Synthesis and characterization of calcium fluoride added zirconia toughened alumina composite powder

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Abstract. The present paper aims to synthesise a composite powder consisting of zirconia toughened alumina (ZTA) and calcium fluoride (CaF2) together followed by their morphological study and characterization. Yttria-stabilized zirconia toughened alumina added with CaF2 was fabricated in the laboratory with the aid of co-precipitation method. The morphological and elemental studies are carried out by means of field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray analysis (EDS). Presence of different phases are investigated using the X-ray diffraction (XRD) analysis. The temperature at which the powder decomposes are obtained by differential thermal analysis/thermo gravimetric analysis (DTA/TGA).

1. Introduction

Application of ceramics in industrial, aerospace manufacturing areas such as cutting tool inserts, dies, slip rings, fittings etc. increases to a significant level because of their promising mechanical properties such as flexural strength, hardness and fracture toughness at harsh operating conditions. Among all the classes of ceramics, zirconia toughened alumina (ZTA) have drawn special attraction to the researchers since it can be utilized in many industrial applications along with its chemical stability. Synthesis of ZTA powder with addition of other phases has become an important stage of research. The synthesis of yttria stabilized ZTA shows the optimum values of hardness and fracture toughness when the composite has 90 wt% Al2O3 and 10 wt% YSZ [1]. Nevertheless, it has some limitation in application where high friction and wear come in to picture. To decrease the frictional and wear components, the addition of solid lubricant is a good choice in current practice. Some solid lubricants such as CaF2, CuO, MoS2 can work under a variety of operating conditions while they are being incorporated into the Al2O3/ZrO2 based ceramics [2-4]. Among all the lubricants, CaF2 is a potential solid lubricant having low shear strength, enables tribo-chemical reactions and prevents adhesion to the sliding interfaces. The ceramic composite Al2O3/ZrO2 added with CaF2 shows least coefficient of friction (COF) as compared to the composite with other solid lubricant such as MoS2, BaF2, h-BN, graphite etc. determined in scratch test [5]. A good number of works has already been done on the addition of CaF2 as second phase into the alumina or zirconia based ceramics in order to achieve comprehensive tribo-mechanical properties [6-8]. Now at this stage of research, it has become quite necessary to the material researchers to prepare the CaF2 added composite ceramics in laboratory to control the particle size (nano to micron level) along with desirable purity level and other physical properties. This can be easily achieved by synthesising the entire lubricant added ceramic composite powder in the laboratory itself. Synthesis of CaF2 is already in knowledge and the work led by Tahvildari et al shows how that CaF2 can be synthesized by co-precipitation method [9]. Bensalah et al. successfully developed some Yb and Er doped CaF2 powders by reverse micelle method which were in nano (20nm) level [10]. Sun et al. expressively synthesised nano level CaF2
(41nm) having low crystalline with the aid of spray drying technique [11].

2. Experimental

2.1 Powder synthesis and characterization

The chemical route which is followed in the synthesis of Zirconia toughened alumina (ZTA) and calcium fluoride (CaF₂) is co-precipitation method. For synthesis of ZTA the precursors used are zirconium oxychlorideoctahydrate (ZrOCl₂.8H₂O), Aluminium nitrate nonahydrate (Al(NO₃)₃), Yttrium nitrate hexahydrate (Y(NO₃)₃) is added in the solution of zirconia and alumina to stabilize the metastable phase of zirconia. The weight percentage in which aluminium nitrate and YSZ are added is 90% and 10% as described earlier by Singh et al. [1]. After the co-precipitation process, the precipitate is cleaned by hot water to remove excess ammonia then again allowed to settle down. On the other hand, the precursors used for synthesis of CaF₂ are ammonium fluoride (NH₄F) and calcium nitrate (Ca(NO₃)₂). 160 ml of de-ionized water is taken in a beaker and both the precursors are mixed into it to obtain 0.032 mole CaF₂, i.e., 2.5 g of CaF₂ in 25 g of total composite powder. The solution is stirred for 3 hrs and a white opaque solution is formed. The solution is kept stagnant for 3 hrs to settle down the particulate matter. This precipitate is therefore mixed with the earlier prepared precipitate of ZTA. The mixture of ZTA and CaF₂ precipitate is stirred for 4 hrs and then sonicated for 15 minutes using an ultra-sonicator instrument (GTSONIC, Antech, China) in order to achieve proper dispersion. After that the precipitation of CaF₂/ZTA mixture is filtered with the aid of filter paper and a thick gel is obtained. The thick soft gel is dried in the oven for 10 h at 100°C. The dried mixture is crushed by the mortar pestle to form fine powder particles. The powder is therefore calcined at 800°C for recrystallization under the influence of argon gas in a closed tube furnace (OKAYFURNACE, Bysakh and Co., India). Finally, the powder is further processed for characterization such as XRD, FESEM/EDS and DTA/TGA. The details of all the precursors used are given in Table 1.

