CHAPTER - V

Influence of Ultrasonic Cavitation on Microstructure and Mechanical Response of an Aluminum/alumina Nanocomposite
5.1 Introduction

Metal matrix nanocomposites (MMNCs) have been attracted a lot of attention among the researchers for their numerous applications in automobile, aerospace and military industries [233-247] due to their significant mechanical properties like high specific strength, long fatigue life and improved thermal stability [248]. Several fabrication methods like mechanical alloying with high energy ball milling, nano sintering, vortex process, spray deposition, electrical plating, sol-gel synthesis, laser deposition etc. have been adopted for the synthesis of nanocomposites [235, 237, 239, 246]. The mixing of nanosized particles is time taking, energy consuming and expensive in mechanical alloying technique. However, synthesis of composite by a liquid phase process is very attractive as it can produce light weight nanocomposite with uniform dispersion of ceramic nanoparticles [238, 239]. The uniform dispersion of nano particulate is necessary to enhance the elastic modulus, hardness and tensile strength of the engineering components. Especially, the use of nanocomposite bears measure importance in automobile and aerospace industries, for the fabrication of low density and high mechanical strength equipments which can save the fuel cost [240-243]. This is the reason for which aluminium is chosen as the major industrial components. Aluminium alloys though possess low density, but it is lacking with high strength like steel and titanium alloys. Hence, an attempt has been taken to form nanocomposites of Al by solid state processing route or powder technology route [254-264] to enhance the mechanical strength. However, to form fully bulk sized engineering component [255] by the uniform dispersion of nano particulates in the metal matrix is a challenge in powder technology route. It is known that uniform dispersion of fine ceramic particles in the metal matrices increase the strength and wear resistance of the materials [257]. However, it is almost difficult to find the uniform dispersion of particles in solidification route due to the difference between the interaction of liquid and solid particles [259]. In this view, ultrasonic casting [260-262] is a suitable technique to forbid the agglomeration of nanoparticles in the metal matrix and to distribute nano sized particulates uniformly in molten melt to enhance the mechanical behaviour of the nanocomposite. High yield strength in cast Al-7wt% Si alloys by reinforcing with 2wt% nano sized (30nm) SiC particles has been observed by Yang et al [135] with the advantage of the density close to...
pure Al. Hence, the non-contact ultrasonic method was almost able for uniform dispersion of nano particulates in metal matrix to increase the strength of the composites with the same density of the pure metal.

In this paper, metal matrix nanocomposites were synthesized by ultrasonic full cavitation technique by two ways mixing process to avoid the agglomeration and clustering of nanoparticles. The structural and mechanical properties have been studied using various experimental tools to prove that the ultrasonic cavitation technique is a novel technique for the synthesis of metal matrix nanocomposites.

5.2 Experimental Details

For the production of nano sized Al$_2$O$_3$ particulates of average size 10-12 nm, commercial available alumina powder of micron size were ball milled for 72h using a high energy Fritsch Pulverisette-5 planetary ball mill with WC grinding balls. The ball milling was done at 300 RPM and the tollune was used as the reagent. Commercial available aluminium of composition of 0.96%Fe-0.43%Mg-0.26%Si was reinforced with this nanosized Al$_2$O$_3$ by the non-contact full cavitation method. The schematic diagram of the experimental setup is shown in Fig. 5.1, consists of an ultrasonic generator (MAKE: RK-100H BANDELIN-GERMANY). The mixing of nanosized powders with aluminium melt has been performed by primary and secondary mixing process. In primary mixing, the nano particulates were mixed up with molten aluminium melt with the help of a vibrating motor. Aluminium was melted at a temperature of 760 °C and the melt had been placed in the ultrasonic chamber. An ultrasonic chamber consists of a steel die of 60 mm length, 40 mm diameter and 1.5 mm thick and a primary mixing unit. Sufficient water circulation facility has been provided around the die for transmission of ultrasonic waves from all sides of the chamber. The mould was heated with an ambient temperature to avoid thermal cracking and was placed in an ultrasonic chamber under frequency of 35 KHz. Further, nearly 350 g of liquid aluminium and 1.5 weight % of alumina nano particulates were poured into vibrating mould. The vibration was continued for five minutes. The mould inside the ultrasonic chamber is surrounded by water for proper transmission of ultrasonic waves. Within few minutes solid nanocomposite was formed.
Figure 5.1: Schematic Diagram of ultrasonic full cavitations experimental setup.

The nanocomposite ingot was cylindrical in shape and cut along the transverse direction in two equal halves. Then one half of the composite was cut longitudinally into five small pieces nearly of equal size of 1 cm² cross sectional area and 0.5 cm thickness (shown in Fig. 5.2).

