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Influence of Processing Parameters on Corrosion Behavior of Metal Matrix Nanocomposites

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Abstract

Present paper reports an overview on the processing, corrosion behavior and applications of various metal matrix composites with a special focus on iron based metal matrix nanocomposites. As iron has a much higher melting temperature compared to aluminum, copper and magnesium therefore it is synthesized using powder metallurgy technique. P/M technique is widely used because it provides microstructural control of the phases with or without less excessive interactions between matrix and the reinforcement. Gupta et al. have reported that Fe-Al_2O_3 metal matrix nanocomposites show improved properties which include density, hardness, wear, deformation and corrosion respectively. This research work shows that due to reactive sintering an iron aluminate ($FeAl_2O_4$) phase is formed and hence various properties have been found to improve. It is anticipated that the results of these investigations will be useful in developing better technology for producing higher grade metal matrix nanocomposites.

Keywords: Metal Matrix Nanocomposites (MMNCs); Powder Metallurgy; Corrosion; Scanning Electron Microscopy (SEM); Applications

1. Introduction

With the advancement in technology, natural materials have become incapable of meeting desired capabilities on product. Thus, there is a need of relatively better material which can serve with improved structural, mechanical and electrochemical properties [1-2]. Nanomaterials have emerged as a new class of material where the size of each constituent lies in the range of 1-100 nm. Metal Matrix Nanocomposites (MMNCs) are promising nano materials widely used in transport, aerospace, marine, automobile and mineral processing industries, owing to their improved strength, stiffness and resistance to wear, abrasion, erosion and corrosion [3]. MMNCs employ ductile metallic matrix and brittle ceramic material as the reinforcement [4]. Several processing techniques have been employed for the synthesis of MMNCs which include powder metallurgy (P/M), stir casting, squeeze casting, chemical vapor deposition (CVD), physical vapor deposition (PVD) etc [5-6]. Powder Metallurgy technique makes use of milling of constituent powder followed by compaction in the die to form a green body. Sintering of the green body is then carried out at a high temperature usually in an atmosphere controlled furnace [7]. P/M processed specimen yields homogenized properties and also involves low processing temperature. It also provides better control over the interfacial kinetics which is not possible by any other route [8-9]. Another important factor which plays an important role in determining the properties of composites is the morphology of the particle i.e. distribution and size [10].

Corrosion is an environmental degradation phenomenon which occurs due to the chemical reaction. Moreover, it reflects electrochemical oxidation of metals or metal based composites in reaction with oxygen [11-12]. Electrochemical reaction generally leads to the formation of rust on the surface of the specimen. There have been a lot of reports with respect to the study on the corrosion characteristics of various metals and polymers. However, no systematic attempt has been made to present a review on the corrosion behavior of various metal matrix nanocomposites.

The present paper is an attempt to report the influence of processing parameters on the corrosion characteristics of various metal matrix nanocomposites. A special focus is given towards the study of iron-alumina metal matrix nanocomposites synthesized via powder metallurgy technique. Various electrochemical properties such as corrosion potential (Ecorr), corrosion current density (Icorr), corrosion rate (Cr) and corrosion protection efficiency (μ_p) were evaluated. Structural and surface characterization such as XRD and SEM of various MMNC specimens was also carried out after corrosion studies. It was revealed that the improvement in corrosion characteristics of iron-alumina nanocomposites is due to the formation of iron aluminate ($FeAl_2O_4$) phase.

2. MMNC Production Technologies [13-14]

Production route adopted for the fabrication of MMNC plays a very important role as it determines the properties of the final product. Variation in the processing route with the same composition and amount of the component will lead to different results and characteristics. The technique which uses no final machining or finishing is the most suitable one i.e. the specimen obtained has the final dimensions very much close to the final product. Various production technologies involved for the fabrication of the composites include:

2.1 Solid State Processing

Solid state processing makes use of raw powder processed at high load and temperature. High temperature is employed as it allows the flow of reinforcement in the matrix. During solid state processing there should not be generation of undesirable secondary phases. These undesirable secondary phases may lead to the reduction in the properties of the final product. Two widely used solid state processes are:

2.1.1 Diffusion Bonding

Diffusion bonding technique basically makes use of long ceramic fibers with metallic matrix. This technique uses high loading of pressure along with high temperature as it facilitates tight binding of matrix and fibers. Foil-fiber-foil is a new type of diffusion bonding technique in which sheet of fiber reinforcement and matrix material is used alternatively and then the entire assembly is combined at the last. This joining of the entire assembly takes place with the help of sintering in two steps:
(a) Fabrication of matrix laminates via plastic flow.
(b) Joining mechanism at the interface of fiber and matrix.
This technique produces composites with improved tensile and compressive strength. Only problem associated with this technique is that it employs extremely high compaction load and temperature which makes it uneconomical.

