Research Article

Effect of Processing on Mechanically Alloyed and Spark Plasma Sintered Al-Al₂O₃ Nanocomposites

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Metal matrix nanocomposites are advanced materials developed using ceramic nanoreinforcements and nanocrystalline metal matrices. These composites have outstanding properties and high potential for large number of functional and structural applications. In this work, nanocrystalline aluminium and Al-Al₂O₃ nanocomposites were synthesised using mechanical alloying and consolidated through spark plasma sintering technique. Scanning electron microscopy, X-ray diffraction, and mapping were used to characterize the powders and sintered samples. Density and hardness of sintered samples were measured using densimeter and hardness tester, respectively. It was found that milling of pure aluminium for 24 h reduced its crystallite size to less than 100 nm. For Al-Al₂O₃ nanocomposites, milling for 24 h decreased the crystallite size of the aluminium phase and resulted in uniform dispersion of the reinforcement. Sintering of the synthesised powders led to grain growth. Al₂O₃ contributed to growth inhibition when samples were sintered for 20 minutes and improved the hardness but reduced densification. The Al-10 vol.% Al₂O₃ nanocomposite had the highest Vickers hardness value of 1460 MPa.

1. Introduction

The growing demand for light-weight and high-performance structural materials, in the aerospace, military, and automotive industries, to reduce energy consumption and air pollution [1, 2], is gradually leading to a shift from conventional metallic alloys to metal matrix composites [3] and nanocomposites [4]. Among these composites, particle reinforced aluminium matrix composites received the serious attention of researchers and engineers. This is due to the fact that reinforcing a metal with ceramic particles improves its mechanical and physical properties. However, although the addition of the reinforcement improves hardness, stiffness, and strength of the matrix, it decreases the ductility and toughness of the composite. This is due to cracking of ceramic particles during loading which leads to early failure of the composites. Fortunately, reducing the size of the reinforcement and/or matrix grains from micro- to nanodimensions to produce nanocomposites [4] led to significant improvement in ductility, toughness, and strength [5, 6]. Grain size is a key microstructural factor that significantly affects the

properties and mechanical behaviour of polycrystalline materials; and one way to design materials with desired properties is controlling their grain size [7]. Moreover, it is known that grain refinement is the only method that improves the strength of the material without compromising the ductility and flow properties [8]. Severe plastic deformation processes can be used to reduce matrix grain size to submicrometer or nanometer dimension. These processes include equal channel angular extrusion/pressing (ECAE/ECAP) [9], multiaxial forging [10], cyclic extrusion and compression (CEC) [11], high pressure torsion (HPT) [12], accumulative roll bonding (ARB) [13, 14], and mechanical alloying (MA) [5]. However, all these processes, except ARB and MA, suffer from two main drawbacks. The first is the fact that they require large load capacity machines and expensive tools. The second is the limited productivity and amount of produced material. In addition to grain size refinement, addition of nanoparticles to metals leads to the enhancement of toughness because of the reduced particle volume fraction needed to achieve high strength. However, the development of nanoparticle reinforced metal matrix nanocomposites for commercial

TABLE 1: Chemical composition of pure aluminium powder [15].

Elements	Al	Fe	Si	Ti	Ga	Ni	Cu, Mn, Pb, Zr, Zn, and Cr
wt.%	99.88	0.074	0.024	0.006	0.006	0.005	0.001 each

