Spark plasma sintering of CNT-NiAl nanocomposites – Process parameter, densification mechanism, and grain analysis

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Abstract. The densification process and grain analysis of consolidated NiAl-CNT composites at 1000 °C, and at varied heating rates from 50 °C/min to 150 °C/min was investigated. The results revealed the effect of heating rate on the densification behaviour of the samples. The displacement of the composites decreased from 3.39 mm to 2.63 mm with increasing heating rate, while the porosity increased by 69% at rapid heating rate. The grain analysis of the sintered samples through the electron backscattered (EBSD) technique indicates the evolution of bigger grains as the heating rate proceeds higher. Furthermore, the mean grain size of the consolidated composites increased from 3.93 μm , to 8.05 μm due to the concentration of defects. Interestingly, there was no texture or predominance of any color evolution in the sintered materials.

Keywords: Grain size / electron backscattered diffraction / porosity / densification and heating rate

1 Introduction

Spark plasma sintering (SPS) is a promising sintering technique which has captivated the attention of a lot of researchers in the field of science and engineering because of the advantages it provided over the traditional sintering processes (TS) [1]. The TS methods are characterized with long sintering temperatures and provides limited control over the properties and microstructures of the material. On the contrary, SPS can fabricate materials at rapid heating rate and short sintering time, thus resulting into uniform microstructures [2,3]. The SPS technology uses a pulsed DC (direct current) under the application of uniaxial pressure [4], to bring about the consolidation of powders. The process allows the acceleration of material transfer and diffusion phenomena due to plasma generation between the powder particles. This results to breakdown and cleaning of oxide impurities from the material surface. Furthermore, pressure assisted plastic deformation and joule effect aid sinterability and densification [5,6]. Owing to the characteristics of SPS, parameters such as pressure, sintering temperature, holding time and heating rate, plays a role in the densification mechanisms of a consolidated sample [7].

The heating mechanism of SPS technique comprises of cooling time and lower sintering temperature, rapid sintering process due to its good heat distribution and great heating rate (up to 1000 K/min) on fabricated samples at microscopic level and macroscopic level [8,9]. Researchers have reported that the use of fast heating rates can limit coarsening for some samples that possesses high-level activation energy for densification than grain growth [10,11]. Therefore, by utilizing a higher heating rate where the non densifying mechanisms prevail, densification takes place by volume diffusion and grain boundary, this allow the possibility of having a fine grain retention. However, this could be a challenge for other samples, due to their elevated activation energy for grain growth than that of densification, in this process the heating rate lacks the expected positive effects [12]. Nevertheless, the studies on the effect of heating rate on grain growth and densification of materials prepared by the SPS technique have given rise to several conflicting outcomes [13]. Investigation by Stanciu et al. [11] on the effect of heating rate on the grain size and densification of SPSed Al_2O_3 and MoSi_2 from 50 °C/min to 700 °C/min was observed, and the final density of SPSed Al_2O_3 was not affected by the heating rate, but it had little effect on the grain size. In the case of the sintered MoSi_2 , the grain size of the sample was independent of the heating rate value.

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Table 1. The starting materials used for the study.

Powder	Particle size	Purity	Supplier
Carbon nanotubes	9.5 nm	99.8%	Nanocyl
Nickel	<3.0 μm	99.5%	Wear Tech Limited
Aluminium	<25 μm	99.8%	Technik GmbH

Similarly, the consolidation of alumina powders at different sintering temperatures, heating rate at 50 °C/min and 300 °C/min respectively was reported by Zhou et al. [14]. The results showed that the sintered samples at 300 °C/min had higher densities, with decreased grain sizes as compared to the sintered samples at 50 °C/min. Contrary to the previous investigations, Shen et al. [15] shows that the density of sintered alumina decreased by 0.6% with increasing heating rate, especially at 350 °C/min, and the grain size was smaller due to the higher heating rate. Recently, the role of heating rate was examined on the transparency and microstructure of sintered alumina powder from 2 °C/min to 100 °C/min, at 1150 °C. The results indicated that the porosity, transparency, and grain size increased as the heating rate increased. The grain size of the sintered alumina increased by 89% from 2 °C/min to 100 °C/min [16].

