Mechanical properties and Corrosion Resistance of nano-Ceria doped Aluminium

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ABSTRACT

Nano Ceria (CeO_2) powder was synthesized by low temperature combustion method using citric acid as fuel. The final product was characterized by means of Scanning Electron Microscopy (SEM) and Powder X-Ray Diffraction (PXRD). The powder blends of nano-CeO2/Al were prepared by low energy ball milling and the composite blocks of nano-CeO2/Al were fabricated with powder metallurgy technique. The microstructure, micro hardness, wear resistance and corrosion resistance of the nano-CeO2/Al blocks were studied by the means of SEM, Vickers Micro hardness Tester, Pin on disk apparatus and Weight Loss Method respectively. From the comparison of powder metallurgy samples bearing different nano-CeO2 contents for corrosion resistance, micro hardness, wear resistance and microstructure, the optimum content of nano-CeO2 was evaluated. The results show that micro hardness, grain structure and wear resistance can be improved significantly with addition of nano-CeO2; at the same time, the optimal micro hardness and microstructure are obtained when the mass fraction of nano-CeO2 is 1.0% where as sample with 5wt% of Nano-CeO_2 showed best wear resistance. Corrosion tests reveal that there was no mass loss due to corrosion.

***Keywords* - Corrosion resistance, Microhardness, Microstructure, Nano CeO2, Wear resistance

1. INTRODUCTION

Among the composites, Aluminum matrix composites attract much attention due to their lightness, high thermal conductivity, and moderate casting temperature. Engine pistons, engine blocks and other automotive and aircraft parts operating under severe friction conditions are fabricated from reinforced aluminum matrix composites. Various kinds of ceramic materials, e.g. SiC, Al_2O_3, MgO and B_4C, are extensively used to reinforce aluminum and its alloys [1]. Superior properties of metal oxides such as refractoriness, high hardness, high compressive strength, wear resistance etc. make them suitable for use as reinforcement material in metal matrix. Incorporating ultra fine particles of metal-oxides significantly improves mechanical properties of the metal matrix by reducing the inter-particle spacing and providing their inherent properties to the metal matrix since they get embedded uniformly into it. However, fine particles represent higher tendency toward agglomeration. Therefore, optimum particle size, amount of reinforcement and processing parameters (compaction pressure, sintering temperature, sintering time) should be determined for each technique and matrix. Nano-particles represent appropriate wettability with metal at the time of sintering and good stability as well [2].

The improvement of corrosion resistance by rare earth elements added to pure Zn has been the purpose of studies by Hilton et.al and Wilson et.al firstly in 1980s. It is suggested that the $CeCl_3$ of 1.0 g/L can make the corrosion velocity of the pure zinc as low as 1/10 of original, and that of the electroplating zinc as low as ½ of original. After the corrosion experiments, there is a layer of yellow film on the surface of both the pure Zn and electroplating zinc. And then Hilton et.al studied the composition and structure of the film thoroughly, and discovered that the main compositions in the film were CeO_2 and Zn. In this work, the nano-CeO_2/Al powder blends were used to prepare nano-CeO_2/Al blocks by cold pressing followed by sintering, and the performance of the fabricated blocks was studied [3,4].

2. EXPERIMENTAL

2.1. Synthesis of nano-CeO_2 powder

The CeO_2 nanopowder was prepared by dissolving cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) and citric acid ($C_6H_8O_7$) in a minimum quantity of double distilled water in a Pyrex dish. The dish containing the solution was introduced into a pre-heated muffle furnace maintained at 400 ± 10 ºC. The solution initially boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases. At the point of spontaneous combustion, the solution begins burning and releases lot of heat; all the solution vaporizes instantly and becomes a burning solid. The entire combustion process for producing CeO_2 powder takes only 5 min. The formation of CeO_2 can be represented by the following reaction:

$2Ce(NO_3)_3$ (aq) + $C_6H_8O_7$ (aq) → 2 CeO_2 + $6CO_2$ (g) + $2H_2O$ (g) + 3 N_2 (g) .... (1)

2.2. Preparation of nano-CeO_2/Al powder blends.

Nano-CeO_2 powder produced by combustion method was added to 99.5% pure commercially available aluminium powder with wt% of nano-CeO_2 varying from 0 to 5%. Aluminium powder which was used had average particle size of 74 microns. Powders were mixed for 30 minutes by hand mixing and loaded in metal die for compaction.