2.1.2 Powder Metallurgy [15-17]

Fabrication of specimen via Powder Metallurgy technique is carried out in the following steps. Initially weighing of the metal and ceramic powder in requisite quantities and as per the desired composition is done. Secondly, ball milling of the metal, ceramic powder and binder is carried out in order to achieve homogeneity and reduction in particle size. Binder is used to provide binding strength. Compaction of the powder mixture is done in a die using a hydraulic press so as to achieve a green body of required dimensions. Sintering of the green compact is done in an atmosphere controlled furnace. During sintering closer coming of the powder particles takes place along with the removal of the porosities. Sometimes, in order to remove left over porosities some secondary processes such as stamping, rolling or extrusion can be employed. With the help of these processes shear deformation takes place between the grain and grain boundaries which leads to strong interfacial kinetics. Fig. 1 shows the schematic layout of powder metallurgy process. The characteristics of powder metallurgy processed metal matrix composites are greatly influenced by:

1. Percentage of the reinforcement.
2. Phase and microstructure which depend on the processing parameters and heat treatment schedule.
3. The bonding between the dispersoids and the matrix.

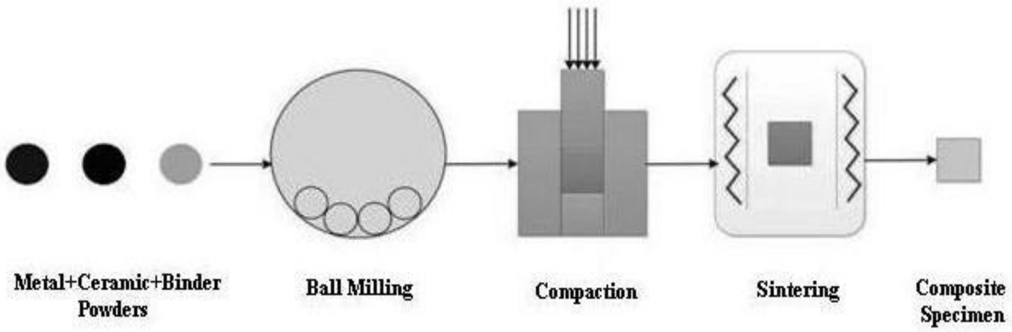

Figure 1: Schematic Layout of Powder Metallurgy Process

2.2 Liquid State Process

Liquid state processes are used in the industrial application where the production rate is extremely high. This technique uses the matrix material in the molten state. Several liquid state process are being widely used and some of them are illustrated below:

2.2.1 Stir Casting

In stir casting technique ceramic reinforcement is added in the molten metal via stirring. The liquid mixture is then poured in a die and the whole assembly is left to solidify. Thereafter the solid block is removed from the die and machining is done so as to get the desired shape. Viscosity of the melt and reactivity of the particle plays a very important role in determining the properties of the final product. This is a very economical technique but is indeed having certain disadvantages as well. Molten mixture may have some entrapped inclusions and gas holes which is a defect and thus reduces the property of the final product. Fig. 2 shows the schematic layout of stir casting process.

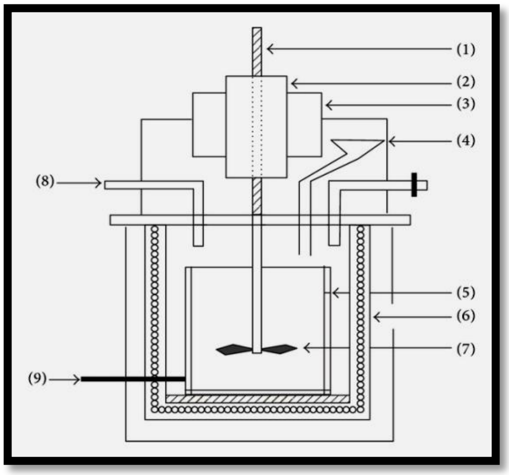

Figure 2: Schematic of stir casting process (1) Stirrer spindle, (2) Sliding mechanism with impeller position control unit, (3) Electric motor, (4) Sprue, (5) Crucible, (6) Electric furnace, (7) Impeller, (8) Argon gas inlet, and (9) Thermocouple

2.2.2 Squeeze Casting [18]

Casting of liquid metal in a pre heated die and forging of the melt during solidification is termed as squeeze casting. Forging load is applied on the melt as soon as the onset of the solidification starts and is continued until its entire solidification. The property achieved by this technique is comparable to the plastically deformed specimen due to presence of negligible amount of porosity. Squeeze casting is more applicable for discontinuously reinforced composites. This technique is totally automated and requires no post machining operations. As this technique is almost pore free thus a small equiaxed recrystallized grain type microstructure is obtained.

