ Mg_2Si and MgO were identified using X-ray diffraction (XRD), energy dispersive spectrometer (EDS), and thermodynamic analysis. The results show that the cenosphere particles distributed homogeneously in the matrix alloy. Moreover, most of the cenosphere particles were filled with the matrix alloy. The preliminary discussion was carried out on the growth mechanism of the in situ Mg_2Si.

1. Introduction

Mg and its alloy are considerable promising materials owing to the combination properties of high specific strength and specific stiffness, low density, and excellent castability, so they are widely used in the automotive and aerospace industries and electron products [1–3]. However, the utilization of Mg alloys was limited because of their poor heat resistance compared with other materials currently widely used [4,5]. Therefore, it is necessary to develop new high performance Mg matrix composites.

In recent years, Mg matrix composites reinforced by in situ compound Mg_2Si particles have been attracting attention as heat resistant light metal materials [6,7]. This is because Mg_2Si is of low density (1.99 g/cm^3), high melting point (1085 °C), high hardness, low thermal expansion coefficient (0.75×10^{-5} °C^{-1}), and high Young's modulus (120 GPa) [8]. More recently, it was reported that Mg_2Si and MgO phases could be in situ formed by the reaction between SiO_2 originated from rice husks and Mg alloys [9,10]; the study results indicated that the magnesium composites reinforced with Mg_2Si/MgO particles showed a good wear resistance and anti-offensive performance in sliding wear test under oil lubricant. The morphologies of primary Mg_2Si were improved through lots of methods such as incorporating modifying agents Sr, P, etc. [11,12], hot extrusion [13], rapid solidification [14], and mechanical alloying [15]. The fly ash cenosphere (FAC) composed of silica, alumina and other materials is the by-product during the combustion of coal in thermal power plants, and its density is about 0.6 g/cm^3. Some researchers added FAC particles to metallic or polymeric matrices to make foam composites [16,17]. FAC particles are extremely attractive materials because of their relatively low price and excellent physical and mechanical properties. On the other hand, the application of FAC particles is a kind of consumption of industrial garbage and can reduce the environmental pollution. As can be speculated on the basis of thermodynamic analysis, the in situ compound Mg_2Si and MgO particles can also be obtained by adding FAC particles to Mg alloys. Unfortunately, few reports can be found on preparing Mg alloy/Flyash composites by incorporating FAC particles up to now [17–19].

Compared with die casting technique [18], in situ composites fabricated using compocasting technique are very interesting for researchers owing to clean interface between reinforcement and matrix, excellent properties, simple fabricating procedure, and low cost. Accordingly, the present paper reports the fabrication of in situ AZ91D/Flyash composites by incorporating FAC particles in Mg alloy using compocasting technique. The microstructure and in situ compound phases in the composites were characterized. The formation mechanism of the reaction product Mg_2Si was discussed.

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Table 1
The chemical composition of the commercial AZ91D Mg alloy (wt.%).

Al	Zn	Mn	Si	Be	Fe	Cu	Ni	Mg
9.07	0.62	0.21	0.034	0.0013	0.0022	0.003	0.00033	Balance

Table 2
The contents of various phases in FAC particles (wt.%).

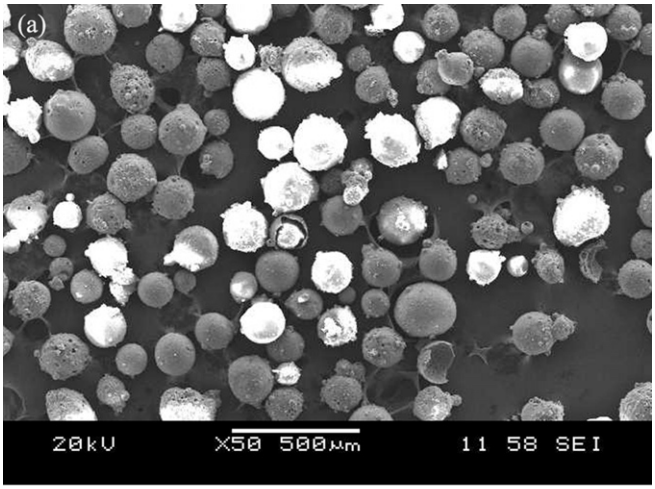
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Others
62.79	24.24	3.86	1.78	1.28	Balance

2. Experimental

2.1. Preparation of AZ91D/Flyash composites

AZ91D Mg alloy and FAC particles were used as raw materials to prepare AZ91D/Flyash composites. The chemical composition of AZ91D Mg alloy and the contents of various phases in FAC particles were listed in Tables 1 and 2, respectively. Fig. 1 shows the morphology and component of FAC particles. The average diameter of FAC particles was about 100 μm.