2.3. Preparation of nano-CeO_2/Al blocks.

Nano-CeO2 doped Al blocks are fabricated with powder metallurgy technique. Powder blends were cold pressed at 150 Mpa to approximately 90% compression and then sintered at 520 °C for 1hour. The sintered nano-CeO_2/Al blocks were polished with emery papers with grit size ranging from 200 to 2000 followed by diamond paste polishing for obtaining mirror finish surface on the specimen blocks.

2.4. Microstructure analysis of nano-ceria/ Al blocks.

Light and Scanning Electron Microscopy (SEM) were employed to analyze the microstructure of the polished nano-CeO_2/Al blocks.

2.5. Micro-hardness test.

Micro hardness was tested using Vickers Micro-hardness tester with diamond indenter in the form of right pyramid and a square base shown in Fig1. An optical microscope with up to 400x magnification along with a Micrometer attachment in the eye piece was used to observe and measure the length of the diagonal of indentation. Microscope attachment helps in determining the distribution of nano-CeO_2 dopant in the samples doped at percentages ranging from 0-5%.

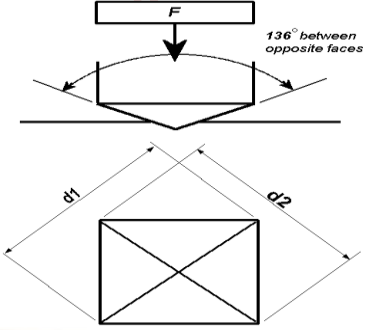


Figure1 Geometry of diamond indenter

Formula used:

$$HV = \frac{2F\sin\frac{136^{o}}{2}}{d^{2}} \qquad HV = 1.854\,\frac{F}{d^{2}}\ \text{approximately} \qquad \text{... (2)}$$

Where 'F' is Load applied in N, 'd' is the average diagonal of indentation and 'HV' represents Vickers Hardness Number.

2.6. Wear resistance test.

Pin on disc apparatus was used to measure the wear resistance of the samples. Nano-CeO_2/Al samples of size 12x12x20 mm^3 were fabricated and mounted on Pin on disk apparatus and made to rub against the rotating stainless steel disk. Area exposed to wear was 12x12 mm^2. Relative velocity of wear test sample with respect to the rotating disk was 2.6 ms^{-1} and sliding distance was 1.57 km. Mass loss due to wear was calculated for each sample after completion of wear test.

2.7. Corrosion resistance test.

Two separate tests were performed to evaluate the corrosion resistance of the nano-CeO_2/Al blocks-

2.7.1 The specimens were soaked in the spray tank with 3.5% NaCl solution for 40 hr and then were rinsed, dried and weighed. The corrosion resistance was evaluated by the mass loss per area, $\Delta m/S$ (Δm is the mass loss and S is the surface area).

2.7.2 The specimens were soaked in the spray tank with 0.5 mol $MgSO_4$ solution for 6 hr and then were rinsed, dried and weighed.

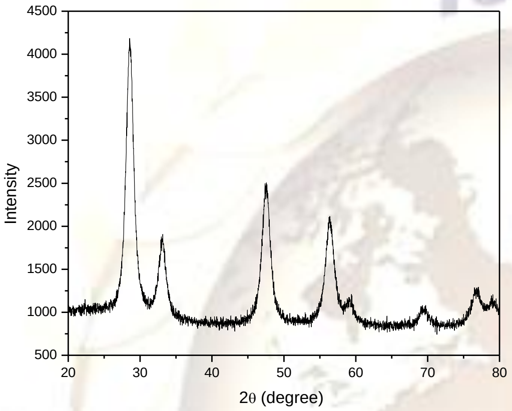
3. RESULTS AND DISCUSSIONS

3.1. XRD and SEM analysis of nano-ceria synthesized by combustion method.

The crystallinity and purity of the prepared product has been confirmed by powder X-ray diffraction. Fig. 2 shows PXRD of CeO_2 nanoparticles which shows a well defined peaks located at 2θ = 28.5, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7, 79.1 are corresponding to (111), (200), (220), (311), (222), (400), (331), (420) planes respectively. All these peaks can be indexed to the face centered cubic phase of CeO_2 (JCPDF cards no 81–0792). No other peak related to impurities was detected. The average crystallite size was estimated using the Debye–Scherer's equation:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \text{...............} \qquad (3)$$

where β is FWHM (rad), λ is wavelength of X-rays,



θ is diffraction angle. The average crystallite size (d) as formed CeO_2 nanoparticles is 10 nm.

