Impact of Ground Nut Shell Ash on Cobalt-Chromium metal matrix composites synthesized using Powder metallurgy process.

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Abstract. Co-based composites are extensively utilized in the field of prosthesis and dental implants. Hybrid composites made using Powder metallurgy process, Co-10Cr-GNSA were studied. The surface morphology of the hybrid composites were studied using Scanning Electron Microscope. The elemental analysis was carried out using X-Ray Diffraction technique. The hybrid composites were analyzed for its various mechanical properties like microhardness, compressive strength, and density. Value of micro hardness of the composite materials showed slight improvement with addition of GNSA reinforcement. The value of density of the hybrid composites was found to be decreasing linearly with the addition of GNSA. Compressive strength of the materials showed a reasonable increment. Wear analysis to study the tribological characterization of the hybrid composites were done with the help of a pin on disc wear testing machine. The wear and COF studies show that with a rise in GNSA content, wear resistance increases because of the presence of oxides of GNSA particles. From the worn out surfaces of the hybrid composite it is concluded that the deformation of the composites takes places initially due to abrasive wear followed by plastic deformation. An electrochemical workstation was used to understand the corrosion characteristics of the hybrid composites in the presence of 3% NaCl electrolytic solution. Co-5Cr-5GNSA hybrid composites exhibit better electrochemical corrosion resistance compared to other specimens.

Keywords: Powder metallurgy, Wear, Corrosion, GNSA

1. Introduction
Now a days more and more people suffer from osteoarthritis disorder, which makes them experience severe pain and discomfort. Recent survey suggests that there are nearly 50 million cases worldwide who are suffering from osteoarthritis disorder and in need of joint replacement surgery [1]. Co-Cr-Mo alloy is the extensively used artificial prosthetic material considering its higher value of wear, hardness and corrosion resistance. Even though Co-Cr-Mo alloys are excellent prosthetic material, still there are certain disadvantages such as wear of implants in the hip joints and problems related to bio compatibility since Mo is not a bio degradable material[2–5]. Therefore it is the need of the hour to
produce a composite with much better wear and corrosion resistance which is also bio degradable and compatible to human body.

The ground Nut Shell Ash (GNSA) which is primarily a biological waste and is available in abundance all over the world. Moreover the GNSA particles have presence of MgSiO3 and AlSiO3 in high concentration .Hence it can be used to replace the hazardous Mo reinforcements[6].

There are many conventional methods to produce wear resistance artificial prosthetic implants such as plasma spraying, physical vapor deposition, electro deposition and chemical vapour deposition. Since these manufacturing processes includes more complex steps and requires costly equipments, the cost of the implants is high. The powder metallurgy technique has its own advantages which include uniform dispersion, low processing cost and ability to manufacture high melting point materials. Hence the powder metallurgy process possesses great potential for producing Co-Cr based hybrid composite materials with highly desirable mechanical properties along with wear and corrosion resistance[7–13].

This work aims to develop a Co-Cr-GNSA hybrid composite material with better wear, corrosion resistance and mechanical properties. In this study, four different compositions based on weight percent is formulated as follows Co-10Cr, Co-10Cr-2.5GNSA, Co-10Cr- 3.5 GNSA and Co-10Cr-5GNSA. The composite powders are mechanically milled and compacted and sintered in order to develop specimens of 8mm cylindrical pellets. The hybrid composites are then studied in order to explore their morphological properties using SEM. The mechanical behavior along with tribological and corrosion resistance behavior were studied and their mechanisms were reported.

