

Chapter 7

Tribological and Corrosion Behavior of Al-TiB₂ Metal Matrix Composites—An Overview



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1 Introduction

Impact of a new material on society is immense. A common saying is that we are only as good as our best materials. From stone to silicon, iron to shape memory alloys, materials have experienced a long journey. If growth of civilization is closely observed, it is revealed that development of materials and their applications are the milestones in civilization and economic progress. At the initial stages of mankind, raw materials availed from nature were processed to end products for the purpose of achieving some useful value in daily life. That end product had a definite shape and size based on very primitive knowledge. With time, findings of newer materials added newer dimensions on those end products which primarily resulted in betterment of life. For instance, the introduction of iron as material in mankind made struggle for survival comparatively easy and quality of life improved accordingly. But the quest for easier daily life with more comfort reproduced existing operations in different modified forms. For instance, a man moving on a wooden wheel at a very nominal speed was obsolete with time. Requirements became higher load-bearing capacity of the wheel as well as more speed. To cater to those requirements in end products, materials other than wood were started to be developed industrially.

Before opting for different materials for useful products, initial efforts were made on mechanics and design of products to enhance the load-bearing capacity. At that time, the material was considered homogenous. In accordance with need, strength of material as a subject was developed where the role of external force on material performance was tried to be understood in a simplified form. Shape and size of

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the product were then modified accordingly. The target was to increase the functioning of the material without yielding. But the industrial revolution in the nineteenth century opened up various fields where structural materials started to be used in sufficient number. Unfortunately, at the same time, several catastrophic failures of boilers and railway equipments took place which resulted in major loss of life. Such incidents coerced better choice of material and increased understanding of material performances at adverse operating conditions. Meanwhile, in the twentieth century, communication became an important parameter and materials of that time were not ready to be adopted. Space research and automobile sectors started to flourish which additionally pushed researchers to find out or develop newer materials capable to perform without failures in extreme conditions.

It is understandable that historically applications played a prominent role in defining and directing the focus of fundamental research on materials. For any product development, materials selection was based on evaluating a series of performance characteristics, process characteristics and sustainability issues. But that approach got changed with time. In recent times, the tremendous advances in understanding of material behavior succeed an increasing trend of using material consisting of various properties together in a balanced way. In automobile industry, some materials are chosen based on better electromagnetic properties in addition to good mechanical properties. In packaging industry, especially for computer hardware and drives, good shock absorption property along with the capacity of electromagnetic interference shielding is desired. In aerospace industry, materials must possess good mechanical strength as well as less overall weight because weight reduction in milligram level even increases sufficient fuel efficiency. Depending on such demands, two important classes of materials have been developed. They are composite materials and electronic materials. From the day of development, those two genres of materials have been considered by industry with great interests. Composites and electronic materials are majorly different from three fundamental classes of materials, e.g., metallic materials, polymeric materials and ceramic materials. A multitude of complex electronic circuits has been transformed into a single 2 cm² chip areas or less than that nowadays and it is possible only because of electronic materials. Similarly, improved mechanical properties like transverse strength, stiffness, shear strength, compressive strength along with enhanced wear resistance of composite materials with respect to monolithic metal alloys made these suitable for versatile range of applications. Mass market products of composite materials are increasing progressively and area of applications are spreading accordingly. Besides, day by day, increasing obligation for reduction in fuel consumption and emissions in ground is pressing composite materials into newer challenges. This leads to a journey based on better understanding of composite materials from different approaches. Composite materials also should be evolved accordingly.

2 Composite Materials

The term 'composite' philosophically designates to 'something combining the typical or essential characteristics of individuals making up a group' [11]. Composite materials have been made by combining different type of materials holding different properties and shapes to achieve new properties changed from either of the constituents. Such combination does not hold any atomic level mixture of different constituent materials, rather it is a thermodynamically unstable mixture containing large amount of interface [51]. If any chemical reaction happens at the interface leading toward thermodynamically stable molecular level mixture of elemental materials, then that material cannot be called 'composites.' That is why, constituents of composite materials are chosen accordingly so that stable interface can be achieved. Elements of composite materials are classified by two ranks, matrix and reinforcements. Matrix is the 'softer' phase in which 'harder' phase holding high stiffness and strength is embedded. Matrix portion in composites is relatively higher in amount while reinforcements play pivotal role to change the properties of matrix. Therefore, matrix is the principal phase of composites which possess a constant character and binds the reinforcing phase. The transverse properties, inter-laminar strength and high-temperature strength of the composites are being held by the matrix portion as it is the continuous phase [21]. Additionally, matrix phase is responsible for utilization of the full potential of reinforcement through transferring some portion of external load successfully into it.