Figure 5.2: Cross sectional view of the ingot.
Each of the specimens is numbered as ‘a’, ‘b’, ‘c’, ‘d’ and ‘e’ respectively from left to right. Then each sample surface was ground and polished with submicron size emery paper of 100 and 200 grits. These grounded and polished specimens were considered for the characterization to have a physical and mechanical feature of the nanocomposites. To study the distribution of nanoparticles in the Al matrix and the microstructure, transmission characterization has been carried out including the selected area electron diffraction analysis. X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a VG ESCA system using the Mg Kα X-ray source with pass energy of 20 eV at a base pressure of $1.0 \times 10^{-10}$ Torr. To have a detailed idea about hardness and Young’s modulus, nano-indentation tests have been performed with respect to penetration depth for each of the specimens using a UMIS nanoindentation system (Fisher Cripps, Australia). The load vs penetration depth, hardness vs penetration depth and Young’s modulus vs distance have been measured for each location of the sample one by one with the help of nano-probe indentation using a diamond Bekovich indenter. The maximum load of the nano-probe indentation was restricted to 20 mN. The mathematical expression used for the determination of hardness and Young’s modulus using nano indenter has been described in literature [265, 266].

5.3 Results and Discussion

![Figure 5.3: (a)TEM picture and (b) selected area electron diffraction patterns of Al and Al₂O₃ nanocomposites.](image)

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Fig. 5.3a shows the transmission electron micrograph of Al and Al$_2$O$_3$ composites. The micrograph shows the uniform distribution of nanocomposites of Al$_2$O$_3$ throughout the Al matrix. The white coloured spot represents the nanoparticles of Al$_2$O$_3$ whereas the black coloured surface represents the Al matrix. The average size of alumina nanoparticles is within the range of 5 nm. Even the size of the nanopowders of alumina is taken in the order of 10-12 nm in the Al matrix but during mixing, there is a possibility of fragmentation of nanoparticles due to ultrasonication which gives rise to the decrease in particle size of the composite. Similar type of micrographs has been observed throughout the matrix with a slight variation of particle size. This confirms that the ultrasonic cavitation technique is a well mixing technique for the formation of nanocomposites of Al and Al$_2$O$_3$ in comparison to the conventional technique. To confirm about the presence of Al and Al$_2$O$_3$, selected area electron diffraction pattern has been shown in Fig. 5.3b.

The SAED pattern always provides information about the crystallographic idea of Al and Al$_2$O$_3$. The pattern clearly establishes the long range ordering of Al and Al$_2$O$_3$ matrix in a particular crystallographic orientation. The crystallographic plane of the nanocomposite Al$_2$O$_3$ is very difficult to be established from X-ray diffraction analysis with consideration to the Al. The maximum interplanar spacing between two atomic planes is of the order of 2.337 Å in Al [267] whereas the same interplanar spacing in Al$_2$O$_3$ is of the order of 2.551 Å [268]. Hence, X-ray diffraction pattern is unable to establish the presence of Al and Al$_2$O$_3$ within the resolution of X-ray. However, the selected area electron diffraction pattern is a novel tool to distinguish the presence of Al and Al$_2$O$_3$ that has been clearly reflected in Fig. 5.3b with the crystallographic planes. The crystallographic planes representing Al$_2$O$_3$ are indexed in the SAED pattern. The TEM picture and SAED patterns reflect the uniform distribution of nanopowders of Al$_2$O$_3$ in Al matrix which may enhance the mechanical performance of the composites.

The survey spectrum with the individual spectrum of C, O and Al are shown in Fig. 5.4. The survey spectrum (Fig. 5.4a) reveals the presence of Al and O including a high intensified peak of C1s. The signature of the C1s is coming from the environment and from the sample holder in which carbon tape is used to stick the sample. The C1s peak is taken as a standardised binding energy to analyse other elements present in the sample. The C1s spectrum is shown in Fig. 5.4b. The binding energy at 284.6 eV attributes to free
carbon [213] which means that the signature of C found in the composite is not a contaminant of the nanocomposites.

![Figure 5.4: X-ray photoelectron (a) survey spectrum; (b) C1s core level; (c) O1s core level; and (d) Al2p core level X-ray photoelectron spectrum of Al/Al₂O₃ nanocomposites.](image)

The X-ray photoelectron spectra for Al2p and O1s are shown in Fig. 5.4c &5.4d. The maximum intensity of the O1s peak is centered at 531.1 eV (Fig. 5.4c). This binding energy is attributed to the bonding of Al with O. It infers that alumina is present in the sample with Al matrix. However, the presence of Al matrix is established from core level spectrum of Al. The core level spectrum of Al2p is shown in Fig. 5.4d. The characteristic curve is deconvoluted into three peaks. The lower binding energy and medium binding energy at 70 eV and 72.9 eV are attributed to the Al whereas higher binding energy at 74.6
eV is attributed to the bonding of Al and O [213]. This infers that both Al and Al$_2$O$_3$ are present in the nanocomposites.