2. Materials and Method
The materials CoCr (99.5% purity) which is used in this study were purchased from Mepco Ltd Tamil Nadu, India. The ground nut shell ash (GNSA) powder used in this work is prepared using heat treatment method which is discussed in our pervious paper [6]. Mechanical ball milling process was used for alloying the Co-Cr- GNSA hybrid composites. The process was carried out for two hours and was then compacted into 8 mm diameter pellet which is cylindrical in shape. The value of compaction pressure was set to 750 MPa consistently. After this, the soft green compacts were hardened by forcing them to sintering process at 1000°C for 2h. The morphology of the hybrid composites were studied using a Field Emission Scanning Electron Microscope (FE-SEM). ASTM: B962-13 standards were used to calculate the density of the Co-Cr- GNSA hybrid composites. The ASTM E384 standards were used to study the micro hardness of the hybrid composite pellets at a uniform load and dwell time of 1 kgf and 10 seconds respectively. Compressive strength of the hybrid composites were studied at a scan rate of 5 mm/min, with the help of a Universal Testing Machine (UTM). ASTM G99-05 standards were used to study the wear and friction behavior of the composites. EN 32 steel of hardness 65 HRC was used for the analysis. The specimens were cleaned using acetone solution before and after the wear test. The wear analysis of the composites was done at various sliding conditions such as the load, sliding distance and sliding speed. The electrochemical corrosion tests were simulated on a three electrode workstation using 3% NaCl solution as electrolyte[14–16].

3. Results and Discussion
3.1 Field Emission Scanning Electron Microscope Analysis
FE-SEM images of Co-10Cr- 3.5 GNSA & Co-10Cr-5GNSA hybrid Composites respectively are shown in Figure 1. There is a homogenous mixture of GNSA Particles with Co and Cr particles. The wettability of the GNSA particles was the major factor in achieving uniform amalgamation. It can be noted that due the milling operation the size of Cr particles have reduced to around 500 nm in size and are bonded strongly with Co matrix.

3.2 Microhardness
The microhardness test was done using a Vickers Micro Hardness Testing Machine with the test being conducted at five different points. Figure 2 shows the variation in the average value of microhardness
of the composites at different configurations based on its composition, i.e. Co-10Cr, Co-10Cr-2.5GNSA, Co-10Cr-3.5 GNSA and Co-10Cr-5GNSA. The microhardness of the composites varied from 320 HV to 340 HV. The hardness of Co-10Cr was found to be 320 HV and the introduction of GNSA resulted in an increase in the microhardness. The maximum microhardness was found to be in Co-10Cr-5GNSA composite with a value of 340 HV. The uniform amalgamation of GNSA particles was the major reason for this improvement in microhardness.

3.3 Compressive Strength and Density

With the addition of the GNSA reinforcement the density of the Co-10Cr –GNSA hybrid composites were found to be decreasing. The value of density for Co-10Cr composites was recognized as 8.1 g/cm³ whereas the density of the Co-10Cr-5GNSA hybrid composites were around 7.65 g/cm³ as shown in Figure.3. This reduction in density was attributed by the relatively soft nature of the GNSA particles. With the addition of GNSA particles, the compressive strength of the hybrid composite materials showed slight increase in its value. Figure.3 helps us understand the compressive strength of different combinations of Co-10Cr-GNSA hybrid composites. The compressive strength of Co-10Cr composite was established to be in the region of 380 MPa. The compressive strength has slightly increased to 401 MPa for the Co-10Cr-5 GNSA hybrid composites which is due the presence of AlSiO₃ particles in the GNSA ash content.

Figure 1. FESEM images of Co-10Cr-3.5 GNSA & Co-10Cr-5GNSA hybrid Composite.

Figure 2. Graphical Representation of Co-10Cr-GNSA hybrid composites.