Based on different matrix and reinforcements, composite materials are classified into six categories, viz., metal matrix composites (MMC), fiber reinforced plastics (popularly known as FRP), fiber reinforced ceramics ((popularly known as FRC), fiber reinforced glasses (popularly known as FRG), intermetallic compound matrix composites (popularly known as IMC) and carbon fiber reinforced carbon (popularly known as CC) composites [51]. Depending on the size of reinforcements, composites are of three types, viz., particulate reinforced composite, whisker reinforced composite and continuous/discontinuous fiber reinforced composite. With progress in research, various combinations of matrix and reinforcements have been introduced leading to newer classification in composite materials. But, basic approach behind the introduction of composites is fixed which is load-bearing capacity of matrix along with adverse condition stability must increase by incorporation of reinforcements.

To understand the contribution of matrix and reinforcement in composites, fiberglass is taken as an example. Plastic is the matrix in this case while glass is reinforcement. Glass is strong but brittle in nature. Plastic possesses very little strength in comparison with glass but when it binds glass, bending of composites becomes easier and breakage of glass does not happen. Additionally, fiberglass withstands much more load than plastic does independently. Hence, fiberglass as composite material is used vividly nowadays in sports gear, building panels and bodies of automobile [21].

Composites are already established as a better alternative to monolithic metals or alloys. To meet the challenging needs of special design, proper choice of composites

material is an effective method. Major points in composites are that yield strength and tensile strength at room temperature are improved and this performance is also maintained at high temperature, while toughness and ductility are prolonged properly [28]. Creep resistance, wear resistance, fatigue strength and Young's modulus of composites are better than popular alloys or metals at ambient temperature and at elevated temperature also [62].

3 Metal Matrix Composites

The idea of MMCs lies in the principles of dispersion hardening and precipitation hardening where strengthening mechanism depends on restricting the dislocation motion by incorporation of fine oxide particles into metallic matrix. In the year of 1970, 'dual phase steel' has been evolved where martensite particles are distributed over ferrite matrix phase and this phenomenon is very much like the material which is currently referred as discontinuous particulate reinforced MMCs [11]. With time, the definition of MMCs has been modified and it excludes any directionally solidified eutectics or Al-Si alloys or alloys containing any precipitates or segregated inclusions. A material can be called as MMCs only when distinct phases co-exist together throughout its total processing history [15].

Lots of studies reported that MMCs are better than other composite materials. Among other composites, carbon-carbon composites are very popular as material in aerospace applications but they suffer severe high-temperature oxidation which causes rapid degradation and erosion [48]. Oxidation in such composites becomes severe when temperature hits 350 °C. So, an oxidation resistance coating is necessary for the purpose of proper utilization of such composites. MMCs are free from such difficulties. Chawla and Chawla [10] reported that MMCs are more advantageous than polymer-based composites due to several reasons. As per them, metal matrix composites show higher strength, higher stiffness and better service temperature than polymer-based composites. Metal matrix composites also show better electrical and thermal conductivity than polymer composites. Transverse properties of MMCs are also better. MMCs possess better survivability against radiation like laser, UV or nuclear. MMCs also hold little or no contamination.

Evans et al. [15] discussed some more advantages of MMCs over polymer matrix-based composites. Metals as matrix can maintain strength along with toughness at high temperatures. Metals do not soak up moistures. Metals are not degraded by radiation. Melting point of metal is higher than polymers which make them safer as matrix. Heat and electricity can pass through MMCs which helps in many applications to take advantage over polymer-based composites. It is also fact that MMCs are easily joined or can be easily fastened to other metallic components. Over carbon-based, polymer-based, glass-based or ceramic-based composites, MMCs have snatched its position as material in military fighter aircraft, helicopter rotor blades, fuselage struts in the space shuttle orbiter, selected components on the Hubble Space Telescope and enormous applications like this [8]. Basic advantages of MMCs come from the matrix

as metals. But it can be comprehended that MMCs are directed to some specific applications where other composites are not suitable to be used.