The effect of heating rate was studied by Lee et al. [17] during the formation of titanium aluminide through the reactive sintering of Ti-48%Al powders. It was reported that increasing heating rate favoured the formation of TiAl, Ti₃Al and TiAl₃ intermetallic compounds. The densification of SPSed TiAl was further assessed by Zofia et al. [18] and they reported that densification of TiAl can be attributed to bulk diffusion of Al, through its contribution in dislocation climb. The process of dislocation glide and twinning are being active in small interparticle regions at the start of the densification cycle. In this present study, carbon nanotubes (CNT) has been used to reinforce the matrix metal (nickel aluminide) because of its promising mechanical properties, and wide-ranging benefits of the composites in energy and transportation industries. However, the densification mechanisms and grain size analysis of intermetallic material especially CNTs reinforced NiAl has not been sufficiently examined from the literature. This is the reason that motivated the authors to focus on the evaluation of heating rate on the densification and grain size of the composites.

2 Experimental procedure

The starting materials utilized are presented in Table 1. Planetary ball milling machines were used to disperse the carbon nanotubes (CNT) within the admixed matrix powders at the speed of 150 rpm. The milling was accomplished in a steel-container consisting different steel balls. Then, the milled powders were charged in a 20 mm sintering die, enclosed with the sintering punches. The consolidation of the powders took place in the spark plasma sintering machine. The details of the dispersion of

nanotubes within the matrix metal and the consolidation process of the samples have been reported [19]. As sintered composite samples were used in this investigation. The data retrieved from the SPS was utilized in evaluating the densification mechanism during the sintering procedure. Tescan Mira 3 XMU (Scanning Electron Microscope; SEM) equipped with Electron Back-scatter Diffraction (EBSD) was utilized to determine the microstructural evolution in the fabricated samples. The Consolidated samples were polished with Eposil M Colloidal Silica for the duration of an hour to achieve a smooth surface, and to depict the features of the microstructures. The grain analysis of the consolidated samples was observed using the EBSD at a tilt angle of 70° for dynamic focus, step size of 0.5 μm and with a voltage of 20 kV. The crystallographic orientation was analyzed with AZtecHKL software (Denmark) and the EBSD maps were obtained. The porosity of the consolidated sample was determined with the formula:

$$\text{Porosity} = (1 - \text{relative density}) * 100\%.$$

3 Results and discussion

3.1 Densification behaviour and fractured surface of the samples

The sintering profile obtained from the SPS was used to assess the densification behaviour of the consolidated samples (NiAl/CNT) and unreinforced NiAl at different heating rates from 50 °C/min to 150 °C/min, and at the sintering temperature of 1000 °C. Figure 1 depicts the displacement-time graph of all the consolidated samples respectively. The mechanisms of the densification observed can be described by the following stages [20]: (a) sample activation and refining, (b) sintering neck formation, (c) growth of neck, and (d) plastic deformation. the first and second steps occurred due to plasma discharge between the particles, which leads to the removal of impurities due to voltage breakdown. Therefore, the sample surface heats up, promoting neck formation by evaporation and diffusion. The last two steps materialized because of electric current passage through the necks by joule heating effect. This favored rapid densification and enhanced by the effect of pressure in the fourth stage. Figure 1a indicates the displacement-time graph of the consolidated NiAl at different heating rates. From the graph, the displacement of the consolidated sample at 50 °C/min was observed at 3.62 mm, the sample at 100 °C/min showed displacement at 3.22 mm, and the sample at 150 °C/min had the highest displacement at 4.15 mm. The displacement decreased as

Fig. 1. The plot of the displacement against time at different heating rate (a) NiAl, and (b) NiAl-CNT.

Fig. 2. SEM fractured morphology of the consolidated samples from 50 to 150 °C/min (a–c) NiAl, and (d–f) NiAl-CNT.

the heating rate was increased, but it further increases at the heating rate of 150 °C/min. This depicts that the rapid heating rate promoted high densification because of the large displacement observed.

