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Tribological behavior of carbon nanotube/aluminosilicate composites prepared through TEOS/boehmite catalyst sol–gel and CVD process

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ABSTRACT

The carbon nanotube (CNT)/aluminosilicate composites were fabricated by the TEOS/boehmite catalyst sol–gel and chemical vapor deposition (CVD) method in this study. Two different CVD growing processes were carefully controlled. One is the continuous process, the other is the CVD growing/calcining process. Different process temperatures for different CVD growing/calcining processes were also adopted to fabricate different CNT/aluminosilicate powders. Furthermore, the mechanical properties, the tribological properties and the microstructure observation of the CNT/aluminosilicate composites, which synthesized by hot pressing of powders generated as described above were studied in depth.

Experimental results indicate that the TEOS/boehmite catalyst sol–gel with different CVD growing/calcining processes generate different products. The final products from the TEOS/boehmite catalytic sol–gel via the two-step CVD growing/calcining process are mainly Mullite, α-Al_2O_3, cristobalite and CNTs. The hardness tests reveal that the composite made by those products through the two-step CVD reaction show higher hardness than others. In addition, it is found that the CNT/aluminosilicate composites prepared via the two-step CVD growing/calcining process exhibits lower weight losses and friction coefficient.

1. Introduction

Mullite is known to be an advanced high temperature ceramic due to its remarkable physical and chemical properties [1,2]. Many methods are available for mullite synthesis. Among these developed methods, sol–gel method provides maximum homogeneity of alumina and silica species resulting in the formation of mullite at relatively lower temperatures compared to the other conventional methods [3–5]. To synthesize stoichiometric mullite ($3Al_2O_3$–$2SiO_2$), boehmite (AlOOH) and tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) are often used as precursors for alumina and silica, respectively.

Carbon nanotubes, discovered by Iijima in 1991 [6], with outstanding chemical and physical properties have become the potential reinforced materials in various technological applications [1]. Many deposition methods [7–11] have been reported on the CNT synthesis. The chemical vapor deposition (CVD) process, one very popular and low cost method for growing CNTs, adopts transition metal particles such as Fe, Co or Ni as the reaction catalyst to reduce the growth temperature. The transition metal catalysts were often found to be incorporated into the silica or alumina framework substrate [12–14] when TEOS is selected as the precursor for silica substrate to synthesize CNTs. A high performance braking materials is often required to have good mechanical property, high wear resistance and high tribological performance. Our previous work has shown that the CNTs have better tribological performance, which stabilized the friction coefficient. Therefore, the paper intend to integrate both merits of the mullite which provides rather good mechanical properties and high wear resistance and the CNTs which can stabilize the friction coefficient using a simple process. Since the boehmite and tetraethoxysilane are often used as precursors for mullite, and $Fe(NO_3)_3$ and tetraethoxysilane are applied as the catalyst in substrate for growing CNT, we mixing them three at once to grow both the mullite and CNTs through CVD process at the same time. In this study, we prepared the $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel with different CVD growing processes to generate fabricate different CNT/aluminosilicate powders. The performances of these CNT/aluminosilicate composites were also investigated.

2. Experimental procedures

2.1. $Fe(NO_3)_3$/TEOS/boehmite catalyst powder preparation

There were two steps in preparing the $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel. Firstly, boehmite (AlOOH) was used as the precursor for alumina and tetraethoxysi-

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lane (TEOS, $Si(OC_2H_5)_4$) as the precursor for silica. TEOS was first mixed with ethanol and hydrolyzed by deionized water under controlled acidic condition (pH = 1.4–1.6) by HNO_3 solution. After being fully hydrolyzed, the solution was mixed with boehmite sol–gel and stirred for 45 min. The stoichiometric concentration ratios of boehmite/TEOS were carefully prepared corresponding to the constant molecular ratios of Al/Si = 3. Secondly, the $Fe(NO_3)_3$ aqueous solutions were mixed with TEOS/boehmite sol–gel and ultrasonic stirred for 45 min. After then, the mixture was air dried at room temperature for 168 h and dried stepwise in the oven at 70 °C for 24 h to remove excess solvent. After then, these dried mixtures were ground into powder.