4 Particulate Reinforced MMCs

Particulate (or particle) reinforced MMCs (PRMMCs) are combinations of matrix phase (metal or metallic alloy) with second phase that is purposely introduced into the metallic phase for improving properties. Second phase of PRMMCs may be more than one. PRMMCs have been fabricated in universities and R&D laboratories since 1960s for research purpose [45, 85]. Almost two decades later, major productions through several new processes were started.

Among whisker reinforced, particulate reinforced and short/long fiber reinforced composites, particulate reinforced composites are isotropic in nature like metals. Whisker or fiber reinforced composites are anisotropic and properties are dependent on the orientation of the whiskers/fibers. Isotropic materials also can be made from whiskers and fibers through desperate random orientation, but further processing of them like extrusion will again re-orient whiskers resulting in anisotropic properties. In anisotropic materials, mechanical properties, e.g., strength, stiffness, are unidirectional while coefficient of thermal expansion (CTE) is specified in another direction. Additionally, for aligned fiber reinforced composites, strength and stiffness are more in the direction of fiber orientation than perpendicular to them. Being isotropic, PRMMCs are free from such orientation in properties. It is true that PRMMCs show lower strength than the strength of fiber reinforced composites in direction parallel with fiber orientation. But it is also granted that PRMMCs do not show different strength and stiffness in different directions.

Regarding other advantages of PRMMCs over others, it is observed that whiskers cost more than particulate and they are brittle in nature. Whiskers break into shorter lengths at the time of processing and reduce the reinforcement efficiency which makes difficulties in cost justification. In fiber reinforced MMCs, higher difference in coefficient of thermal expansion between constituents yields higher residual stresses at the time of significant temperature change. Those stresses result yielding at the time of cooling. Kainer [28] discussed vividly that PRMMCs are the best in capability to offer targeted applications, and additionally, they are cost effective, show high isotropy of properties and large-scale production is possible for this case. As per literatures, the following advantages of PRMMCs are prominent [15].

- Equiaxed reinforcements are less costly
- Fabrication methods are simple and cost effective
- Material properties are isotropic in nature
- General metal working processes like machining, joining, forming can be applied in this case

5 Fundamental Knowledge on Particulate Reinforced Composites

Composites especially discontinuous particulate reinforced composites are inhomogeneous. That is why basic strength of materials cannot explain the behavior of composites. When load is applied externally on composites, non-uniform distribution of stresses occurs. Such distribution is tried to understand using several models as it determines the behavior alternatively called characteristics of the material. Characteristics of MMCs with nature of stress distribution are very much dependent on microstructures and matrix/reinforcement interfaces. Microstructure and interfaces are results of production processes as well as thermal and mechanical pre-history of matrix and reinforcements. Chemical compositions along with grain size, textures, precipitation behavior and lattice defects are the concerned factors of matrix for determining composite characteristics. While for reinforcing phases, amount, size, distribution and orientation are the related factors. Factors of reinforcements and matrixes along with production processes are approached differently in different models for the sake of the closest prediction of composite behavior. Basic models have been developed by assuming the ideal conditions, e.g., optimal boundary surface formation, uniform distribution with a very small amount of clustering and no influence of the reinforcement phase on matrix phase. In reality, the situation differs from the ideal one because a strong interaction occurs between reinforcement and matrix at the time of mixing. Models are appropriated accordingly with the deviation from reality and several new factors are introduced in the model with increase in understandings. Models based on long fiber reinforcement or short fiber reinforcement, e.g., the slab model, the shear lag model, continuous coaxial cylinder model, finite difference and finite element models are not discussed here though they are vividly presented in several literatures (Clyne and Withers 2014). Focus is kept on understanding the strengthening mechanism of discontinuous particles reinforced MMCs as this study deals with such type of MMCs only. The following discussion is progressed from simple model to very recent observations regarding mechanisms of particulate reinforced MMCs characteristics.

'Rule of mixtures' is the simplest and basic model of predicting composite behavior based on known properties of constituents (matrix and reinforcement). If U_c signifies the property of PRMMCs, V_f as the reinforcement phase volume and U_m as the property of matrix, then following equation is obtained using 'rule of mixtures' [51].

$$U_c = V_f U_f + (1 - V_f) U_m \quad (1)$$

For more than one reinforcement phase in composites (hybrid composites), Eq. 1 will be modified into general form, which is

$$U_c = \sum_1^n V_n U_n + \left(1 - \sum_1^n V_n\right) U_m \quad (2)$$

In Eq. 2, n is the number of reinforcement types. In this model, matrix reinforcement interactions are idealized too much. From this model, CET, thermal conductivity, ultimate tensile strength like properties cannot be predicted accurately as these properties depend on shape, size distribution, interface like several discussed parameters. In further, to predict the behavior of composites with better accuracy, understanding on surface and interface energy was increased. Following equation was developed regarding that purpose [17].