Figure 1b describes the displacement-time graph of the consolidated composites (NiAl-CNT) at different heating rates. The displacement of the consolidated composite at 50 °C/min was observed at 3.39 mm, the composite at 100 °C/min showed displacement at 2.85 mm, and the composite at 150 °C/min attains displacement at 2.63 mm. The displacement of the consolidated composite decreased with increasing heating rate. It further suggests the detrimental effect of heating rate on the densification of

the composites. This is in line with the result reported by Singh et al. [6]. The decrease in displacement at increasing heating rate may be attributed to the lower thermal transfer. The presence of CNT in the composite may induce pores at higher heating rate which retards the sintering mechanisms [9].

The SEM fractured morphology (Fig. 2) was used to buttress the densification mechanisms of the consolidated samples. The fractured surface of the consolidated NiAl (Fig. 2a–c) is characterized with cavities (pointed with white arrows). Figure 2a describes the fracture morphology of the consolidated NiAl at the heating rate of 50 °C/min, indicating necking of particles as represented with red arrow.

Fig. 3. The illustration of the porosity with heating rate (a) NiAl, and (b) NiAl-CNT.

Similar behaviour was observed for the consolidated NiAl at 100 °C/min (Fig. 2b), with the presence of pronounced cavities. This suggests that the particles are not well bonded which is an indication of the low displacement seen in Figure 1. The consolidated sample at 150 °C/min (Fig. 2c), had a fractured surface with reduced cavities and the particles are well metallurgically bonded. This occurrence maybe attributed to rapid neck formation of the particles and it maybe responsible for the high displacement observed in Figure 1. The fractured morphology of all the consolidated NiAl at different heating rate displayed a rock candy features which indicates intergranular fracture.

The fracture morphology of the consolidated NiAl-CNT composites (Fig. 2d–f) displayed the presence of neck formation (pointed with white arrows), cavities (pointed with red arrows) and cracks (pointed with blue arrows) at different heating rate. The consolidated composites at the heating rate of 50 °C/min (Fig. 2d) showed presence of cavities, with a few neck formations [21]. These cavities became bigger as observed in the composite (Fig. 2e). At this stage (100 °C/min), there were fewer necks formed as compared to Figure 2d. In Figure 2f, more distinct cavities and cracks were seen. This explained why the displacement decreases with the heating rate. The cavities noticed from the sintered composites maybe due to the agglomerated CNTs. The fractured morphology of all the consolidated composites at different heating rate may have displayed transgranular fracture.

3.2 Porosity of the samples

Figure 3 shows the porosity of the consolidated samples at 1000 °C at different heating rates. The porosity of the consolidated NiAl at 50 °C/min was observed to be 5.1%. When the heating rate was increased to 100 °C/min, the porosity had increased to 9.2%. This indicates that the

pores in the consolidated samples increases with heating rate. However, the porosity of the consolidated sample at 150 °C/min was found to be 3.8% which depicts high relative density and less pores. Furthermore, the porosity of the consolidated composite increased with increasing heating rate from 50 °C/min to 150 °C/min. The porosities of the composites were observed to be 4.3%, 11.6%, and 14% respectively. This could be accredited to decrease in neck formation and lack of particle arrangements at high heating rate which hinders good metallurgical bonding. Also, the presence of CNT agglomerates could create pores which hinders diffusion during the SPS process [22].