Figure2 PXRD pattern of as-formed and CeO_2 nanoparticles

Fig.3 shows the SEM micrograph of CeO_2 nanoparticles. The as-formed nanoparticles are agglomerated from few microns to a few tenths of microns, fluffy and plate like clusters in nature.

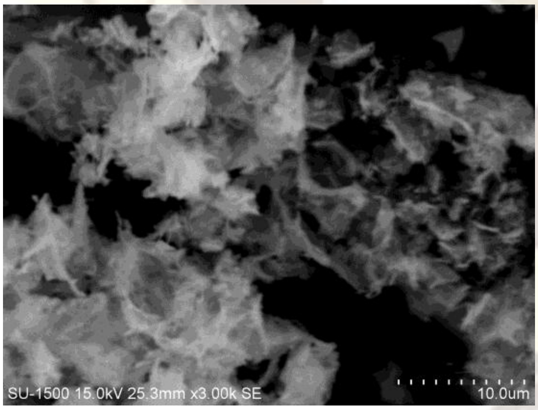


Figure3 SEM micrographs as-formed nano-CeO_2

The agglomeration of nanoparticles is usually explained as a common way to minimize the surface free energy. The voids and pores present in the sample are due to the large amount of gases produced during combustion synthesis.

3.2. Micro structure analysis of sintered nano-CeO_2/Al blocks.

Nano-CeO_2 particles can be seen well embedded in the grains of aluminium matrix in Fig 4, as a result of which the structure becomes denser and grains compact. Nano-CeO_2 particles are evenly distributed in Al matrix in case of lower doping percentages (0% to 1%) and agglomeration of nano-CeO_2 cannot be seen in major part of the Al matrix as shown in Fig4. This indicates that the material has uniform structure and steady performance at doping percentages less than 1%. At higher doping percentages (2.5% and 5%), agglomeration of nano-CeO_2 is more common in the Aluminium matrix and the nano-CeO_2 particles are not evenly distributed as shown in Fig5 and Fig6. This uneven distribution and agglomeration of nano-CeO_2 in the Al-matrix leads to density variations from one region of the matrix to another, porosity, non-uniform structure and unsteady performance. Agglomeration of nano-CeO_2 can lead to increase in porosity of the Al-matrix around the agglomerations as a result of difference in thermal expansion coefficient from one location in the matrix to another. Porosity is more commonly seen in the sample with 2.5wt% of nano-CeO_2 and lesser in 1wt% since pore formation took place mostly around the nano-CeO_2 reinforcement embedded in the host matrix. But due to agglomeration of nano-CeO_2 in the aluminium matrix at high wt%, the porosity in the matrix around sights of agglomeration is high and leads to reduction in uniformity in the matrix.

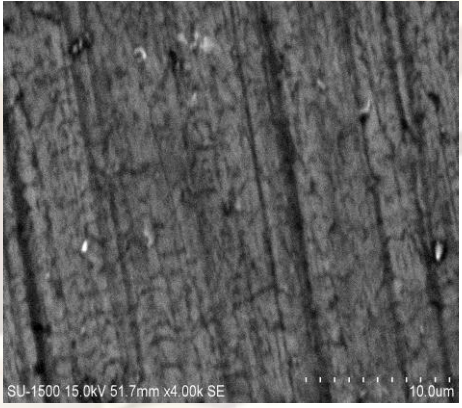


Figure4a SEM of Pure Al matrix

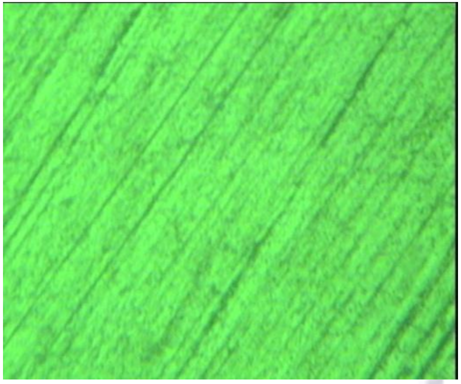


Figure4b Optical Microscopy of Pure Al matrix (400x magnification)