About 500 g of AZ91D Mg alloy was molten and heated to 720 °C at a graphite crucible in an electric resistance furnace, and then cooled to 590 °C at which the Mg alloy was in the semi-solid state. After that, about 25 g of FAC particles preheated to 200 °C were added to the semi-solid Mg alloy, and the slurry was stirred at a rotation speed of 700 rpm for 15 min to ensure the homogeneous distribution of FAC particles in the matrix alloy. Then, the slurry was rapidly reheated to 720 °C, held for 15 min, and poured into a steel mould preheated to 200 °C, forming cylindrical castings with 20 mm in diameter and 90 mm in height. The mixed SF_6 and N_2 protective gas was used to prevent the oxidation and combustion of the Mg alloy during all processes. Besides, the solution treatment of the samples was carried out at 420 °C for 16 h in order to observe clearly the phases in the composites.



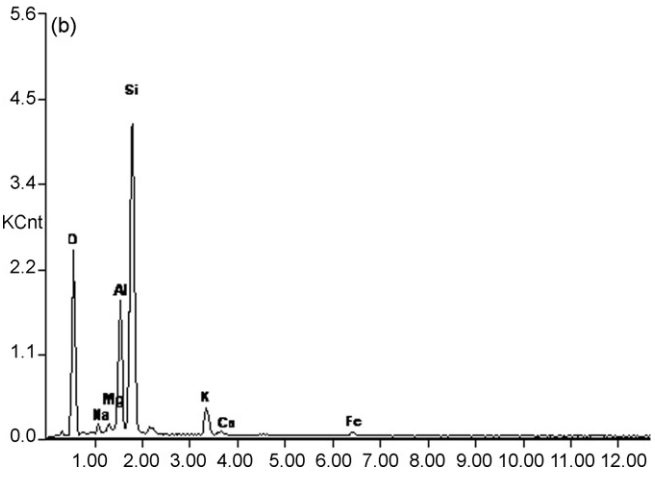


Fig. 1. Morphology (a) and composition (b) of fly ash cenospheres.

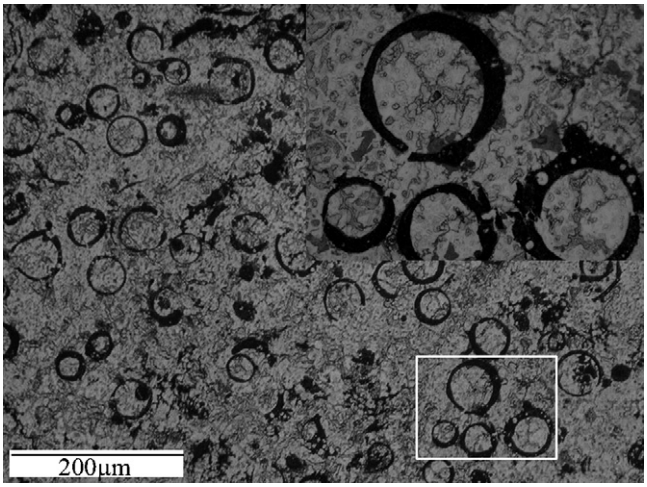


Fig. 2. Microstructures of AZ91D/Flyash composites.

2.2. Microstructure analysis

The microstructures of the composites were observed using Olympus GX51 optical microscopy (OM) and scanning electron microscopes (SEM, JSM-6360LV) with energy dispersive spectrometer (EDS). The sizes and volume fraction of in situ products were statistically measured by quantitative metallographic analysis method. X-ray diffraction (XRD, D/MAX2500PC, Cu Kα, Japan) analysis was carried out to identify the phases in the composite samples.