Figure 5.5: Load vs penetration depth of Al and Al$_2$O$_3$ nanocomposites for all five specimens taken from the half of the cylindrical cross section.

The load vs penetration depth is shown in Fig. 5.5 for the entire specimen specified in Fig. 5.2 for Al and Al$_2$O$_3$ nanocomposites. The maximum load of 20 mN is applied in all specimens with a variation of 1mN for each set of measurements having a drift rate of 0.06nm/s. With the increase of load, penetration depth increases. Fig. 5.5 (a), (b), (c), (d) & (e) show that in first cycle of applied load for a maximum load of 20mN, the penetration depths are 0.55 $\mu$m, 0.52 $\mu$m, 0.57 $\mu$m, 0.58 $\mu$m and 0.54 $\mu$m respectively. For the same maximum load of 20mN, the penetration depth varies in a range of ± 0.03 $\mu$m. It is observed that at the periphery regions (location ‘a’ and ‘e’), the penetration depths are almost constant whereas in the middle regions, the penetration depth is slightly more. This is because of the distribution of more nanoparticles or presence of more agglomerates in periphery region in comparison to the middle portion. It is occurring due to the action of centrifugal force on nanoparticles during the mixing of matrix and nano powders. So nearer the periphery region, the depth of indentation is less in comparison to the middle region of the bulk composite. For the first cycle of the measurement, it is observed that the
penetration depth is almost equal (0.55±0.03 μm). This means that distribution of nano alumina powder is uniform throughout the matrix for which the penetration depth does not alter which may enhance the hardness and elasticity modulus. The study infers that nanoparticulates are mostly having even distribution throughout the aluminium metal matrix which is evidenced from the TEM picture.

Figure 5.6: Hardness vs penetration depth of Al and Al₂O₃ nanocomposites for all five specimens taken from the half of the cylindrical cross section.

Figure 5.6 shows the hardness vs penetration depth of Al and Al₂O₃ nanocomposites for five specimens. It is observed that the monotonic variation of hardness as the penetration depth increases with the application of load and pertain the same line profile for all five location of the sample. It is observed in Figure 5.6 that when penetration depth is small, hardness is more. As penetration depth increases, hardness gradually decreases. It is observed that for a constant penetration depth of each of the location, the hardness value is almost same. For all five samples from different locations hardness is almost same which signifies the uniform distribution of nanoparticles in the aluminium matrix. This gives isotropic mechanical properties of the composites.
Figure 5.7: Young’s modulus vs penetration depth of Al and Al₂O₃ nanocomposites for all five specimens taken from the half of the cylindrical cross section.

Figure 5.7 (a, b, c, d and e) show the plots between Young’s modulus vs penetration depth for all the locations of the sample. These figures show that when the penetration depth is less, Young’s modulus is more. The elastic property is more in a nanoparticle system in comparison to the bulk sample. As penetration depth increases, Young’s modulus gradually decreases due to clustering of nanoparticles in some locations. In periphery region (a) and (e), for a depth of 0.55 μm, the difference of elasticity value is not significant. That means for a particular depth of applied load, values of Young’s modulus are almost same for each location. This also ensures that nanoparticles have almost even distribution throughout the metal matrix. The load, hardness and Young’s modulus vs penetration depth establish a fact that the ultrasonic full cavitation technique is most suitable technique for the preparation of nanocomposites with uniform distribution of nanoparticles throughout the matrix. In addition to this, the restriction of agglomeration of
the nanoparticles in the matrix is also another advantage to enhance the physical and mechanical behaviour of the metal matrix nanocomposites.

5.4 Conclusions

Following conclusions have been made from our experimental observations:

- Non-contact full cavitation technique is a novel route for synthesis of nanocomposites.
- TEM analysis indicates the uniform arrangement of nanoparticles through the metal matrix and the average size of the nanoparticles are in the order of 5nm. The SAED analysis shows the presence of both Al and Al₂O₃.
- The hardness, Young’s modulus results infer that alumina nano particulates are distributed uniformly over the aluminium metal matrix.
- This uniform distribution will increase the strength, light weight and hardness of the nanocomposite more than the metal matrix and micrometric composite.