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\emptyset(\gamma_a\gamma_b)^{1/2} \quad (3)$$

In above equation, \emptyset is a constant depends on the characteristics of the system. γ_a and γ_b are the surface energy of constituents (a is matrix and b is reinforcement). Composites contain a large amount of interface. A strong adhesion without chemical reaction at the interface is required for achieving better properties. To achieve that type of interface, idea about the work of adhesion (W_{ab}) is required. Following equation was developed to predict work of adhesion (W_{ab}) for making 'ab' composites.

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab} \quad (4)$$

From Eqs. 3 and 4, it is comprehended that interface characteristics majorly depend on the parameter $2\emptyset(\gamma_a\gamma_b)^{1/2}$. The value of \emptyset can be experimentally obtained as well as theoretically following method proposed by Girifalco and Good [17]. Equations 3 and 4 mainly direct interface characteristics for various matrix/particle combinations. Interface characters finally direct in finding out suitable particles compatible with matrixes like Al/Mg.

Llorca and Gonzalez [39] tried something more than simple rule of mixture thing or basic energy exchange thing at the time of fabrication. They predicted tensile behavior of one particulate reinforced composites using the following equation

$$\sigma(\varepsilon) = \sum_i \gamma_i [\sigma_i^I(\varepsilon)(1 - \rho_i) + \sigma_i^F(\varepsilon)\rho_i] \quad (5)$$

In this equation, σ is the average compressive stress, ε is plastic strain. Subscript i signifies one small unit which holds same volume fraction of reinforcement. $\sigma_i^I(\varepsilon)$ is the average stress acted on unit where reinforcement is intact, while $\sigma_i^F(\varepsilon)$ is the stress of the unit where reinforcement gets fractured. ρ_i is the fraction of total units containing fractured reinforcements. In this model, the material was considered as three-dimensional array of hexagonal prisms whose height and base were equal. The particle was assumed to be positioned at the center of each unit and shape was either spherical or cylindrical. They got partial success in terms of accurate prediction.

At the same time, Young modulus of particle reinforced composites was tried to be estimated by several models. Tsai Halpin model was pioneer in this aspect. Voigt model and Reuss model were also effective to estimate Young's modulus but those models are applicable to those fiber reinforced composite materials whose

stress direction is parallel with the orientation of fiber and also to those layer composite materials when acting load is perpendicular to the layers. As per Tsai Halpin model, the composites Young's modulus, E_c can be effectively assumed with the help of geometry factor [22]. This geometry factor takes the shape and size of the reinforcement into consideration. The concerned equation in Tsai Halpin model is

$$E_c = \frac{E_m(1 + 2S \cdot q \cdot f)}{1 - q \cdot f} \quad (6)$$

where

$$q = \frac{\left(\frac{E_p}{E_M}\right) - 1}{\left(\frac{E_p}{E_M}\right) + 2S} \quad (7)$$

In above two equations, E_p signifies particle Young's modulus and E_M signifies matrix Young's modulus; the term 'f' signifies the total volume content of the particles. Though geometry of reinforcement is considered in this model, basic assumptions about production process like no pores, no agglomerations or no non-reinforced areas are still there.

Hence, it is seen that in the initial period of research, separate factors were accommodated one by one in a model. Consideration of one factor with more priority than others results in the development of separate mechanisms like grain refinement, Orowan strengthening, CTE strengthening, Hall–Petch mechanism, etc. To accommodate all factors, nowadays, researchers are inferring such micromechanical model where contributions of all strengthening mechanisms considered together [31]. Conglomerations of several factors in one model to estimate the strengthening mechanism of particles in PRMMCs are quite common findings in literatures [28]. Among those models, following equation is used mostly for combining different strengthening factors.

$$\Delta\sigma = \sqrt{(\Delta\sigma_{\text{load}}^2) + (\Delta\sigma_{\text{CTE}}^2) + (\Delta\sigma_{\text{EM}}^2) + (\Delta\sigma_{\text{Orowan}}^2) + (\Delta\sigma_{\text{Hall-petch}}^2)} \quad (8)$$

Several researchers claimed that Eq. 8 provides best validation of experimental results but it is noteworthy that there is no convergence or generalization among researchers regarding this approach [12].

