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Synthesis of SiAlON Ceramics with Novel Magnetic Properties

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ABSTRACT

This paper presents a study on the magnetic behaviour of selected doped SiAlONs with various compositions including Y, Yb, Sm, Gd, and Er. The resulting crystalline phases were confirmed by X-ray diffraction. The magnetic hysteresis data for the samples were collected at room temperature using a vibrating sample magnetometer. The study revealed that doped SiAlONs experience an appreciable level of magnetic hysteresis. Although the parameters corresponding to hysteresis loops in doped SiAlONs are less than those of common ferrites, their magnetic properties of SiAlONs may open up new potential areas of application as the host SiAlON ceramics have excellent structural properties.

Key words : SiAlON ceramics, Magnetic properties, Magnetic hysteresis

1. Introduction

SiAlON ceramics are considered promising materials for many special engineering applications requiring mechanical and chemical stability at elevated temperatures and high resistance to wear. The solid solution of β-Si_3N_4, in which Si and N are substituted by Al and O, respectively, is known as β-SiAlON (β′)[1-2] and is expressed by the general formula $Si_{6-z}Al_zO_zN_{8-z}$, where z is the Al substitution level and $0<z<4.2$. α-Si_3N_4 forms a more limited solid solution, α-SiAlON (α′), which results from a similar substitution to β-SiAlON but its stability requires the addition of metal cations (M = Ca, Y and selected rare-earth elements) which partially occupy two large interstitial sites in the α-Si_3N_4 unit cell.[3] The metal cation should be just large enough to occupy the interstitial volume and the suitable ionic radius is about 1 Å. The solid solution α-SiAlON is expressed by the general formula,

$$M^{v+}_{m/v}\ Si_{12-(m+n)}\ Al_{m+n}\ O_n\ N_{16-n}$$

where v is the valency of the metal cation M.

Densification of both α- and β-SiAlONs occurs via liquid phase sintering, which requires a metal oxide additive as the basis for the formation of an oxynitride liquid. SiAlON ceramics have been widely explored for structural properties[4-9] but less research work has been done on their functional properties.[10-12] In particular, the magnetic properties of doped SiAlONs have not been explored at all thus far. As SiAlON ceramics have excellent structural properties, SiAlONs with magnetic properties may open up new potential areas of application. As such, the broad aim of this work was to synthesise a series of SiAlON ceramics with different dopants (Y, Yb, Sm, Gd and Er) and to investigate their resulting magnetic behaviour.

2. Experimental

The starting powders used were α-Si_3N_4 (UBE grade SN E10), AlN (Starck HC, Grade B), Al_2O_3 (Sumitomo, AKP-30), and rare-earth oxides of Y, Yb, Sm, Gd and Er (99.9% purity, Sigma-Aldrich).

The appropriate amounts of initial powders for different compositions were mixed and milled in a rotating polyethylene bottle in ethyl alcohol with silicon nitride balls as the milling media. These compositions correspond to 10 wt% to 19 wt % of the dopant depending on the atomic weight of the rare-earth oxide. High m values and compatible n values were selected to insert a high amount of rare-earth cations in SiAlON ceramics. The precursor charge was 30 grams and the milling time was about 60 h. The milled wet powder was sieved through a 38 μm grid and then dried.

The dried powder was isostatically pressed (200 MPa) to form disc-shaped pellets (diameter=16 mm, thickness=3.5 mm) and cylindrical pellets (diameter=6 mm, height=5 mm). The disc pellets were prepared for analytical studies and cylindrical pellets were prepared for investigation of magnetic properties. The pellets containing rare-earth cations were gas pressure sintered for 3 h at 1800°C in a graphite crucible in a carbon resistance furnace under a static nitrogen gas pressure of 0.9 MPa.

X-ray diffractometry (XRD) was conducted on polished

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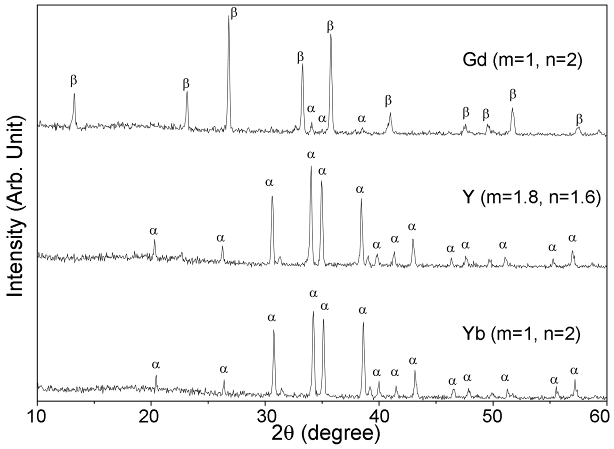

Fig. 1. XRD pattern of SiAlON.

sintered disc samples using Cu-K_α radiation (Rigaku D/Max 2200, Japan). Sample densities were determined using Archimedes' principle.

The magnetic hysteresis data of the doped SiAlON samples were collected at room temperature using a vibrating sample magnetometer (7400 series, LakeShore). With this technique, magnetic properties can be measured as a function of the magnetic field, temperature and the frequency of vibration of the sample. The sample is placed within suitably placed sensing coils and made to vibrate mechanically. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetic moment of the sample.