2.2. CNT/aluminosilicate powder growth

CNT/aluminosilicate powder growth was conducted in a simple CVD setup made of a tube furnace and gas flow control units. The $Fe(NO_3)_3$/TEOS/boehmite catalyst powder was placed in a graphite boat before sending into a horizontal alumina tube reactor. The catalyst powder was first calcined in the vacuum atmosphere at 450 °C for 2 h. After then the catalyst powder was chemically reduced at 550 °C with a H_2/N_2 (10/100 sccm) atmosphere for 2 h. Two different CVD growing/calcining processes were designed specifically to fabricate given CNT/aluminosilicate powders. For the one-step reaction (continuous) process, the catalyst powder was finally calcined at 750 °C (or 1300 °C) for 30 min by introducing a mixture of C_2H_2/N_2 into the reactor at flow ratio of 30/70 sccm. Whereas, the two-step reaction process calcinated. The catalyst powder firstly at 750 °C for 30 min by introducing a mixture of C_2H_2/N_2 into the reactor at flow ratio of 30/70 sccm, then the temperature was increased to 1300 °C and kept at 1300 °C for 30 min by introducing nitrogen at 100 sccm. After the growing/calcining process, the nitrogen was fed into the reactor to purge the acetylene from the tube and prevent back flow of air into the tube. The furnace was then allowed to cool to room temperature before exposing the CNT/aluminosilicate powders to the air.

2.3. Sample preparation

80 wt.% CNT/aluminosilicate powders with 20 wt.% phenolic resin powders were mixed and press-molded at 180 °C under a unidirectional pressure of 100 MPa to make round disks of 25.4 mm in diameter and 10 mm in thickness CNT/aluminosilicate composites. The specimens made by CNT/aluminosilicate powders prepared through one-step reaction process at 750 or 1300 °C, and two-step reaction process at 750–1300 °C were designated as FTB 750, FTB 1300 and FTB 750–1300 individually.

2.4. Characterization of the catalyst and the CNTs

X-ray diffractometer (Scintag, X-4000, USA) with Ni-filtered Cu Kα radiation was operated at 30 kV and 20 mA. Data were collected between 10 and 90° (2θ) in a scanning speed of 2°/min to identify the various phases of CNT/aluminosilicate powders prepared through $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel adopted by different CVD growing/calcining processes. Those various phases were identified by matching each characteristic XRD peak with that compiled in JCPDS files.

The morphologies and microstructure of the CNT/aluminosilicate powders were observed using the Hitachi S-4700 (Tokyo, Japan) field emission scanning electron microscopy (FE-SEM) and electron dispersive spectroscopy (EDS). Some CNT/aluminosilicate products were also examined by FEI transmission electron spectroscopy (TEM, Tecnai G^2 20 S-Twin, Holland). The TEM specimens were prepared by ultrasonically dispersing grinded the CNT/aluminosilicate products in alcohol and then making several droplets on TEM copper grids. The samples were observed at various TEM power up to 200 keV.

2.5. Hardness test

Hardness values of all specimens were determined at HRR (Rockwell, R scale) levels by a hardness test machine (Akashi, ATK-600, Japan). The used indenter was a 12.7 mm spherical steel ball, the applying load was 60 kgf and the testing position was along the radial direction of the specimen. At least, five positions were tested for each set of samples and the average values of hardness were measured.

2.6. Friction and wear tests

Friction and wear tests were conducted using a homemade disc-on-disc sliding wear tester. The square-shaped (32 mm × 32 mm) counterface material is SAE-G2500 gray cast iron (the rotor material). Prior to testing, the wear test specimens (included cast iron disc and CNT/aluminosilicate composites) were polished through a level of #1200 grit paper, followed by ultrasonic cleaning and drying. A fixed load of 1.2 MPa, constant rotor speed of 1000 rpm (linear speed is 0.67 m/s) and testing time of 300 s (sliding distance is 200 m) were used in every wear test. A strain gage-equipped LRK-100K load cell (NTS Technology, Nara, Japan) was used to determine the friction coefficient. The weight loss was measured and averaged from the CNT/aluminosilicate composites for each run.