applications is still facing some challenges and the race for better materials performance is never ending [7]. These challenges include inhomogeneous microstructures because of nanoparticles' agglomeration, grain growth if sintering is required, and limitations on the amount of the produced material. Fortunately, overcoming the above challenges is possible through proper selection and combination of processing techniques. In this regard, mechanical alloying is used to process homogenous nanocomposite powders [5]. It allows not only the design of specific microstructures with uniform dispersion of the reinforcement and small grain size of the matrix, but also the elevation of the limitations on the amount of the produced material. On the other side, spark plasma sintering (SPS) also named field assisted sintering (FAST) is a binderless and a direct process to consolidate powdered materials in short times at relatively low temperatures. It involves the application of uniaxial force and high intensity current at low voltage [16]. The advantages of the process include the ability to sinter the material at low sintering temperature and in short sintering time which allows the retention of the initial fine structure of the material that leads to superior properties. In addition, SPS is a cost-effective process due to the fact that it is binderless process and direct, does not require a precompaction step, and can be performed at low temperatures for short times compared to other powder metallurgy processes. The MA and/or SPS techniques were used to process nanostructured aluminium [17–20], aluminium alloys [21–23], and Al-Al₂O₃ nanocomposites [24, 25]. Despite the importance of Al-Al₂O₃ nanocomposites, work dedicated to their processing using MA and SPS is very scarce in the literature. In a previous review paper [26], the authors concluded that reaching uniform distribution of the reinforcement in the matrix, which could be achieved through optimization of processing parameters, is vital for the development of nanocomposites with the anticipated properties. In another work [15], the authors successfully synthesised and consolidated Al-SiC nanocomposites using MA and SPS techniques. The objective of the present work is to synthesize nanocrystalline aluminium and homogenous Al-Al₂O₃ nanocomposite powders using mechanical alloying and consolidate them through spark plasma sintering technique. The second objective is to investigate the influence of milling and sintering conditions on the microstructure, densification, and hardness of the developed materials.

2. Materials and Experimental Procedures

Aluminium powder, 99.88% purity supplied by Aluminium Powder Co. Ltd., and α -Al₂O₃ (with an average particle size of 150 nm), 99.85% purity, supplied by ChemPUR Germany, were used in this investigation. The chemical composition and particle size distribution of the aluminium powder are presented in Tables 1 and 2, respectively.

TABLE 2: Particle size distribution of aluminium powder [15].

Size (μm)	%
63	0
53	1
45	11
38	11.4
<38	76.6

Mechanical alloying was used to synthesize Al-Al₂O₃ composite powders reinforced with 2, 10, and 15 vol.% Al₂O₃ nanoparticles. In addition, pure aluminium, as a reference material, was milled for 24 h. A planetary ball mill (Fritsch Pulverisette, P5, Idar-Oberstein, Germany) was used to perform the milling experiments. The powders were milled in argon inert gas to avoid oxidation. Milling conditions of ball to powder weight ratio of 10:1 and speed of 200 rpm were maintained constant in all experiments. Stainless steel vials (250 mL in volume) and balls (10 mm in diameter) were used. Each powder mixture was milled for 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, and 24 h. The sticking of the powder to milling balls and vials was minimised using stearic acid (1.5 wt.%). Spark plasma sintering machine (FCT Systeme, Germany), model HP D 5, was used to consolidate the mechanically alloyed powders. More details on SPS process were reported in [16]. Disc shaped specimens were prepared using a graphite die of 20 mm diameter. A compaction pressure of 50 MPa and heating rate of 200°C/min were used in all sintering experiments. Aluminium unmilled and milled for 24 h and Al-Al₂O₃ nanocomposite powders containing 2, 10, and 15 vol.% Al₂O₃ milled for 24 h were sintered. The samples were sintered at a temperature of 550°C for holding times of 5 and 20 minutes. FE-SEM equipped with EDS was used to characterize both mechanically alloyed powders and sintered samples. X-ray elemental mapping, using 20 frames, was performed to examine the distribution of the reinforcement in the matrix. X-ray diffraction experiments were carried out using a diffractometer (Bruker D8, USA, with a wavelength $\lambda = 0.15405$ nm) to characterize the crystallite size of the aluminium matrix. The bulk density of the consolidated samples was measured according to the Archimedes principle using Mettler Toledo balance density determination KIT model AG285. Digital microhardness tester (Buehler, USA) was used to measure the microhardness of the developed materials. The obtained hardness values were the average of 12 readings. Conditions of a load of 100 gf and a time of 12 s were maintained in all measurements.

3. Results and Discussion

FE-SEM micrograph of aluminium powder is shown in Figure 1(a). Its particles have various sizes and shapes. A TEM

FIGURE 1: (a) FE-SEM micrograph of Al powder and (b) TEM micrograph of Al_2O_3 nanopowder.

micrograph of the as-received Al_2O_3 nanopowder is presented in Figure 1(b). The Al_2O_3 nanopowder has particles with different shapes and average particle size of 150 nm. It can be noticed that Al_2O_3 nanoparticles are agglomerated because of their small particle size.