Figure 3. Comparison of Density and Compressive Strength of the Co-10Cr-GNSA hybrid composites.
3.4 Wear and COF Analysis
The loss of material due to wear of the Co-10Cr-GNSA hybrid composites is shown in Figure 4. The variation of wear loss of Co-10Cr-GNSA hybrid composites is depicted as graphical plots. The Figure 4 (A) indicates the wear analysis data of the Co-10Cr-GNSA hybrid composites at different loads (10N, 15N and 20N). The sliding speed (1.5 m/s) and sliding distance (1000 m) were kept constant. The Co-10Cr-5GNSA hybrid composites have witnessed very minimal wear loss at all loading conditions. The wear loss of Co-10Cr-GNSA hybrid composites at various sliding distance and speed is shown in Figure 4 (B&C) respectively. The wear loss has experienced similar trend. With the increase in GNSA concentration in the matrix there is definite resistance to wear and thereby the wear loss is very minimal for the Co-10Cr-5GNSA hybrid composites. The variation in coefficient of friction at different loads, sliding distance and sliding speed for Co-10Cr-GNSA hybrid composites is depicted in Figure 5 (A, B & C). It was observed that with an increase in load, the COF of the hybrid composites increased. Whereas, it reduced with an increase in sliding speed. Overall the Co-10Cr-5GNSA hybrid composites displayed better COF value. This improvement in Wear and friction characteristics is may be attributed to the presence of AlSiO3 compounds in the composite material and also due to the tribo oxide surface layer formation on the surface of the composite specimen. The worn out surface analysis of the Co-10Cr-GNSA hybrid composites after wear analysis is represented in Figure 6. From the worn out surface analysis it can be concluded that there is plastic deformation experienced in hybrid composites which is preceded by abrasive wear.

![Figure 4. Wear Loss plot of Co-10Cr-GNSA hybrid composites.](image-url)
Figure 5. COF plot of Co-10Cr-GNSA hybrid composites.
3.5 Electrochemical Corrosion Analysis.

The corrosion analyses of the Co-10Cr-GNSA hybrid composites were done using an electrochemical work station with three electrodes. The electrolyte which was used in this study is 3% NaCl solution. The polarization curves are obtained by using tafel extrapolation methods as shown in Figure 7. The test results exhibit that the corrosion potential value, Ecorr and the corrosion current value, Icorr of Co-10Cr-5GNSA hybrid composites was found to be better compared to other combinations of hybrid composites. The Ecorr value of Co-10Cr-5GNSA hybrid composites was found to be -0.419 V and Icorr value was around -0.12 mA/cm². The corrosion performance of Co-10Cr-3.5 GNSA was also similar to that of Co-10Cr-5GNSA hybrid composites. The Co-10Cr composite shows lesser corrosion resistance than the hybrid composites as shown in Table 1.

Table 1. Tafel plot fallouts of Co-10Cr-GNSA hybrid composites.

| S.No | Specimen         | Ecorr (V) | Icorr (mA/cm²) |
|------|------------------|-----------|----------------|
| 1    | Co-10Cr          | -0.442±0.051 | 0.5±0.020      |
| 2    | Co-10Cr-2.5 GNSA | -0.437±0.044 | 0.4±0.011      |
| 3    | Co-10Cr-3.5GNSA  | -0.420±0.021 | -0.1±0.003     |
| 4    | Co-10Cr-5GNSA    | -0.419±0.0191| -0.1±0.002     |

Figure 6. Worn out Surface analysis of Co-10Cr-GNSA hybrid composites.

Figure 7. Potentiodynamic polarization plot of Co-10Cr-GNSA hybrid composites.
4. Conclusions
The Co-10Cr-GNSA hybrid composites were studied and their mechanical, wear and corrosion mechanisms were reported.
- The addition of GNSA reinforcement resulted in an increment in the Microhardness of the Co-10Cr-5GNSA hybrid composites (340 HV) compared to Co-10Cr composites.
- The compression strength of the Co-10Cr-5GNSA hybrid composites (401 MPa) has improved considerably than the Co-10Cr composites.
- The value of density of the Co-10Cr-5GNSA hybrid composites showed a considerable decrement due to the addition of less dense GNSA reinforcement.
- The Co-10Cr-5GNSA hybrid composites exhibited a higher resistance to wear.
- Corrosion resistance of Co-10Cr-5GNSA hybrid composites was found to be better than the Co-10Cr composites from the electrochemical corrosion analysis.

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