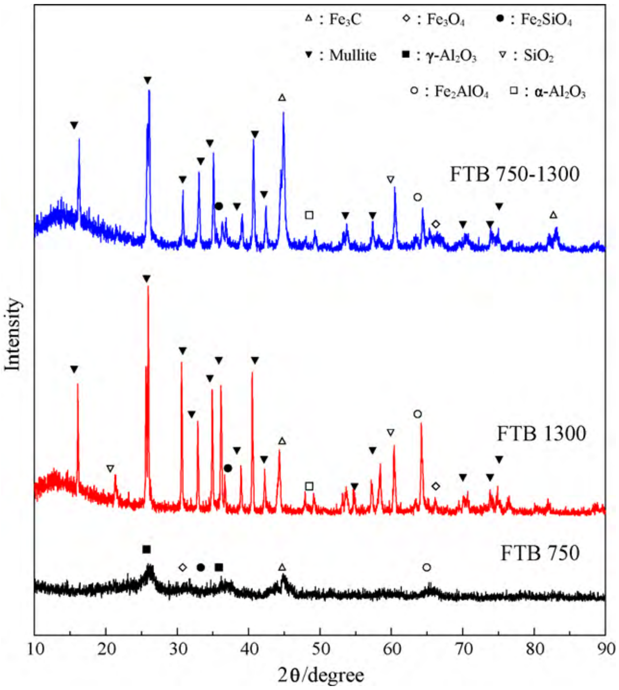

Fig. 1. XRD patterns of different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes. For the FTB 750 specimen, the spectrum gives weak and broad bands of Fe_3C, Fe_2AlO_4, Fe_2SiO_4, Fe_3O_4, and γ-Al_2O_3. The XRD patterns of FTB 1300 and FTB 750–1300 specimens are approximately similar. Some XRD peaks of FTB 1300 and FTB 750–1300 specimens were also observed in FTB 750 specimen. Nevertheless, the XRD patterns reveal the degree of crystallization of FTB 750 specimen is weak. Typically broad and weak crystallized γ-Al_2O_3 reflections were observed in FTB 750 specimen. To compare with the diffraction pattern of the FTB 750 specimen, both FTB 1300 and FTB 750–1300 specimens show better degree of crystallization. In the XRD patterns of FTB 1300 and FTB 750–1300 specimens, mullite crystalline were developed as main phases at temperatures as high as 1300 °C. SiO_2 and α-Al_2O_3 crystalline phases were also detected. The different patterns between FTB 1300 and FTB 750–1300 specimens were Fe_3C peak intensity. The Fe_3C peak intensity of FTB 750–1300 specimen was stronger and more obvious than that of FTB 1300 specimen. The phenomena reflected that CNTs were seldom observed in FTB 1300 specimen in follow-up microstructure observation.

3.2. Microstructure

The microstructures of CNT/aluminosilicate powders prepared through different CVD growing/calcining processes are shown in Figs. 2 and 3. In FTB 750 specimen, many entangled CNTs were found (Fig. 2(a) and (b)). TEM also showed that these CNTs were multiwalled nanotubes. The inner diameter of the CNTs is about 10 nm and outer diameter is about 18 nm (Fig. 3(a)). The selected-area diffraction (SAD) patterns demonstrated that the basal planes of the CNTs were highly aligned to the tube axis.