2.3 Vapor State Process

Vapor state process is used when the molten materials are used in the spray form. This technique provides large scale adhesion on the interface of matrix and reinforcement. Major advantage of this technique is that different alloys can be used and rate of evaporation is controlled by the variation in the composition. At times vapor state process is also termed as the sputtering. Vapor state processes are of following types:

- Chemical Vapor Deposition
- Physical Vapor Deposition.
- Spray Forming
- Low Pressure Plasma Deposition
- Electric Spray Arc Forming

3. Corrosion Behavior of Metal Matrix Composites

A lot of work has been done using aluminium, copper, magnesium and iron as the matrix material synthesized via stir casting and powder metallurgy process. Corrosion characteristics of composites depend upon the type of reinforcement and size of the particle. A few of the investigations are illustrated below:

He et al. [19] investigated the corrosion characteristics of 2024 aluminium alloy reinforced with SiC_p rolled as a sheet and synthesized via powder metallurgy technique. The composition contained 17% by volume of SiC_p. Corrosion behavior of the specimens was studied using 3.5 wt% of NaCl solution. It was revealed from the study that the coating on 2024Al gives a corrosion protection to 3.5 wt.% NaCl solution. Anodized coating on the SiCp/2024Al MMC also provides corrosion protection. But, it is not as effective as for 2024Al because of non-uniformity in thickness and cavities associated with the SiC particulates. SiC particle anodizes at a significantly reduced rate compared with the adjacent Al matrix which gives rise to alumina film encroachment beneath the particle and occlusion of the partly anodized particle in the coating. New formation mechanisms of coating growth during anodizing of a SiCp/2024Al MMC were proposed.

Palta et al. [20] investigated the effect of Cu addition on the wear and corrosion properties of ‘‘in situ’’ Mg_2Si particle reinforced Al–12Si–20Mg matrix composites produced with help of the nucleation and growth of the reinforcement from the source matrix in order to overcome the disadvantages of composites produced by externally reinforcing ceramic particles. Composites such as Al–12Si–20Mg–XCu were produced by adding 1%, 2%, and 4% Cu, to the Al–12Si–20Mg alloy in order to achieve this purpose. The microstructural characterization, hardness, wear and corrosion properties of composites were correlated and analyzed. Weight loss in test specimens under the action of solution containing 30 g/l NaCl + 10 ml/l HCl, and the tafel extrapolation method were used to analyze corrosion behavior of these composites. Results of microstructural characterization concluded that as the amount of Cu added to the Al–12Si–20Mg alloy increased, the size and volume of the Mg_2Si particles formed within the matrix decreased and $CuAl_2$ intermetallics formed in the matrix. According to the results of corrosion experiment, corrosion resistance increased with the addition of Cu.

Tiwari et al. [21] investigated the corrosion behavior of magnesium reinforced with SiC particles fabricated using mechanical disintegration deposition technique. Composition was kept as 6 and 16 vol% of SiC particulates reinforced in the magnesium matrix. Specimens were synthesized using a graphite die and using a pressure of 40 MPa and temperature of 2100°C. Corrosion characteristics of the specimens were carried using 1M NaCl solution and in the ambient condition. Corroded surface of the specimen was also characterized using

X-ray diffraction for phase analysis and using SEM with EDS for morphological and elemental profile respectively. From structural studies it was found that after corrosion magnesium hydroxide [$Mg(OH_2)$] forms as a major product. SEM studies reveal that the matrix was not attacked whereas the region near SiC is attacked more by NaCl which is due to the cathodic nature. Fig. 3 shows the SEM micrographs of (a) Mg and (b) Mg-6SiC after corrosion in 1M NaCl solution. It was also found that more amount of oxygen was present near SiC particles. On an overall basis it can be concluded that there was less amount of corrosion on the Mg-SiC composite whereas the entire surface of Mg was found to be corroded.