3. Results and discussion

3.1. The microstructures of AZ91D/Flyash composites

Fig. 2 shows the microstructures of AZ91D/Flyash composites. It can be found that FAC particles distributed homogeneously in the Mg alloy matrix and were almost completely filled with Mg alloy. Some FAC particles fractured at the thinnest regions or concentrating porosities on their walls because of the difference of the thermal expansion coefficients between FAC particles and matrix alloy and the stress during the collection of FAC particles (Fig. 1(a)) and the preparation of the composites. Rohatgi et al. reported that the FAC particle wall was embrittled by the reaction between Mg matrix and FAC particle [18].

The XRD pattern indicated that the composites contained $Mg_{17}Al_{12}$, Mg_2Si, MgO and α-Mg phases (Fig. 3). It was worth noting that the earlier report about AZ91D–fly ash cenosphere thought there was no significant reaction at the interface between the fly

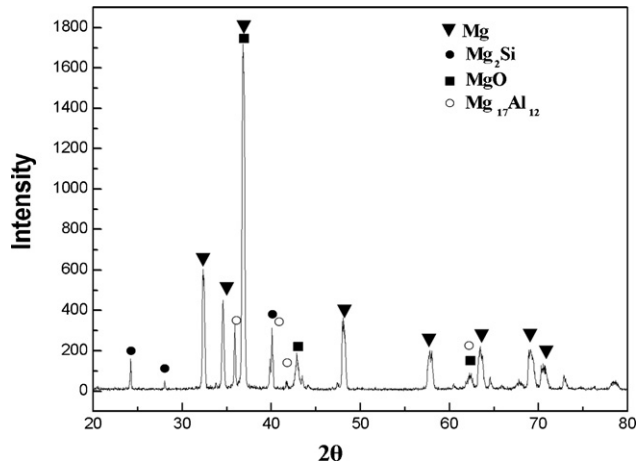


Fig. 3. XRD pattern of AZ91D/Flyash composites.