The Al- Al_2O_3 powders were milled for different milling times to achieve uniform dispersion of the reinforcement in the matrix. Figure 2 shows typical FE-SEM micrographs of Al-10 vol.% Al_2O_3 powder milled for (a) 3 h; (b) 6 h; (c) 20 h; and (d) 24 h. The morphology and size of aluminium particles changed with milling time. Initially, milling led to flattening of particles and increase in their size. However, at long milling time of 24 h, Figure 2(d), milling led to particle size decrease and particles had smaller size compared to the size of unmilled particles as presented in Figure 1(a). In addition, particles became more equiaxed.

Figures 3(a) and 3(b) show FE-SEM micrographs of powders containing 2 and 15 vol.% of Al_2O_3 , respectively, milled for 24 h. The nanocomposite powders reinforced with 2 and 15 vol.% of Al_2O_3 nanoparticles showed similar behaviour compared to the Al-10 vol.% Al_2O_3 composite. Analysis of the size and morphology of aluminium particles in powders containing 2, 10, and 15 vol.% Al_2O_3 and milled for 24 hours, presented in Figures 3(a), 2(d), and 3(b), respectively, shows that the higher the Al_2O_3 content the smaller the particle size; and more equiaxed particles were formed. Therefore, it can be concluded that, under the same milling conditions, the increase in Al_2O_3 content enhanced the milling effect. The same effect was observed in Al-SiC nanocomposites where SiC was reported to enhance the milling effect in mechanically alloyed Al-SiC nanocomposites prepared under milling speed of 200 rpm, milling time up to 20 h, and BPR of 10:1 [15]. This is due to the fact that the increase in reinforcement volume fraction leads to the increase in milling rate and reduces the time to reach a balance between fracturing and rewelding of the milled particles [15].

Elemental mapping of aluminium and oxygen in Al-10 vol.% Al_2O_3 composite mechanically milled for 2 h; 8 h; 15 h; and 24 h and corresponding FE-SEM micrographs are

shown in Figure 4. The micrographs confirm the decrease of particle size and formation of more equiaxed particles with the increase in milling time from 2 to 24 h as discussed above. It can be noticed that after milling for 15 hours, from the one hand, the size of aluminium particles remained relatively large, and from the other hand, Al_2O_3 nanoparticles remained relatively agglomerated as it is evident from the mapping of Al and O, respectively. However, a homogenous composite powder with small aluminium particles and uniform distribution of Al_2O_3 nanoparticles was obtained when the milling time was increased to 24 h. The uniform dispersion of Al_2O_3 particles is clear from the mapping of aluminium and oxygen at 24 h. This time is the same time used to obtain a uniform distribution of SiC nanoparticles in mechanically alloyed Al-SiC nanocomposite powders prepared under similar conditions [15]. It is worth mentioning here that the time to reach uniform dispersion of the reinforcement in mechanically alloyed nanocomposites strongly depends on the nature of the matrix, amount and type of the reinforcement, and milling conditions. Yadav [27] obtained uniform dispersion of SiC particles in Al-SiC composites (containing 5, 10, and 20 wt.% SiC) at a milling time of 30 minutes. In his work, acetone and polyacrylic were used as process control and dispersive agents, respectively; and a ball to powder weight ratio (BPR) of 5:1 and a speed of milling of 500 rpm were employed. Homogenous distribution of SiC nanoparticles was achieved in Al-SiC composites containing 2.5, 7.5, and 12.5 vol.% SiC after 10 h of milling [28] at milling conditions of a speed of 320 rpm and BPR of 20:1 and 10:1.

The composite powders reinforced with 2 and 15 vol.% of Al_2O_3 displayed similar behaviour. Uniform distribution of Al_2O_3 particles was reached after milling for 24 h as can be seen from mapping of oxygen presented in Figure 5. The Al_2O_3 particles remained fairly distributed despite the increase in their volume fraction to 15%.

Analysis of Figures 4(d), 5(a), and 5(b), showing elemental mapping in composite powders reinforced with 10, 2, and 15 vol.% of Al_2O_3 , respectively, indicates that under

FIGURE 2: FE-SEM micrographs of Al-10 vol.% Al_2O_3 composite powder mechanically alloyed for (a) 3 h; (b) 6 h; (c) 20 h; (d) 24 h.

the employed milling conditions, a milling time of 24 h was suitable to process homogenous composites with uniform dispersion of the reinforcement. On the other hand, nanostructured aluminium matrix was obtained at this milling time as will be discussed below. Thus, only powders milled for 24 h were consolidated using SPS for subsequent characterization.