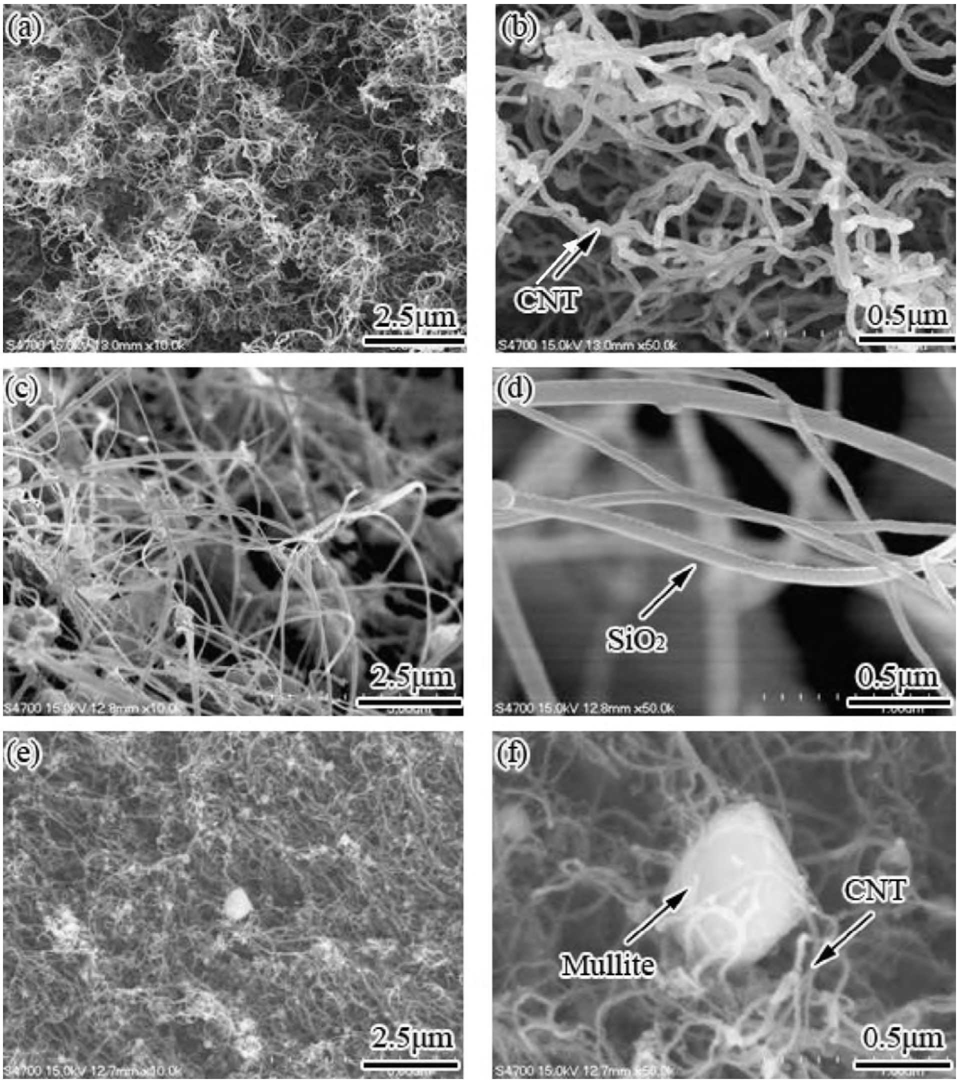

Fig. 2. Microstructures of different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes (a) and (b) FTB 750, (c) and (d) FTB 1300, and (e) and (f) FTB 750–1300.

Some nano-filaments were observed in FTB 1300 specimen (Fig. 2(c) and (d)). These nano-filaments seem to be straighter than the CNTs observed in the FTB 750 specimen. TEM micrographs show that these nano-filaments were not CNTs but amorphous silica nanowires (Fig. 3(b)). The diameter of these silica nanowires were about 50–100 nm. It should be noted that CNTs were seldom observed in the FTB 1300 specimen. It is possible that the reaction temperature at 1300 °C for one-step reaction (continuous) process is too high to synthesize CNTs. At 1300 °C, the elemental carbon decomposed from C_2H_2 is hard to precipitate from Fe_3C to form CNTs because most of the precursor has been transform into liquid iron instead of Fe_3C. On the contrary, the iron atom became as the catalyst for silica nanowires synthesis. TEM observations also showed that mullite and α-Al_2O_3 crystalline phases were also detected at 1300 °C for one-step reaction (continuous) process.