3. Results and Discussion

The sintered SiAlON samples were found to be of high density. Their density value varied around 3200 kgm^{-3} depending on the dopant. The XRD pattern of rare-earth doped SiAlONs is shown in Fig. 1, where the crystalline phase was identified as α′ -SiAlON and β′ -SiAlON.

The experiments with the vibrating sample magnetometer (VSM) the SiAlON samples doped with different rare-earth cations (Y, Yb, Sm, Gd and Er) showed small hysteresis loops. As mentioned earlier, sintered cylindrical SiAlON samples were used for the investigation of magnetic behaviour. No noticeable variation of the hysteresis behaviour was observed when powder samples of doped SiAlON were used for investigations. Fig. 2 shows representative hysteresis loops of rare-earth-doped SiAlONs. This general trend of hysteresis looping was observed for all ceramics containing different rare-earth cations of different compositions. Such hysteresis behaviour is due to the response of orbiting electrons when exposed to an applied magnetic field. The rare-earth atoms or ions in the material may have a net magnetic moment due to unpaired electrons in partially filled atomic orbitals.

It can be seen (Fig. 2) that there is a change in the slope of the curves of the magnetic moment against the magnetic field for different SiAONs containing rare-earth atoms. This indicates the possibility of having different magnetic susceptibilities of different rare-earth-containing SiAlONs. The orders of magnitude of the mass susceptibility values calculated from the slopes of the curves are comparable with the values corresponding to those of the rare-earth elements.[13] However, it is important to realise that the rare-earth atoms bond with the neighbouring atoms in the SiAlON structure. Structural refinement of Y α-SiAlON indicates that Y^{3+} atoms are surrounded by seven (N,O) atoms with different Y-(N,O) distances.[14,15]

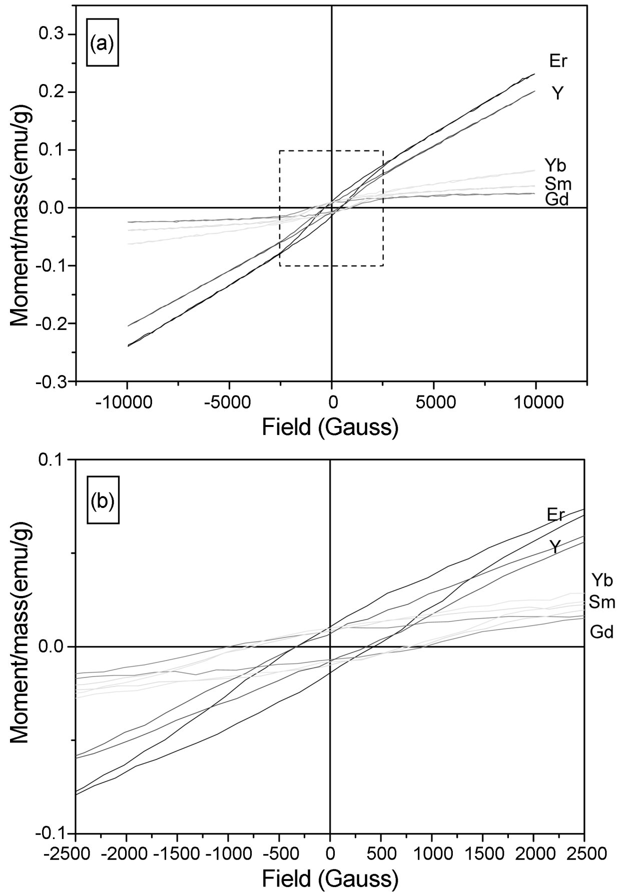

Fig. 2. (a) Magnetic hysteresis loops of rare-earth doped SiAlONs. Varying slopes of the curves indicate different values of magnetic susceptibilities of different SiAlONs. Inset: the central part of hysteresis loops. (b) Enlargement of box area of (a).

The central part of the hysteresis loops is shown in the inset in Fig. 2 (b). As can be seen from this figure, the saturation magnetisation varies from 0.164 to 0.235 emu/g, the coercive field varies from 400 to 900 Gauss and the remanence magnetization varies in the range 0.01~0.02 emu/g. It is also worth noting that the β′ -SiAlONs containing rare-earth atoms also showed a similar magnetic hysteresis behaviour.

The hysteresis behaviour of doped SiAlON samples was also compared with hysteresis loops of powder compacts made from pure oxides of rare-earth samples. This shows that the SiAlON samples and the corresponding pure oxide powder samples exhibit a similar response to an external magnetic field, characterising soft magnetic materials with a small area hysteresis loop. However, the different slopes of the curves of a particular rare-earth-doped SiAlON and the corresponding oxide indicate different values of magnetic susceptibilities.

4. Conclusion

Novel magnetic properties were observed in some rare-earth-doped SiAlON ceramics. The observed parameters corresponding to hysteresis of doped SiAlONs were small. A similar general trend was observed for all the SiAlON samples containing different rare-earth cations. Rare-earth-containing β-SiAlONs also showed a similar magnetic hysteresis behaviour.

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