Figure 6 shows XRD spectra of aluminium, unmilled, Figure 6(a), and milled for 24 h, Figure 6(b). Only reflections from α -Al solid solution are present. The α -Al phase has FCC crystal structure. Mechanical alloying of pure aluminium for 24 h decreased the intensity of the α -Al peaks. This decrease was accompanied with broadening of the peaks, as can be seen in Figure 6(b). This is due to the fact that mechanical milling of metallic powders is usually associated with a decrease in crystallite size and increase in lattice strain [29]. The decrease in crystallite size is believed to take place in three stages, “The first stage is characterized by the formation of shear bands with high density of dislocations. In the second

stage, annihilation and recombination of these dislocations give rise to small angle grain boundaries separating the individual grains. In the last stage, the orientation of the single crystalline grains become random with respect to their adjacent grains” [29]. It should be understood that “in XRD analysis, when the size of a crystal is used, it usually refers to the size of crystallites concerning a factor, which makes a diffraction peak broad” [30].

Figure 7 shows XRD spectra of nanocomposites reinforced with 2, 10, and 15 vol.% of Al_2O_3 nanoparticles and mechanically alloyed for 24 h. It is worth mentioning here that for Figure 6 XRD patterns were recorded for the same powder, that is, aluminium unmilled and milled for 24 h; but, for Figure 7, XRD patterns were recorded for three powders containing different volume fractions of the Al and Al_2O_3 phases and milled for the same time of 24 h. Furthermore, particle size and shape for the three powders are noted to be the same as it is clearly seen in Figures 3(a), 2(d), and 3(b), for

FIGURE 3: FE-SEM micrographs of powders containing (a) 2 and (b) 15 vol.% of Al_2O_3 milled for 24 h.

composites containing 2, 10, and 15 vol.% Al_2O_3 , respectively. This is due to the fact that Al_2O_3 acts as a grinding medium and the increase in its volume fraction contributes to more refinement of the particles as explained above. Therefore, the volume fraction of the two phases present and the size and shape (flattened or equiaxed) of the particles may affect the intensity of peaks in the powders. Figure 7 shows that, for the composite powders, milling reduced the intensity of peaks and led to their broadening, compared with the unmilled aluminium powder presented in Figure 6(a). The crystallite size of the α -Al phase decreased because of milling and addition of Al_2O_3 as explained below.

The formation of secondary phases in the mechanically alloyed nanocomposite powders was not revealed by XRD. This could be attributed to the fact that the composites are processed through a powder metallurgy route and not casting. Moreover, peaks of these phases may not be easily seen on XRD spectra because of the reduced intensity as a result of milling [31] and their small amount which may be below the detectability of the equipment [32]. Peaks of Al_2O_3 phase were not observed in the composite containing 2% alumina and milled for 24 h, Figure 7(a), because of the low volume fraction of alumina. However, the peaks were detected in XRD spectra of composites containing 10 and 15% alumina nanoparticles and milled for 24 h, Figure 7(a and b), respectively. Overall, Al_2O_3 peaks had low intensity which could be attributed to the fact that Al_2O_3 nanoparticles have average particle size of 150 nm and their crystallite size is very small which contributes to peak broadening in addition to broadening that results from plastic deformation and increase in strain as a result of milling [30, 33, 34].

Crystallite size of the α -aluminium phase in pure aluminium and composites milled for 24 h was calculated [15, 30] using

$$B_r \cos \theta = \frac{k\lambda}{L} + \eta \sin \theta, \quad (1)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation ($\lambda = 0.15405$ nm); L and η are crystallite size and lattice strain, respectively; and θ is the Bragg angle. B_r is related to the measured width of the peak (B_{obs}) and peak broadening caused by factors except the particle size effect (B_i), frequently called instrumental broadening factor and calculated using a fully annealed sample, through the following formula [15, 30]:

$$B_r^2 = B_{\text{obs}}^2 - B_i^2. \quad (2)$$

Crystallite size of the α -Al phase is presented in Figure 8. The α -Al phase of the as-received pure aluminium had a crystallite size of 298 nm and decreased to 62.29 nm after milling for 24 h. This size is close to the crystallite size of the aluminium phase reported by other researchers who investigated the effect of milling on monolithic Al powder [22, 23]. It was reported that dry milling of monolithic Al decreased the α -Al crystallite size to 38 nm in 8 h [22] and 75 nm in 20 h [23]. As for the composite containing 2 vol.% of Al_2O_3 , milling for 24 h decreased the crystallite size of the α -Al phase to 39.82 nm. Further increase of Al_2O_3 to 10 and 15 vol.% led to further decrease in the crystallite phase to 32.69 and 27.24 nm, respectively. This clearly shows that Al_2O_3 nanoparticles acted as grinding medium and enhanced the milling effect which contributed to further decrease of the crystallite size of the α -aluminium phase. A summary of the crystallite size of the aluminium phase in mechanically alloyed Al-based nanocomposites is presented in Table 3.

Mechanical alloying of Al-based nanocomposites was reported to decrease the crystallite size of the aluminium matrix to nanodimensions [15, 28, 39]. α -Al crystallite sizes of 175.6 and 97.9 nm were reported for Al-SiC composites reinforced with 12.5 and 2.5 vol.% SiC, respectively, and mechanically alloyed for 10 h [28]. In another work, Al5083-10 wt.% SiC composites were mechanically alloyed for 15 h at a speed of 400 rpm using a BPR of 20 : 1; and a crystallite size

FIGURE 4: FE-SEM micrographs of Al-10 vol.% Al₂O₃ composite mechanically alloyed for (a) 2 h; (b) 8 h; (c) 15 h; (d) 24 h and corresponding mapping of Al and O.

FIGURE 5: Mapping of oxygen in Al-Al₂O₃ composites mechanically alloyed for 24 h: (a) 2 vol.% and (b) 15 vol.%.

FIGURE 6: XRD spectra of aluminium (a) as-received and (b) mechanically alloyed for 24 h.

FIGURE 7: XRD spectra of Al-Al₂O₃ composites mechanically alloyed for 24 h (a) 2 vol.%, (b) 10 vol.%, and (c) 15 vol.% Al₂O₃.

of 25 nm was reported [39]. In Al-SiC composites reinforced with 1, 5, and 10 wt.% SiC nanoparticles, mechanical alloying for 24 h was reported to decrease the crystallite size of the α -Al phase to 140, 50, and 32 nm, respectively [15].

The microstructure of unmilled aluminium sintered for 5 and 20 min is presented in Figures 9(a) and 9(b), respectively. The effect of milling on the microstructure of aluminium

TABLE 3: Crystallite size of α -Al phase in mechanically alloyed aluminium composites.

Composite	Crystallite size (nm)	Ref.
Al-15 vol.% Al ₂ O ₃	27.24	This work
Al-10 vol.% Al ₂ O ₃	32.69	This work
Al-2 vol.% Al ₂ O ₃	39.82	This work
Pure Al MA for 24 h	62.29	This work
Pure Al unmilled	298	This work
Al-10 wt.% SiC	32	[15]
Al-5 wt.% SiC	50	[15]
Al-1 wt.% SiC	140	[15]
Pure Al	298	[15]
Al-SiC	—	[35]
Al-6 wt.% SiC	69	[36]
Al-1.2 wt.% SiC	63	[36]
Al-10 SiC-CNT	32	[37]
Al-5 SiC-CNT	34	[37]
Pure Al	141	[37]
Al-5356/B4C	36	[38]
Al5083-10 wt.% SiC	25	[39]

sintered for 5 and 20 min can be clearly seen in Figures 9(c) and 9(d), respectively. The microstructure of unmilled and sintered aluminium for 5 minutes is characterized by relatively large grains. The increase in sintering time from 5 to 20 minutes resulted in grain growth. The effect of milling for 24 h and sintering for 5 minutes can be clearly seen in Figure 9(c) where a very fine microstructure characterized by elongated grains was obtained. The increase in sintering time from 5 to 20 minutes led to significant grain growth as seen in Figure 9(d). It is well known that sintering time plays an important role in isothermal grain growth, which can be expressed with the formula $G^n - G_0^n = Kt$, where G_0 and G are the grain sizes at initial time t_0 and isothermal holding time t , respectively. K is a temperature-dependent parameter.

FIGURE 8: Crystallite size of α -Al phase in (1) Al MA for 24 h and Al- Al_2O_3 composites (2) 2 vol.%, (3), 10 vol.%, and (4) 15 vol.% mechanically alloyed for 24 h.