| Precursors name                  | Purity level | Manufacturer       |
|---------------------------------|--------------|--------------------|
| Aluminium nitrate nonahydrate,  | ≥ 98%        | Sigma Aldrich      |
| Al(NO₃)₃                         |              |                    |
| Zirconium oxychlorideoctahydrate| 99%          | Loba Chemicals     |
| ZrOCl₂.8H₂O                     |              |                    |
| Yttrium nitrate hexahydrate,    | 99.9%        | Alfa Aesar         |
| Y(NO₃)₃                         |              |                    |
| Ammonium fluoride,               | 96%          | Alfa Aesar         |
| NH₄F                            |              |                    |
| Calcium nitrate,                | 99%          | Alfa Aesar         |
| Ca(NO₃)₂                         |              |                    |

3. Results and discussion

3.1 XRD analysis of synthesized powder

XRD analysis is carried out of both pure CaF₂ and CaF₂/ZTA powder in the range of 2θ = 20° to 80° and the corresponding patterns are given in Fig. 1. The evidences the retention of CaF₂ particles in the synthesized ZTA composite powder. Maximum intensity for CaF₂ is obtained at 2θ = 47.33° which is also present in the composite powder as found from the XRD pattern. In addition to this, there is a CaO phase in the composite powder which may be formed during the calcination of the composite powder at 800°C.
3.2. Morphological characterization and elemental analysis

Powder morphology and the presence of different elements in the composite powder is provided in the Fig. 2 and Fig 3, respectively. The particles are clearly visible in the FESEM micrograph and formed spherical shape. The particles are almost uniform in size. The homogenised distribution of CaF$_2$ particles in the ZTA powder is observed from the EDS analysis. The EDS analysis confirms the presence of the elements Al, Zr, Ca and F in the composite powder.

3.3. Thermal analysis of composite powder

Thermal analysis data are obtained in the temperature range from room temperature to 1500ºC by the DTA/TGA analysis as shown in Fig. 3. The TGA of sample indicate that initially there is a decay till 200ºC, which can be attributed to the removal of moisture of the sample. Afterwards, the sample shows a steady region indicating the stability of the sample till 1300ºC. A decay after 1300ºC can be observed due to the possible fluoride loss at high temperature. The corresponding DSC analysis of sample represents the thermodynamic characterization of the sample. The peak at 965 ºC may be attributed to the $\alpha/\beta$-CaF$_2$ polymorphic phase transition. The sharp peak at 1171 ºC indicates the formation of solid solution and may be considered as the eutectic point of CaF$_2$ and CaO at high temperature [13].
4. Conclusion
The attempt of fabricating CaF$_2$/ZTA composite powder via co-precipitation method is successfully held in the laboratory. The as prepared powder sample has been characterized by XRD, FESEM/EDS and DTA/TGA. The synthesised particles CaF$_2$ and ZTA are uniformly distributed and found almost uniform particle size throughout. As the extension of the current work will include the development of CaF$_2$/ZTA self-lubricating ceramic component for high temperature tribological applications.
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