3.3 Analysis of the grain size

Figure 4 illustrates the grain size analysis of the consolidated samples at varied heating rates from 50 to 150 °C/min. The maps of the consolidated samples were obtained from the electron backscattered patterns (EBSP) after indexing. The maps revealed the grain boundaries of the samples with some black regions. These are the regions where flamenco had difficulties in indexing the EBSPs due to the occurrence of unknown phases or grain boundaries deformed areas, known as low-EBSP areas. The reason for this could be due to the presence of porosity where the CNTs are agglomerated [23]. Figure 4a–c depicts the grain boundaries of the consolidated NiAl. It was observed that the grain arrangement was similar (the differences are not obvious) as the heating rate increases from 50 to 150 °C/min, although the samples had some porosities. However, the grain boundaries of the consolidated composites increased as the heating rate increases, as represented in Figure 4d–f. The composite at 50 °C/min had similar grain boundaries with the consolidated NiAl, maybe because it had enough power input for particle bonding. The presence of the agglomeration of CNTs could have created some pores in the composites which hinders diffusion. It depicts that at high heating rate, more porosities were observed in the composite which could have been responsible for improper particle bonding, resulting into large grains in the composites at 150 °C/min. Studies have shown that rapid heating rate impedes surface diffusion for coarsening processes, thereby leading to the decrease in grain size [15,24]. However, this study agrees with Murayama et al. [25], which reported that high heating rate results in grain size increase because of high defect concentration formed during densification and rapid particle deformation. Furthermore, fast heating rate produces large direct current which may cause defect formation because of high temperature plasma formed on the surface of the particles, which induced dynamic grain growth [26]. Similarly, the microstructures of the consolidated NiAl and NiAl-CNT depict the presence of pores as observed from Figure 2. This is because consolidated samples go through non-thermal and thermal effects, rearrangement of sample particle, and deformation (both localized and bulk) during SPS mechanisms which affects the densification, grain growth and mechanical properties of the samples [27]. However, rapid heating rate results into the formation of large thermal gradients which may lead to the sinterability of the outer region of the sample before the inner region of the sample, leading to residual porosity [28].

Fig. 4. Illustration of the grain boundaries of the sintered samples (a–c) NiAl, and (d–f) NiAl-CNT.

Fig. 5. Inverse pole maps of the consolidated samples.

Figure 5 describes the inverse pole figure (IPF) of the consolidated samples at different heating rates. IPF is used to show the alignment of the crystal directions with the consolidated samples' axes at different heating rates. It can also be utilized to predict the texture of a sample. Figure 5 shows the IPF maps of the consolidated samples, which

indicated that there is no predominance of any colour. This suggests that the consolidated samples do not have texture or show the intensity of any colour [29].

The mean grain size of the consolidated samples was evaluated using the line intercept method, according to ASTM E112 (Fig. 6). The mean grain size (μm) of the consolidated NiAl from 50 °C/min to 150 °C/min was measured as $3.24 \pm 2.5 \mu\text{m}$, $3.14 \pm 2.1 \mu\text{m}$, and $3.27 \pm 2.4 \mu\text{m}$ respectively. It could be seen that there is little disparity in the grain size of the NiAl samples. However, the mean grain size of the consolidated composite (ball milled after 60 min) from 50–150 °C/min was measured as $3.93 \pm 2.5 \mu\text{m}$, $4.78 \pm 3.4 \mu\text{m}$, and $8.05 \pm 5.8 \mu\text{m}$ respectively. Furthermore, the distribution of the grain size of the consolidated samples is presented in Figure 7. The length of the grain was used to compute the grain size of the consolidated samples, Figure 7a–c shows the distribution of the consolidated NiAl. The highest count of the grain size was observed at 17 μm , 11 μm , and 14 μm from 50 °C/min to 150 °C/min. In the case of the consolidated NiAl-CNT (Fig. 7d–f), the highest count of the grain size was observed at 10.5 μm , 16.5 μm , and 29.5 μm respectively from 50 °C/min to 150 °C/min. Large grain size was observed at 150 °C/min from Figure 7f.

Fig. 6. The mean grain size plots of the consolidated specimens.

Fig. 7. The grain size distribution of the consolidated specimens at different heating rate.

4 Conclusions

This research work evaluated the role of sintering parameter on the densification mechanism and grain analysis of the fabricated composites. The displacement of the consolidated samples are dependent on the heating rate. The punch displacement of the sintered NiAl decreases with the heating rate until it further increases at the heating rate of 150 °C/min. The trend observed for the sintered composites are different

because the punch displacement decreases with increasing heating rate. The use of EBSD technique was also helpful in revealing the arrangement of the grains of the sintered samples. It depicted the influence of heating rate on the grain analysis because of the presence of high defect concentration formed during densification and rapid particle deformation. This phenomenon caused the increase in the grain sizes of the sintered composites as the heating rate was increased. The variation of grains of the sintered NiAl was non conspicuous.

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