It can be concluded that grain growth in the milled nanocrystalline aluminium was much less compared to the unmilled aluminium. This may be due to recrystallization of the heavily milled and deformed structure. Moreover, it is claimed that nanocrystalline materials often exhibit a remarkable resistance to grain growth [40].

Typical microstructures of Al-15 vol.% Al_2O_3 sintered for 5 and 20 min are presented in Figures 10(a) and 10(b), respectively. The increase in sintering time from 5 to 20 minutes led to marginal grain growth. Analysis of the microstructure of aluminium, Figure 9(c), and Al-15 vol.% Al_2O_3 , Figure 10(a), milled for 24 h and sintered for 5 minutes shows that both materials have microstructures with similar features and very elongated grains. The grains in the composite material have relatively large size compared to the monolithic material. However, for the same samples sintered for 20 minutes, the monolithic material, Figure 9(d), had a microstructure with relatively large and equiaxed grains while the composite material, Figure 10(b), had a microstructure with relatively small and elongated grains. It can be concluded that Al_2O_3 significantly contributed to grain growth inhibition when samples were sintered for 20 minutes.

Relative density of the consolidated samples is presented in Figure 11. The as-received pure aluminium consolidated at 550°C for 5 minutes had a relative density of 98.88%. The increase in sintering time to 20 minutes increased its relative density to 100%. The pure aluminium milled for 24 h and consolidated at 550°C for 5 minutes had a relative density of 95.92%. The increase in sintering time to 20 minutes resulted in a minor change of density to 95.18%.

The Al-2 vol.% Al_2O_3 composite consolidated at 550°C for 5 minutes had a relative density of 98.16%. The increase in sintering time to 20 minutes decreased its relative density to 95.50%. The Al-10 vol.% Al_2O_3 composite consolidated at 550°C for 5 minutes had a relative density of 100%. The increase in sintering time to 20 minutes did not change its density. The Al-15 vol.% Al_2O_3 composite consolidated at 550°C for 5 minutes had a relative density of 91.69%. The increase in sintering time to 20 minutes did not affect its density.

Analysis of density results presented above shows that relative density of 100% was achieved for pure unmilled

aluminium sintered for 20 min; that is, it was fully densified. However, milling for 24 h reduced its densification to 95%. The addition of 2 vol.% of Al_2O_3 increased the densification compared to pure aluminium milled for 24 h. Further increase of Al_2O_3 content to 10 vol.% led to full densification of the sample. However, the increase in Al_2O_3 content to 15 vol.% reduced the densification to 91%.

Generally, it is believed that “compaction of powder containing grains of nanometer dimensions, especially when ceramic or carbide nanoparticles are incorporated, is more difficult than the compaction of micron-sized powder of the same metal or alloy. This is because plasticity in nanocrystalline samples requires order of magnitude larger stresses and the spring back is more pronounced. Therefore, nanostructured samples are likely to be more porous” [35, 41, 42] and may not sinter to full density easily. On the other hand, conventional sintering involves compaction followed by sintering, but consolidation using SPS is done in one single step which makes sintering and densification behaviours more complex. Overall, sintering time had marginal effect on the densification of samples except the composite reinforced with 2 vol.% of Al_2O_3 which showed a small decrease in its density with the increase in sintering time from 5 to 20 minutes. This small decrease in density could be attributed to the effect of sintering time on the formation and elimination of open and closed pores, which may have been affected by the large size and flattened shape of particles shown in Figure 3(a). It is worth mentioning here that the density of samples was measured according to Archimedes method with the possibility of water intrusion into any remaining open pores [43]; this will slightly affect density values if open pores are present. The increase in Al_2O_3 content to 10 vol.% contributed to the decrease of particle size and led to the formation of more equiaxed particles as seen in Figure 2(d), which may have improved the densification. However, further increase in Al_2O_3 content to 15 vol.% reduced the densification. This could be due to the fact that consolidation of nanocomposite powders becomes more difficult at higher fractions of ceramic nanoparticles.