In Eq. 8, $\Delta\sigma$ is the increment in yield strength due to incorporation of particles into base matrix. $\Delta\sigma_{\text{load}}$ is the contribution of load-bearing effect on yield strength of composites [59]. Following equation is used to measure this certain contribution.

$$\Delta\sigma_{\text{load}} = 0.5V_p\sigma_{ym} \quad (9)$$

In Eq. 9, V_p signifies particles volume fraction while σ_{ym} signifies the matrix yield strength.

$\Delta\sigma_{CTE}$ is related to strain developed by the disparity in CTE of the matrix and reinforcement of composites [18]. Two equations with different parameters are there for estimating $\Delta\sigma_{CTE}$ [12].

$$\Delta\sigma_{CTE} = \sqrt{3}\beta G_m b \sqrt{\rho_{CTE}} \quad (10)$$

and

$$\Delta\sigma_{CTE} = \sqrt{3}\beta G_m b \sqrt{\frac{12V_p \Delta\alpha \Delta T}{bd_p}} \quad (11)$$

In Eqs. 10 and 11, β is the strengthening coefficient, $\Delta\alpha$ is the difference of CTE between particle and matrix, ΔT is the difference in processing temperature and temperature at which tensile tests are performed. V_p and d_p signify the amount in volume and diameter of the particles.

$\Delta\sigma_{EM}$ is originated from modulus mismatch and expressed using following equation [31]

$$\Delta\sigma_{EM} = \sqrt{3} \times G_m b \sqrt{\rho_{EM}} \quad (12)$$

In Eq. 12, α is a coefficient depends on material. ρ_{EM} is a function based on bulk strain of the composites.

$\Delta\sigma_{Orowan}$ and $\Delta\sigma_{Hall-petch}$ in Eq. 8 are the two contributions based on the famous Orowan equation and Hall–Petch equation, respectively [20]. It is noteworthy that Orowan strengthening mechanism is mainly effective for estimating strength of composites with sub-micron-sized particles [46]. Hall–Petch equation is based on contribution of grain refinement on yield strength of composites.

$$\Delta\sigma_{Orowan} = \frac{0.13G_m b}{\lambda} \ln \frac{d_p}{2b} \quad (13)$$

G_m represents the shear modulus of matrix, b signifies the Burgers vector, d_p indicates the average diameter of the particles and λ denotes the inter-particle spacing in Eq. 13.

$$\Delta\sigma_{Hall-Petch} = k_y \left(d^{-\frac{1}{2}} - d_0^{-\frac{1}{2}} \right) \quad (14)$$

In the above equation, k_y is the Hall–Petch slope, the average grain size of matrix before reinforcement is denoted by d_0 and d is the grain size of the composites.

For better understanding of above discussions, a study is chosen as an instance in the following. This study is based on yield strength of PRMMCs (Al–5 wt%TiB₂) and done by Wang et al. [79]. In the study, first yield strength of fabricated composites

is calculated theoretically from three different approaches, e.g., grain refinement strengthening, Orowan strengthening and CTE strengthening. Then ultimate yield strength of composites is calculated as per the proposition of Zhang and Chen [84] using the following equation

$$\Delta\sigma = \Delta\sigma_{\text{grain-refinement}} + ((\Delta\sigma_{\text{Orowan}})^2 + (\Delta\sigma_{\text{CTE}}^2))^{1/2} \quad (15)$$

For finding the contribution of grain refinement in final yield strength, Eq. 14 is used. In Eq. 14, the value of d is calculated using the following formulae [16].

$$d = d_0(1 + pV_p)^{-1/3} \quad (16)$$

In Eq. 16, the refining potency of the reinforcement is p . The value of p is measured empirically by Wang et al. [79] in the study. Regarding contribution of Orowan strengthening, a slight modified version of Eq. 13 is used. Increment in strength by CTE strengthening is estimated by Eq. 10. Value of β is taken as 1.25.