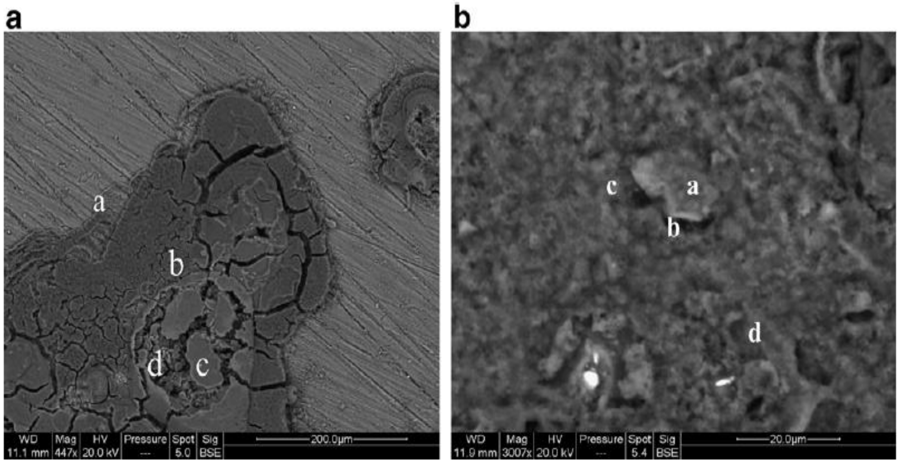

Figure 3: SEM micrographs of (a) Mg and (b) Mg-6SiC after corrosion in 1M NaCl solution [21]

Recently Gupta et al. [22-23] has investigated un-doped and doped Fe-Al_2O_3 metal matrix nanocomposites via powder metallurgy process. Fe-Al_2O_3 (5% and 10%) metal matrix nanocomposite specimens were synthesized by ball milling followed by compaction and sintering in inert atmosphere in the temperature range of 900-1100°C for 1-3 hour. However, few selected compositions i.e. Fe-10% Al_2O_3 were doped with cobalt oxide and sintered at 1100°C for 1 hour. It was found from the investigation that for un-doped iron-alumina metal matrix nanocomposites an iron aluminate phase forms due to which the various structural, mechanical and electrochemical properties were found to improve. However for cobalt oxide doped metal matrix nanocomposites there was a reduction in iron aluminate phase formation.

Corrosion behavior of 5% Al_2O_3 reinforced specimen showed that due to Al_2O_3 reinforcement, the Tafel plots shift towards lower current regions, thereby, denoting the improvement in the corrosion resistance of the specimens. XRD and SEM analysis revealed the formation of the aluminum chlorate ($AlCl_3O_{12}$) phase which is formed as a result of the attack of HCl on aluminum oxide particles. Anti-corrosion efficiency of all the specimens was found to be above 90%. Corrosion behavior of 10% Al_2O_3 reinforced specimen showed that iron aluminate ($FeAl_2O_4$) phase formation improved the corrosion resistance of Fe-Al_2O_3 metal matrix nanocomposite specimens. XRD results showed the presence of aluminum chlorate and iron chloride phases respectively in the corroded specimens. SEM results showed that the specimen having poor corrosion characteristics showed the formation of dark patches on the specimen surface [24-25].

Corrosion behavior of CoO doped Fe-Al_2O_3 nanocomposite specimen showed that CoO doping improves the corrosion resistance of pure Fe as well as of Fe-Al_2O_3 metal matrix nanocomposite specimens. XRD results show the presence of aluminum chlorate and cobalt chlorate phases respectively in the corroded specimens. Presence of nano particles were found in the composite specimens with high percent of cobalt oxide and nano rods in the pure Fe specimen with 0.5% of cobalt oxide. Anti-corrosion efficiency of 1.0% doped nanocomposite specimen and 0.5% doped pure iron specimen was found to be 99.99%. Existence of nano size particles of Al_2O_3 and CoO instantly undergoes passivation forming film on the iron surface which protects the corrosion of iron in HCl solution [26]. Figure 4 shows the Tafel Polarization plots of cobalt oxide doped specimens.