It seems that the two-step reaction process for FTB 750–1300 specimen can synthesize CNTs and mullite successfully (Fig. 2(e) and (f) and Fig. 3(c)). In the first step of the two-step reaction process, CNTs were synthesized firstly at 750 °C. For the second step, the alumina and silica components in $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel were transformed into mullite. It should be noted, although the SiO_2 evidence of were detected by XRD analysis, silica nanowires were also rarely observed in the FTB 750–1300 specimen. A more plausible explanation for the XRD peak of SiO_2 detected by XRD analysis is that the cristobalite is produced from the silica sources at 1300 °C. The result is distinct from the FTB 1300 specimen. There are two possible reasons to explain the phenomena. First, most of catalyst was provided to synthesize CNTs in the first step of the two-step reaction process. The residual catalyst was not enough to synthesize silica nanowires. Second, most of silica sources were transformed into mullite and cristobalite at 1300 °C. The residual silica sources and catalyst were inadequate to meet the needs for the silica nanowires syntheses.

3.3. Hardness

As shown in Fig. 4, the average hardness of each specimen with different CNT/aluminosilicate powders was approximately analogous. However, the specimens with higher growing/calcining temperatures generally showed the higher hardness. This observation implies that the CNT/aluminosilicate powders prepared through higher growing/calcining temperatures could improve the hardness of specimens. Among those specimens prepared through different CNT/aluminosilicate powders, the FTB 750–1300 specimen shows the highest hardness. One possible explanation for the phenomena is that products such as CNTs, mullite,α-Al_2O_3 trans-