The hardness of the developed materials is presented in Figure 12. The as-received pure aluminium consolidated at 550°C for 5 minutes had a Vickers hardness of 369.3 MPa. The increase in sintering time to 20 minutes decreased its hardness to 326.3 MPa. This can be attributed to grain growth observed in Figures 9(a) and 9(b). It is understood that the yield strength of polycrystalline materials depends on the grain size according to the expression $\sigma_{ys} = \sigma_0 + kd^{-1/2}$ (Hall-Petch relationship), where σ_0 is the lattice friction stress and k is a Hall-Petch slope. On the other hand, Vickers hardness and yield strength could be related through a simple formula $H_v/\sigma_{ys} \approx 3$. As a result, hardness can be related to the grain size through $H_v = H_0 + kd^{-1/2}$, where H_0 and k are constants. Therefore, the hardness of a material decreases with the increase in grain size.

Pure aluminium ball milled for 24 h and consolidated at 550°C for 5 minutes had a Vickers hardness of 837.8 MPa. The increase in sintering time to 20 minutes decreased its hardness to 421 MPa. The milled aluminium had similar

FIGURE 9: Optical micrographs ($\times 500$) of unmillied aluminium sintered for (a) 5 min and (b) 20 min and aluminium milled for 24 h and sintered for (c) 5 min and (d) 20 min.

FIGURE 10: Optical micrographs ($\times 200$) of Al-15 vol.% Al_2O_3 composite milled for 24 h and sintered for (a) 5 min and (b) 20 min.

behaviour in terms of sintering time effect. However, milled aluminium had higher hardness compared to unmillied aluminium because of smaller grain size.

It is well understood that reducing the crystallite size in metals results in significant enhancement in their mechanical properties. The reduction in crystallite size corresponds to increased dislocation density which causes higher resistance to the sliding of atomic planes and, as a consequence, the metal becomes stronger. Whereas bulk metals can be strengthened through several cold working methods, metals in the form of powders can be effectively strengthened by reducing their crystallite size using mechanical alloying (MA) process. The crystallite size of ball milled metallic powders

can be effectively reduced to nanometer range. In the process, “the powder particles undergo excessive plastic deformation producing complex dense networks of dislocations. Initially, the internal strain increases with increasing dislocation density. As the dislocation density reaches a threshold value in the heavily strained region, the grains break up into much smaller grains with low angle boundaries. These smaller grains undergo further deformation and disintegration as the milling time is increased. Ultimately, the orientation of the grains with respect to each other becomes completely random and the final grain size approaches nanometer scale” [44]. It is worth mentioning here that once the nanostructure is fully developed, additional decrease of the grain size will be

FIGURE 11: Relative density of sintered samples. (1) Al, (2) Al MA for 24 h and Al-Al₂O₃ composites, (3) 2 vol.%, (4), 10 vol.%, and (5) 15 vol.%.

FIGURE 12: Hardness of sintered samples. (1) Al, (2) Al MA for 24 h and Al-Al₂O₃ composites, (3) 2 vol.%, (4), 10 vol.%, and (5) 15 vol.%.

more difficult because large stresses are usually required for the deformation of nanograins. The creation and movement of dislocations under these circumstances are difficult and hence grain boundary sliding becomes the dominant deformation mechanism. The rate of recovery is another parameter which limits the grain size reduction during milling. Partial recovery may occur during mechanical milling, especially for metals with low melting point. For such metals, the formation of high dislocation density regions is hindered by the increased recovery [45]. Once nanocrystalline powders obtained by milling are consolidated, grain growth may take place; however, grain size will remain relatively small compared to unmilled powders, as seen in Figures 9(c) and 9(d), which leads to improved hardness.

The Al-2 vol.% Al₂O₃ composite consolidated at 550°C for 5 minutes had a Vickers hardness of 1113.6 MPa. The increase in sintering time to 20 minutes decreased its hardness to 1098 MPa. The Al-10 vol.% Al₂O₃ composite consolidated at 550°C for 5 minutes had a Vickers hardness of 1463.3 MPa. The increase in sintering time to 20 minutes

decreased its hardness to 1309.7 MPa. The Al-15 vol.% Al₂O₃ composite consolidated at 550°C for 5 minutes had a Vickers hardness of 923.9 MPa. The increase in sintering time to 20 minutes decreased its hardness to 821.9. Hardness followed the same trend as densification. Overall, the increase in Al₂O₃ content up to 10 vol.% increased hardness; a further increase to 15 vol.% decreased it as a result of poor densification and probably less uniform distribution of the reinforcement. The composite reinforced with 10% vol. of Al₂O₃ nanoparticles displaced higher hardness than other aluminium based nanocomposites reinforced with CNTs [46–48] or SiC nanoparticles [33]. However, its hardness was lower than the hardness of Al-10 wt.% SiC nanocomposite [15] and Al5083-10 wt.% SiC [39]. Table 4 shows hardness values of aluminium based nanocomposites consolidated by spark plasma sintering. Data presented in Table 4 clearly shows that the hardness of aluminium based nanocomposites strongly depends on the nature of the matrix, whether pure aluminium or alloy, sintering parameters, and the amount of the reinforcing phase.