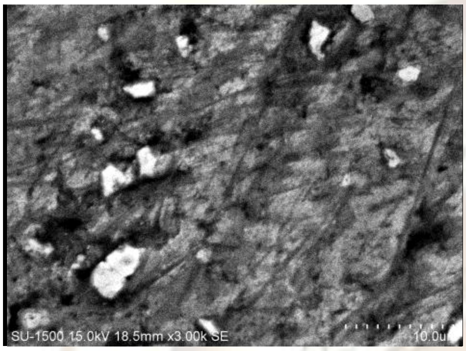


Figure5a SEM image of 1% ceria doped Al matrix

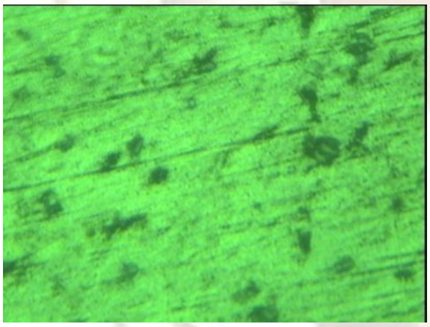


Figure5b Optical Microscopy of 1% Ceria doped Al matrix (400x magnification)

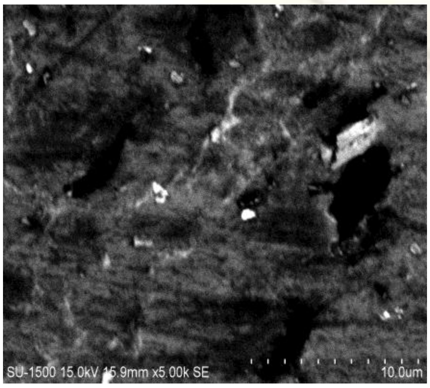


Figure6a SEM image of 2.5% ceria doped Al matrix

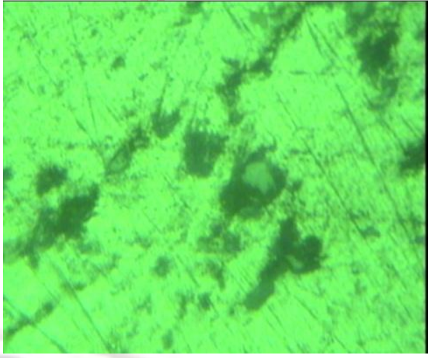


Figure6b Optical microscopy of 2.5% ceria doped Al matrix (400x magnification)

3.3. Micro hardness test.

Fig7 depicts the variation of microhardness with addition of nano-CeO_2. Micro hardness of nano-CeO_2 doped aluminium blocks increased with increase in percentage of nano-CeO_2 from 0-1% concentration by weight and then reduced with further increase in weight percentage. Sample prepared with 1wt% of nano-CeO_2 tested for maximum micro hardness of 618Hv/0.5kg. Sample block of pure aluminium without doping showed micro hardness of 478Hv/0.5kg. Small increase in micro hardness value is observed at lower doping percentages of 0-0.5%. This means that hardness of Al matrix has been increased by the addition of nano-CeO_2 crystals since they can be seen embedded into the Al matrix when observed in the microscope [5]. High interfacial bond strength between the ceramic reinforcement bearing superior hardness and host matrix is also evident due the increased micro hardness value of the doped samples[6]. At low wt% of nano-CeO_2 in Al matrix, many areas of the Al matrix do not receive reinforcement from the nano-CeO_2 since it is not distributed to all parts of the matrix evenly.

1wt% of nano-CeO_2 in Al matrix was determined as the optimum wt% since maximum micro hardness was achieved in this sample block. This is due to the uniform distribution of reinforcement particles into the Aluminium matrix because nano-CeO_2 can be seen embedded in all areas of the matrix uniformly when observed under 400x magnification.

Sample blocks of aluminium with 2.5wt% and 5wt% of nano-CeO_2 as reinforcement material show lower micro hardness than 1wt% sample and show reduction in micro hardness with increase in wt% of nano-CeO_2 beyond 1%. Due to higher wt% of nano-CeO_2, agglomeration of the nano-CeO_2 crystals can be seen at various sites in the matrix and leads to non-uniform distribution of the reinforcement material, non uniform grains in the matrix and non uniform thermal expansion coefficient within the sample blocks which results in matrix with uneven hardness from one region to the other.