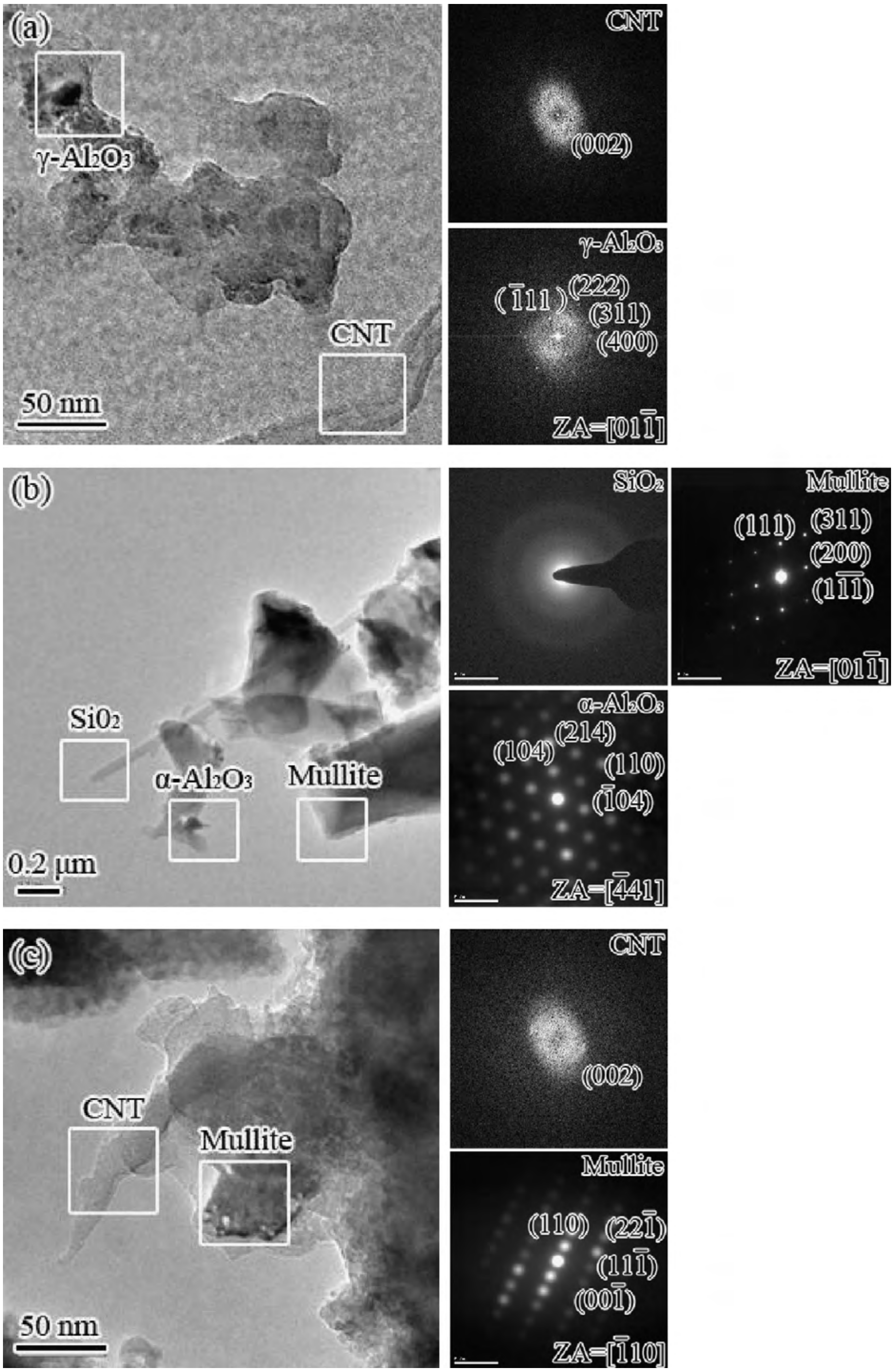

Fig. 3. TEM microstructures and diffraction (SAD) patterns of different CNT/ aluminosilicate powders prepared through different CVD growing/calcining processes (a) FTB 750, (b) FTB 1300 and (c) FTB 750–1300.

formed from the $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel through the two-step reaction process could provide better mechanical properties of the specimens.

3.4. Friction and wear

The friction coefficient curves with respect to time under a 1.2 MPa load and a 1000 rpm sliding speed of specimens with different CNT/aluminosilicate powders through different CVD growing/calcining processes are shown in Fig. 5 (*note*: several tests were repeated for each condition). For all specimens, the friction coefficient always rose abruptly at first and then dropped with time to a steady value. Among those specimens with CNT/aluminosilicate powders during the wear test, FTB 1300 specimen showed the most obvious difference between lowest and highest friction coefficient and the FTB 750 specimen showed the highest friction coefficient curve. The friction coefficient curves during the wear test of FTB 1300 and FTB 750–1300 specimens were approximately similar. Nevertheless, the FTB 750–1300 specimen showed more stable variation in friction coefficient curve than that of FTB 1300 specimen. Base on the observation of microstructure, the difference between FTB 1300 and FTB 750–1300 specimens were the existence of CNTs. Therefore, it implies that CNTs could improve the tribological performance and stabilize the friction coefficient of specimens during the wear test.

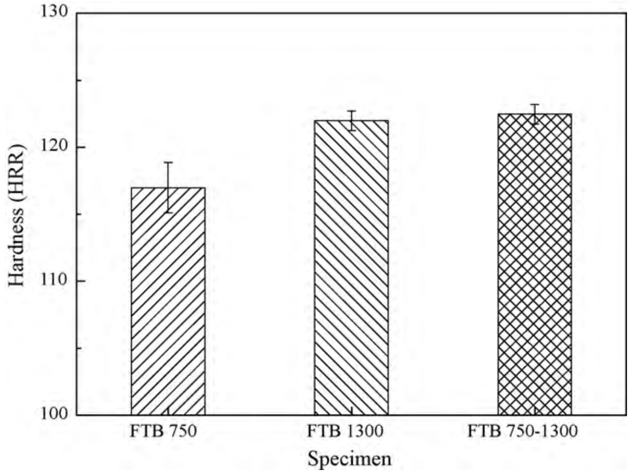

Fig. 4. Hardness of specimens with different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes.