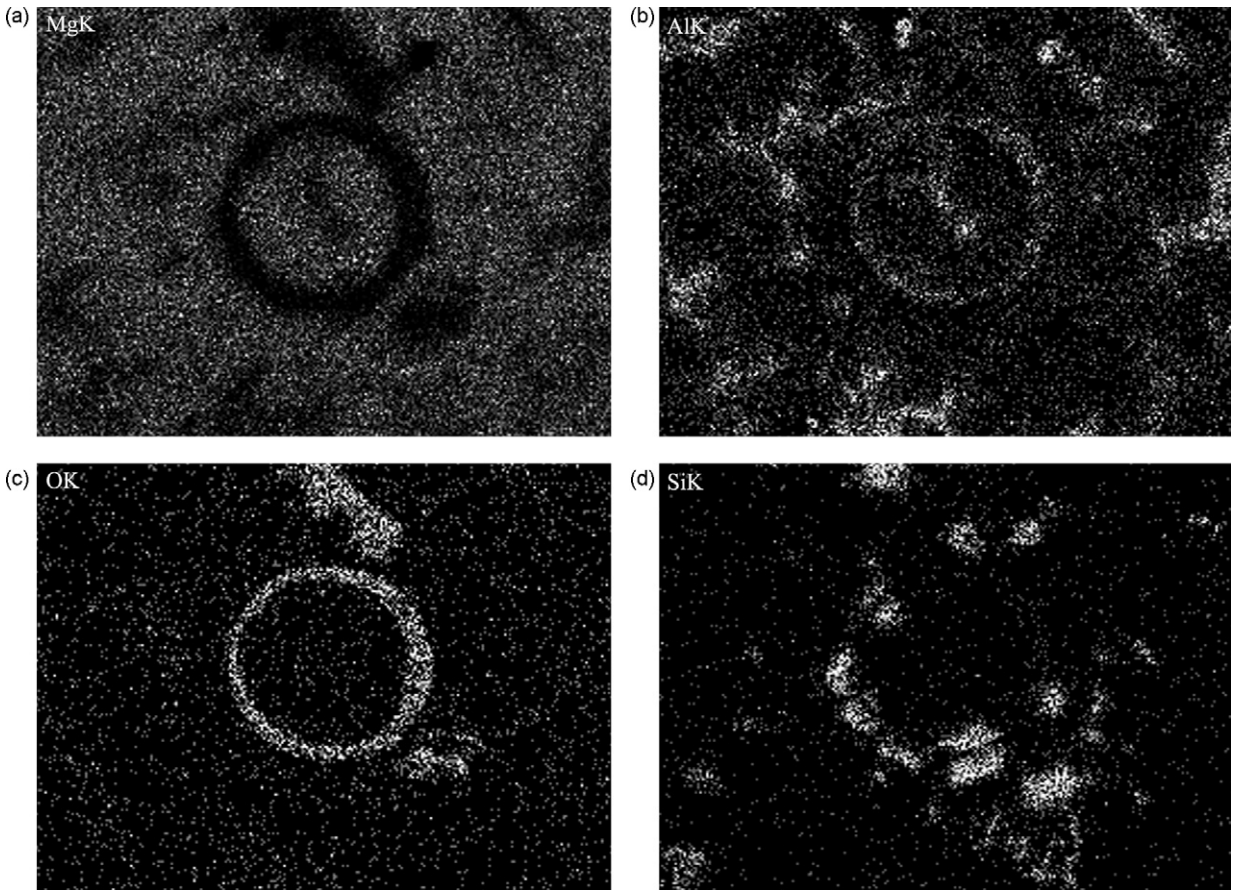


Fig. 4. X-ray mappings of Mg (a), Al (b), O (c) and Si (d) elements in AZ91D/Flyash composites.

ash particle and AZ91D matrix alloy [18]. In order to clearly identify the different phases in the composites, the EDS analysis was carried out, and the distribution of Mg, Al, O and Si elements was obtained from the X-ray mappings (Fig. 4). $Mg_{17}Al_{12}$, Mg_2Si and MgO phases were identified through analyzing the compositions of A, B and C points (Fig. 5). It is worth mentioning that the MgO formed from FAC particles and mainly existed on the walls of FAC particles can cause a volume contraction [19]. However, it is not definite whether this volume contraction would result in the fracture of FAC particles at present investigations or not. It was inevitable for the MgO formed from the oxidation of matrix alloy during processing, however, this MgO was too less to be detected.

The morphologies of Mg_2Si and the interfaces of the composites were shown in Fig. 6 after the solution treatment of the samples was carried out. It was observed that $Mg_{17}Al_{12}$ was almost completely dissolved after being held at 420 °C for 16 h, and a great deal of blocky Mg_2Si phase (dark gray) with about 15 μm in size exists in the matrix, and its volume fraction was about 4%. The compound Mg_2Si grew into matrix from the outer and inside walls of FAC particles, and few formed in matrix owing to the low diffusion capability of Si atom in Mg alloy.

The following reactions should occur based on thermodynamic calculation [17]:

$$4Mg_{(l)} + SiO_{2(s)} = Mg_2Si_{(s)} + 2MgO_{(s)} \quad \Delta G_1^\circ = -412,440 + 96.69T \tag{1}$$

$$5Mg_{(l)} + 2Al_{(l)} + 2SiO_{2(s)} = 2Mg_2Si_{(s)} + MgAl_2O_{4(s)} \quad \Delta G_2^\circ = -714,670 + 164.97T \tag{2}$$

$$3Mg_{(l)} + Al_2O_{3(s)} = 3MgO_{(s)} + 2Al_{(l)} \quad \Delta G_3^\circ = -145,810 + 26.32T \tag{3}$$

$$3Mg_{(l)} + MgAl_2O_{4(s)} = 4MgO_{(s)} + 2Al_{(l)} \quad \Delta G_4^\circ = -110,210 + 28.41T \tag{4}$$

Mg_2Si, $MgAl_2O_4$ and MgO formed after FAC particles were added to Mg alloys according to above thermodynamic calculation. The formation of $MgAl_2O_4$ and MgO was in connection with Mg content [20]. $MgAl_2O_4$ could be obtained in Al alloys containing trace Mg. If Mg content was sufficient, according to Eq. (4), the free energy difference $\Delta G_4{}^\circ \ll 0$ even at 590 °C, and the reaction in Eq. (4) can happen spontaneously. Furthermore, the Mg–O bonds are significantly stronger than the Al–Mg bonds, and MgO phases should form in preference to the compound $MgAl_2O_4$ [17], therefore, the interface products should be MgO, which was in line with XRD and EDS analysis (Figs. 3 and 5). The volume fraction of MgO was about 1.9%.