Overall it can seen that nano-CeO_2 can be used to increase the micro hardness of aluminium matrix since nano particles get embedded into the grain boundaries, result into uniform and finer grain size in the matrix at the time of sintering. Finer and uniform grain size represents higher micro hardness since grain boundary dislocations are reduced.

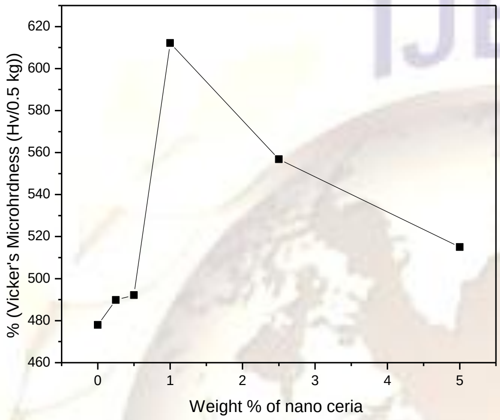


Figure7 Variation of micro hardness with addition of nano-CeO_2

3.4. Wear Resistance.

Wear resistance of the samples was evaluated in terms of mass loss in samples after the wear test was carried out and results are summarized in Table 1. With the increase in wt% of reinforcement in the samples, mass loss due to wear reduced. Pure Al sample showed highest mass loss of 0.0277gm where as the sample reinforced with 5wt% of nano-CeO_2 showed least mass loss of 0.0190gm. Clearly, it can be seen that increase in wt% of nano-CeO_2 in Al matrix improves the wear resistance significantly. This increase in wear resistance can be attributed to addition of ultra fine ceramic reinforcement which posses high hardness, wear resistance and at the same time a strong interfacial bonding with the host matrix [7, 8].

Wt% of nano-CeO_2	0%	1%	5%
Initial Weight (gm)	3.9355	2.6275	2.7621
Final Weight (gm)	3.9078	2.6035	2.7423
Weight Loss (gm)	0.0277	0.0240	0.0198

Table 1 Weight loss in samples after wear test

3.6. Corrosion Resistance.

Corrosion tests reveal that there was no mass loss in the samples after the corrosion testing was carried out for 40 hours with 3.5wt% NaCl solution and 6 hours with 0.5M $MgSO_4$ solution (Table 2 and 3). This can be inferred as high corrosion resistance property of aluminium powder metallurgy products since sample blocks not doped with ceria also exhibit no mass loss after getting exposed to corrosive solutions at the time of testing. Highly compact grain structure and formation of protective alumina layer on the exposed surface can be attributed for the high corrosion resistance of the samples.

Table 2 After corrosion for 40 hours with 3.5% NaCl solution

Wt% of ceria in sample	Initial weight(gm)	Final weight(gm)
0	19.5588	19.5590
0.10	9.7365	9.7364
0.25	8.2445	8.2446
0.50	8.9059	8.9059
1.00	11.0571	11.0573
2.50	16.6144	16.6148
5.00	14.3113	14.3115

Table 3 After corrosion for 6 hours with 0.5M solution of $MgSO_4$

Wt% of ceria in sample	Initial weight(gm)	Final weight(gm)
0.00	19.5590	19.5594
0.10	9.7364	9.7364
0.25	8.2446	8.2449
0.50	8.9059	8.9062
1.00	11.0573	11.0579
2.50	16.6144	16.6145
5.00	14.3115	14.3115

4. CONCLUSIONS

The present study demonstrates CeO_2 nanopowder can be synthesized by a low temperature solution combustion method using cerium nitrate and citric acid. nano-CeO_2 reinforced aluminium matrix showed improved micro hardness and microstructure as compared to pure Al matrix. Nano-CeO_2 crystals are well distributed in the Al matrix when doping percentage is increased from 0.1 to 1% and impart there ceramic properties to the matrix like high hardness, corrosion resistance and strength due to increased densification of the matrix. Optimum wt% of Nano-CeO2 was found to be 1% with regard to uniform distribution of the reinforcement and highest micro hardness value of 612.18Hv/0.5kg among all the samples that were evaluated. Increasing trend in wear resistance of samples with increase in wt% of nano-ceria shows that ceramic particles as nano-reinforcement can impart superior wear resistance to the host aluminium matrix. Metal oxide nano particles are very efficient at imparting their inherent properties to the host matrix like high hardness, refractoriness and strength since they have high surface area to volume ratio. They reduce inter particle spacing in the host matrix and favor the formation of a more compact matrix.

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