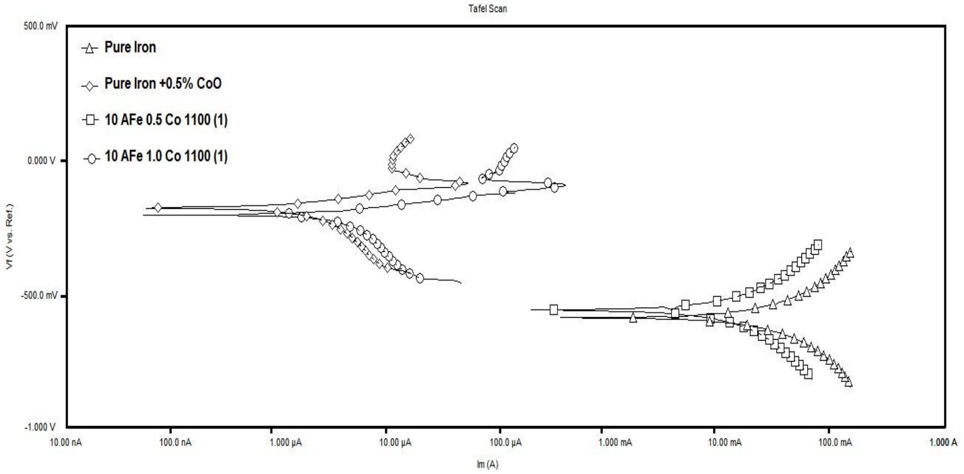

Figure 4: Tafel Polarization plots of cobalt oxide doped specimens [26]

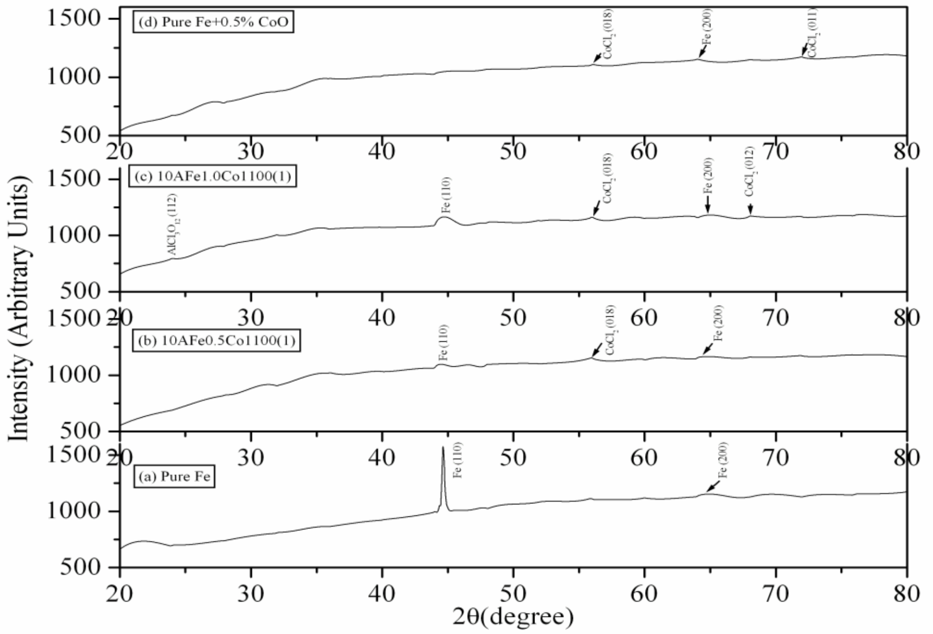

Figure 5: XRD patterns of the corroded surfaces of (a) Pure Fe (b) 10AFe0.5Co1100(1) (c) 10AFe1.0Co1100(1) and (d) Pure Fe+0.5% CoO specimens respectively [26]

Figure 5 shows the XRD patterns of the corroded surfaces of (a) Pure Fe (b) 10AFe0.5Co1100(1) [0.5% doped composite] (c) 10AFe1.0Co1100(1) [1.0% doped composite] and (d) Pure Fe+0.5% CoO specimens respectively. Pure Fe specimen shows the presence of pure iron phase. Specimen 10AFe0.5Co1100(1) shows reduced intensity peaks of iron along with some peak of cobalt chlorate ($CoCl_2$). In the same manner specimen 10AFe1.0Co1100(1) showed presence of aluminum chlorate ($AlCl_3O_{12}$) and cobalt chlorate ($CoCl_2$) phases respectively. Specimen having pure Fe with 0.5% CoO showed presence of some smaller peaks of iron and of cobalt chlorate phases respectively. From the XRD results, it can be concluded that there is more amount of cobalt chlorate phase and at the same time there is a presence of aluminum chlorate phase which is formed on the specimen surface as a result of the corrosion action [26].