It is well known that there are two modes of the crystal growth, faceted and nonfaceted, and the faceted morphology is normally a growing feature of nonmetals, intermetallic compounds, etc. [21]. The growth mode of Mg_2Si is a typically faceted one under conventional solidification condition according to Fig. 7, which showed the morphology of primary Mg_2Si with smooth surface. Slight angular features and growth edges can also be found from Fig. 7 [22]. According to the theory developed by Jackson, if Jackson's factor α exceeds 2, the faceted growth is favored. Kubaschewski et al. calculated α of (1 1 1) and (1 0 0) of Mg_2Si, and the result showed that α is 3.75 and 2.5, respectively [23], which indicated the growth mode of Mg_2Si is normally faceted one. Si can hardly dissolve in Mg matrix

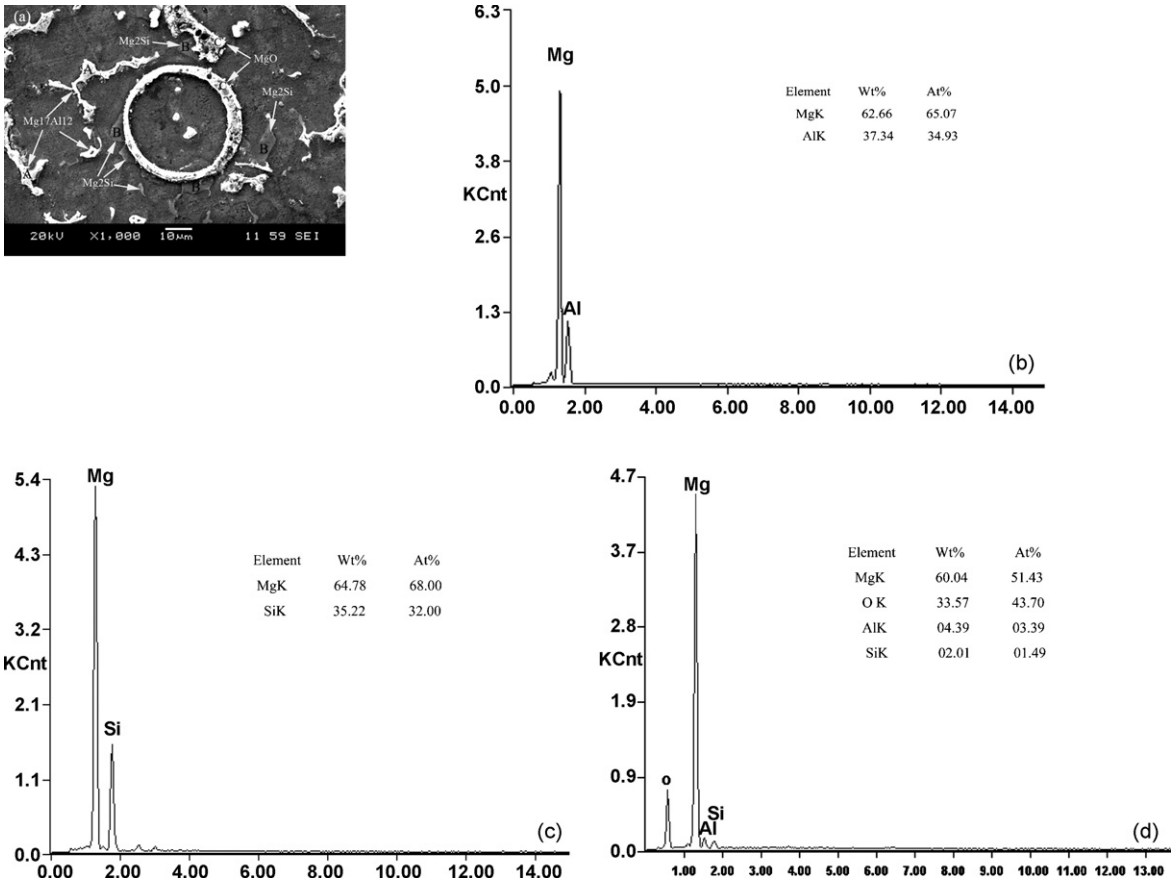


Fig. 5. Microstructures of AZ91D/Flyash composites (a) and the compositions of A, B and C phases ((b)–(d)).