As for the composites, the increase in hardness can be attributed to the same factors which lead to the increase in the strength of particle reinforced metal matrix composites. This includes small grain size of the matrix (Hall-Petch theory), presence of nanoparticles (Orowan strengthening), increase in dislocations' density, load transfer from the matrix to the reinforcement, and strain gradient [49–52].

4. Conclusion

Nanocrystalline aluminium and homogenous Al-Al₂O₃ nanocomposites were developed using MA and SPS techniques. The influence of reinforcement content, milling, and sintering conditions on the microstructure, densification, and hardness of the developed materials was investigated. It was found that milling of pure aluminium for 24 h decreased its crystallite size less than 100 nm. For Al-Al₂O₃ nanocomposites, milling for 24 h decreased the crystallite size of the aluminium phase and resulted in uniform dispersion of the reinforcement. Sintering of the synthesised powders led to grain growth. Al₂O₃ contributed to grain growth inhibition when samples were sintered for 20 minutes. Milling improved hardness of aluminium but reduced its densification. Addition of Al₂O₃ nanoparticles resulted in further improvement of hardness. The Al-10 vol.% Al₂O₃ nanocomposite had the highest Vickers hardness value of 1460 MPa.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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TABLE 4: Hardness of aluminum nanocomposites consolidated by SPS.

Composite	K (deg./min)	P (MPa)	T ($^{\circ}\text{C}$)	Time (min)	HV (MPa)	Ref.
Al-15 vol.% Al_2O_3	200	50	550 $^{\circ}$	5	923.9	This work
Al-15 vol.% Al_2O_3	200	50	550 $^{\circ}$	20	821.9	This work
Al-10 vol.% Al_2O_3	200	50	550 $^{\circ}$	5	1463.3	This work
Al-10 vol.% Al_2O_3	200	50	550 $^{\circ}$	20	1309.7	This work
Al-2 vol.% Al_2O_3	200	50	550 $^{\circ}$	5	1113.6	This work
Al-2 vol.% Al_2O_3	200	50	550 $^{\circ}$	20	1098.0	This work
Pure Al BM 24 h	200	50	550 $^{\circ}$	5	837.8	This work
Pure Al BM 24 h	200	50	550 $^{\circ}$	20	421.0	This work
Pure Al	200	50	550 $^{\circ}$	5	369.3	This work
Pure Al	200	50	550 $^{\circ}$	20	326.3	This work
Pure Al	200	50	600	10	313	[15]
Al-1 wt.% SiC	200	50	600	10	1080	[15]
Al-5 wt.% SiC	200	50	600	10	928	[15]
Al-10 wt.% SiC	200	50	600	10	1715.3	[15]
Al5083	300	50	500	3	1480	[39]
Al5083-10 wt.% SiC	300	50	500	3	2500	[39]
Al2124	100	35	500	20	1102.4	[46]
Al2124 + 1 wt.% CNTs	100	35	500	20	1181.9	[47]
Al6061	100	35	450	20	660	[47]
Al6061 + 1 wt.% CNTs	100	35	450	20	710	[47]
Al-7Si-0.3Mg	100	35	500	20	630	[48]
Al-7Si-0.3Mg + 0.5 wt.% CNTs	100	35	500	20	680	[48]
Al-12Si-0.3Mg	100	35	500	20	680	[48]
Al-12Si-0.3Mg + 0.5 wt.% CNTs	100	35	500	20	830	[48]
Al-7Si-0.3Mg	100	35	500	20	630	[33]
Al-7Si-0.3Mg + 5 wt.% SiC	100	35	500	20	710	[33]
Al-7Si-0.3Mg + 12 wt.% SiC	100	35	500	20	750	[33]
Al-7Si-0.3Mg + 20 wt.% SiC	100	35	500	20	690	[33]

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