Figure 6 shows the SEM and EDAX of full frame of the specimen 10AFe1.0Co1100(1) showing nano size particles after corrosion in 1N HCl at 20000X magnification with the corresponding elemental profile discussed in table 1. The present view shows the presence of carbon (C), oxygen (O), aluminium (Al), chlorine (Cl), iron (Fe) and cobalt (Co) respectively.

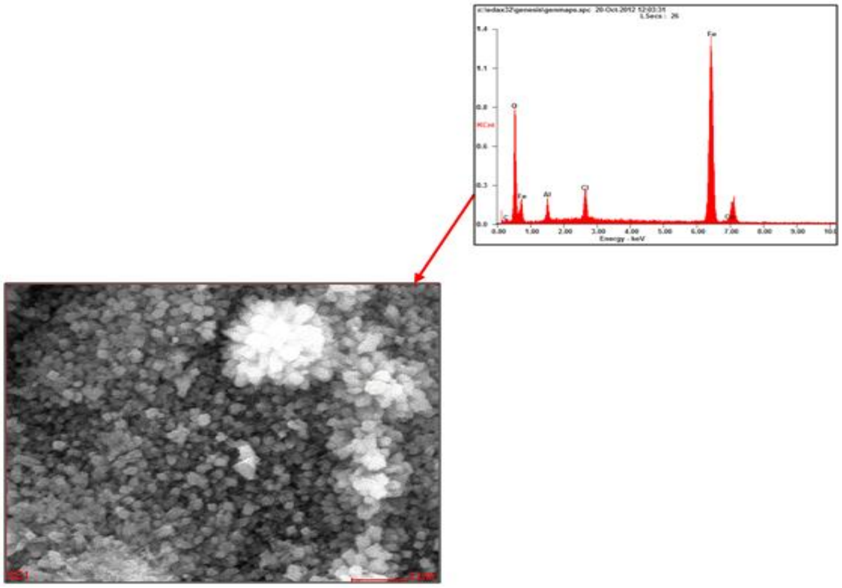

Figure 6: SEM and EDAX of full frame of the specimen 10AFe1.0Co1100(1) showing nano size particles after corrosion in 1N HCl at 20000X magnification [26]

In the present full frame selection carbon is 05.73 wt%, oxygen is 34.26 wt%, aluminium is 04.88 wt%, chlorine is 03.95 wt%, iron is 50.46 wt% and cobalt is 00.73 wt%. It is seen in the present result that there is formation of smaller nano size particles of various constituents present in the nanocomposite specimen. Atomic fractions of various elements indicate the presence of nano size particles of aluminium chlorate and cobalt chlorate. Therefore, it can be concluded from the above discussion that due to the formation of nano aluminium chlorate and cobalt chlorate phases, a passivating film is formed on the specimen surface which reduces the corrosion of the nanocomposite specimens [26].

Table 1: Elemental Profile of full frame 10AFe1.0Co1100(1) specimen after corrosion [26]

Composition	Wt%	At%
C	05.73	12.47
O	34.26	55.96
Al	04.88	04.73
Cl	03.95	02.91
Fe	50.46	23.61
Co	00.73	00.32

4. Applications of Metal Matrix Nanocomposites [27]

MMNCs find application in wide number of areas some of which are listed below:

- Brake Components, discs, rotors etc are made from aluminium-alumina metal matrix composites as it serves with light weight properties.
- Pistons, cylinder bores, intake and exhaust valves are made from aluminium-silicon carbide metal matrix composites.
- Transmission lines make use of copper-silicon carbide metal matrix composites due to improved electrical conductivity.
- Cutting and grinding tools make use of iron-nickel alloys reinforced with titanium carbide.
- Heavy duty components like railway wagon wheels, driveshafts make use of iron-alumina metal matrix nanocomposites.

Conclusion

A systematic study on influence of processing parameters on Corrosion Behavior of Metal Matrix Nanocomposites has been reported in this paper. The following important conclusions have been drawn:

1) Stir casting and Powder metallurgy are the two prominent routes for fabricating metal matrix nanocomposites. Powder metallurgy route produces homogenous composite products.
2) A lot of work has been carried out using aluminium, copper and magnesium as the matrix material but there are only few reports available for iron as the matrix.
3) Iron aluminate phase formation takes place due to reactive formation between iron and alumina particles. Mechanical properties of Fe-Al_2O_3 metal matrix nanocomposites depends upon iron aluminate phase formation which in turn depend upon sintering temperature and time respectively.

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