After yielding final value as per Eq. 15, the real experimental values are fitted into estimated values and results show that 35–56% of reinforcing particles take part in strengthening of composites for different base matrix. Most interestingly, those percentages are quite relatable with the microstructures presented in that study. So it can be comprehended that accuracy of prediction of PRMMCs characteristics through model formation becomes enhanced with time which essentially leads to the fact that behavioral understanding of composites has been increased in a sufficient amount.

6 Aluminum-Based PRMMCs and Related Reinforcements

Properties of constituents are mostly retained even after formation of composites. So, composite properties are majorly determined by constituent properties. Accordingly, choice of base matrix and particles is driven by intended applications of the end products. Nowadays, a wide genre of particles, from ceramic to fine red mud, graphene nano-platelets to fly ash are being incorporated into aluminum/magnesium base matrixes [2, 53]. It raises a pertinent question. Can any type of particle be reinforced into any base matrix? The answer is no [51]. Though the aim of composites is tailoring of matrix properties using particles, chemical reactions arise at the interface resulting degradation or disparity of constituents which yields in degraded PRMMCs. So, proper compatibility of matrix and reinforcements is needed before choosing them as the constituent. Appropriate wetting is a major condition for pairing matrix and particle through liquid metallurgy route. Proper wetting helps in stress transfer and stress distribution in solid state of the composites which prevents fracture. Conversely, occurring of any chemical reactions at the interfaces is usually harmful to the properties.

Literatures reveal that light alloys are popular as base matrix based on costing, availability, recycling, etc. Aluminum, magnesium, copper, titanium and iron metals including their alloys are normally used as base matrixes. Among these, selection of specific base matrix depends on industrial applications of composites. Other alloys can be used but only for specific functional purposes.

Al alloys are chosen as base matrix mainly for two factors. First, aluminum (Al) or aluminum alloys (Al alloys) are majorly popular where energy efficiency is the prime concern. Being lightweight material with noteworthy strength, aluminum or aluminum alloys are easy to process and help to reduce energy consumption. Pure Al due to its lack in strength and other compatibility issues is not first hand choice for major structural applications. But when pure Al is embedded by other phases, it becomes competent with strength of steel and develops versatile properties [79]. In automotive components like pistons, engine blocks, etc., aluminum-based particulate reinforced composites as materials are already in use [57]. Even right now, disks, brakes, rotors, connecting rods are also being made of aluminum-based particulate reinforced composites. Among all commercially produced MMCs, composites based on aluminum (Al) alloys are the highest in volume [61]. Industries of ground transportation, aerospace, recreational, thermal management and automotive actually demand materials which hold high structural efficiency along with excellent tribological behavior. Al-based PRMMCs are that type of materials to fulfill such requirements [47].

Secondly, there is a need to maintain high specific strength with increase in operating temperature. Engine heads, pistons and similar components of automotive and transport field are commonly made of Al alloys in peak-aged condition. Definitely, there are some advantages regarding Al alloys as material from material science point of view. But before introduction of Al based PRMMCs, Al alloys were losing its position because when operational temperature was high, softening of alloys occurred which yielded overaged condition of Al. Ceschini et al. [9] discussed that synergistic combination of tough ceramic particles with Al matrix aided in maintaining strength and stiffness at high-temperature operations. Accordingly, use of Al/Al alloys-based composites has progressed. Study of other characteristics, viz., wear, friction, thermal conductivity, formability of Al-based PRMMCs gets required attention to suitably replace Al alloy.

When a composite material is selected for any specific usage, i.e., tribo-material or corrosion resistant material, than in laboratory scale, it has to go through some steps. Those steps are mentioned in Fig. 1. So depending on the final behavior, reinforcing phase, base alloy and also fabrication routes are selected. Reinforcing phase in PRMMCs actually resists and transfers the load applied externally on the composites [23]. Surappa [70] comprehensively stated that reinforcement in the aluminum matrix is usually non-metallic and commonly ceramic. Till now, lot of reports are available on PRMMCs among which major reinforcing phases are carbide (SiC, TiC, B₄C, WC), nitride (AlN, TiN, Si₃N₄), oxide (Al₂O₃, TiO₂, SiO₂, MgO) or boride (ZrB₂, TiB₂) [32, 65]. Recently, carbon nano-tubes [82] and certain hard intermetallics (MoSi₂ [13], Ni₃Al) are being reinforced in a more focused way, though carbon nano-tubes are not generally categorized as particles. There are some