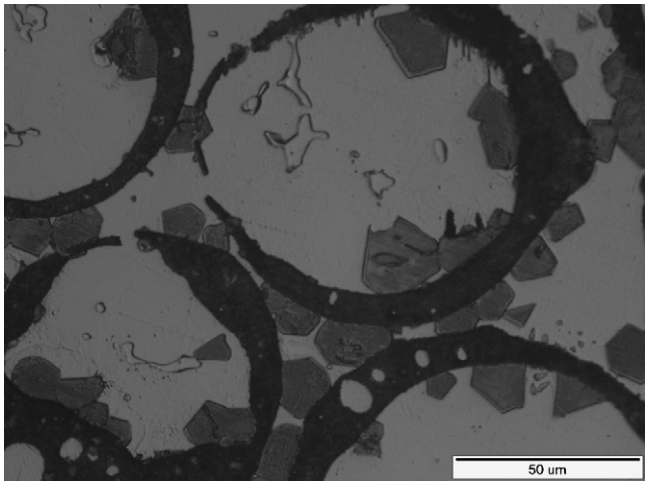


Fig. 6. Morphologies of Mg_2Si and the interfaces in AZ91D/Flyash composites after solution treatment at 420 °C for 16 h.

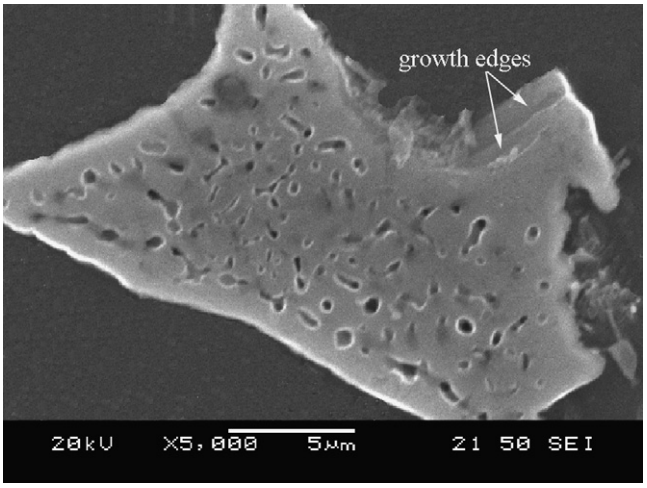


Fig. 7. Morphology of primary Mg_2Si in AZ91D/Flyash composites with growth edges character.

according to Mg–Si binary phase diagram, and precipitate only to form Mg_2Si [24]. With the cooling of the slurry, the primary Mg_2Si formed firstly (about 1.5 wt.% Si in this work), and then the ternary eutectic reaction occurred: $L \rightarrow Mg_2Si + \alpha\text{-}Mg + Mg_{17}Al_{12}$. According to the non-continuous growth mechanism of crystal, Mg_2Si grew into blocky one because the faceted morphology advances largely depend on lateral motion of steps [21]. Certainly, the growth mode of Mg_2Si maybe transforms with the different cooling rates of the composites.

4. Conclusion

It was feasible to form in situ Mg_2Si and MgO reinforcement in AZ91D/Flyash composites by using compocasting technique. The distribution of the fly ash cenosphere particles in AZ91D Mg alloy matrix was uniform. The in situ Mg_2Si and MgO compounds mainly existed on the walls of cenosphere particles, besides, few Mg_2Si formed in the matrix. The primary Mg_2Si showed polygonal morphologies with a mean size of 15 μm and growth edges features.

The growth mode of Mg_2Si was faceted one in conventional solidification condition.

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