Weight losses of specimens with different CVD growing/calcining processes after experiencing the same load (1.2 MPa) and speed (1000 rpm) wear test were compared in Fig. 6. Among all specimens, the FTB 750 specimen had the largest weight losses (17.8 mg) and the FTB 750–1300 specimen had lowest one (4.1 mg). It also shows that the weight losses of specimens are roughly related to their hardness. The higher the hardness, the lower were the weight losses. The probable explanation for this result is that those ceramic products such as mullite, α-Al_2O_3 transformed from the $Fe(NO_3)_3$/TEOS/boehmite sol–gel at higher calcining temperatures could provide better mechanical properties and wear resistance.

Based on the observation of friction and wear results, we can recognize that among those different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes. CNTs could improve the tribological performance and stabilize the friction coefficient of specimens. Furthermore, those ceramic products such as mullite, α-Al_2O_3 transformed from the $Fe(NO_3)_3$/TEOS/boehmite sol–gel at higher calcining temperatures could provide better mechanical properties and wear resistance.

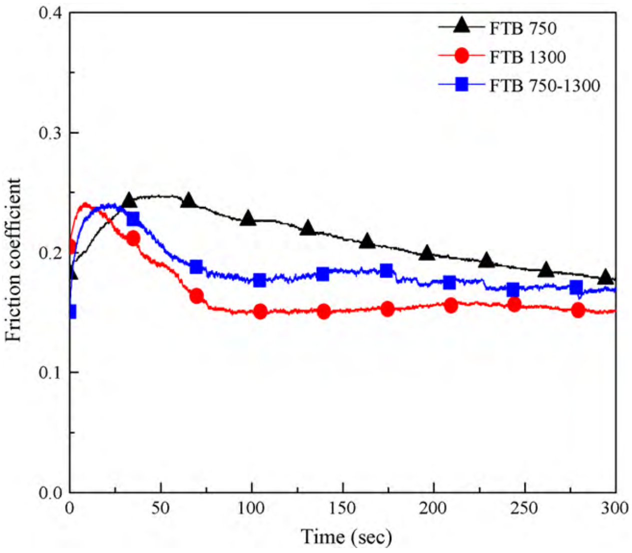

Fig. 5. Friction coefficient curves of specimens with different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes during wear test.

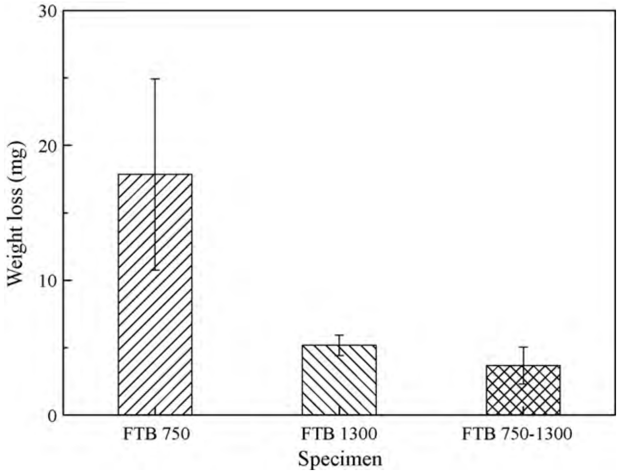

Fig. 6. Weight losses of specimens with different CNT/aluminosilicate powders prepared through different CVD growing/calcining processes during wear test.

4. Conclusion

Different CNT/aluminosilicate powders were synthesized through $Fe(NO_3)_3$/TEOS/boehmite catalyst powders with different CVD growing/calcining processes. By adopting the one-step reaction (continuous) process at 750 °C, the products were CNTs and γ-Al_2O_3. By adopting the one-step reaction (continuous) process at 1300 °C, the products were silica nanowires,α-Al_2O_3 and mullite. In addition, the two-step reaction process could synthesize CNTs, mullite and α-Al_2O_3.

CNTs, mullite,α-Al_2O_3 transformed from the $Fe(NO_3)_3$/TEOS/boehmite catalyst sol–gel through the two-step reaction process could provide better mechanical and tribological properties of the specimens. CNTs could improve the tribological performance and stabilize the friction coefficient of specimens. Furthermore, those ceramic products such as mullite, α-Al_2O_3 transformed at higher calcining temperatures could provide better mechanical properties and wear resistance.

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