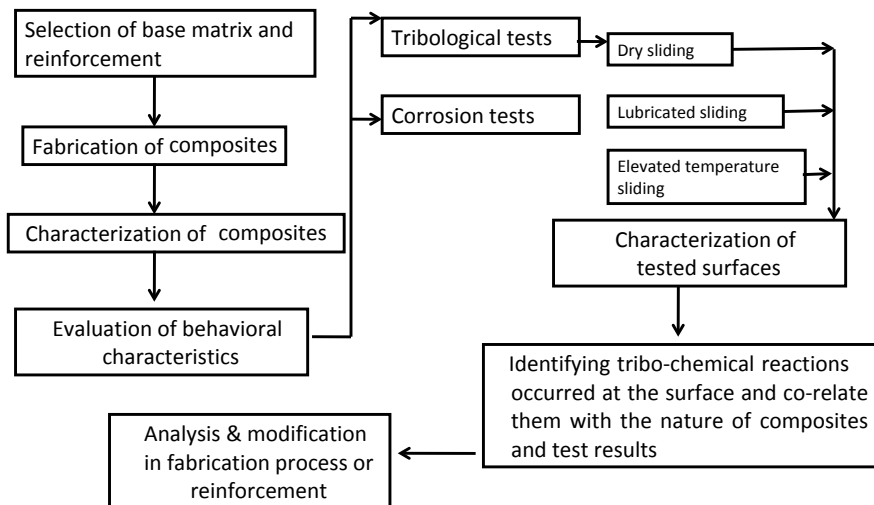


Fig. 1 Block diagram to show how a composite material has been selected for fabrication

common properties among popular ceramic reinforcements. All of them possess density more than 2200 kg m^{-3} , melting point higher than 2000 K, Vicker’s hardness more than 600 HV and Youngs’ Modulus at least 400 GPa [51]. Such high hardness or mechanical strength of particles is being transmitted into Al through reinforcement. Accordingly, composites show intermediate properties between Al and used ceramic particle. Aluminum-based particulate reinforced metal matrix composites are commonly called as aluminum metal matrix composites (AMCs) or PRAMCs, and in rest of the study, it will be referred as AMCs. The term ‘composite’ will also essentially signify AMCs in the following discussions.

7 Fabrication of MMCs

Fabrication of metal matrix composites is the most challenging part. Major cost associated with AMCs/MMCs is involved in fabrication systems. Thorough literature survey on AMCs reveals that composites with same particle along with same shape, size and amounts but fabricated through different routes show different mechanical and tribological behavior under same operating conditions [1]. It happens because orientation and distribution of reinforcements in matrix are affected by the manufacturing processes. Suitable fabrication method depends on two major factors. First, the method needs to be cost effective one to distribute the secondary (reinforcing) phase in the preferred configuration. Second, a strong bond between matrix and the reinforcement is to be achieved at the time of fabrication so that an effective load transfer can occur between phases prior to fracture. Depending on these factors,

Table 1 Processing routes for major three AMCs

Types of AMCs	Fabrication methods	References
Al-SiC	Squeeze casting (liquid state), powder metallurgy (solid state), ultrasonic dispersion (liquid metallurgy)	[35, 36, 83]
Al-Al ₂ O ₃	Cold isotropic pressing (CIP) and sintering (solid state), powder metallurgy (solid state), milling and hot pressing (semi-solid state), vortex method (liquid state)	[19, 26, 27, 29]

fabrication of composites is performed through solid state and liquid state fabrication methods. Some researchers suggested that gaseous state methods like chemical vapor deposition or physical vapor deposition may be used to make composites by depositing a layer of material on the surface of another material (substrate) [51]. In situ and ex situ techniques are two separate fabrication styles commonly used by the researchers and are distinguished by the process of incorporating ceramic particles into matrix. In situ process involves reaction of at least two (or more) elements inside molten metal for producing required ceramic reinforcement inside the matrix. In ex situ process, ceramic reinforcement is incorporated into matrix in particle form and it involves no reaction for purpose of production of reinforcement. Table 1 provides primary processes which are commonly used by researchers for fabrication of two major AMCs.

Solid state fabrication technique includes processes like powder metallurgy, mechanical alloying, diffusion bonding and surface oxidation. Major advantage of solid state fabrication method is less chemical interaction between particles and matrix yielding almost no chemical products at the interface. Among all solid process, most popular one is powder metallurgy techniques. These methods actually deal with discontinuous reinforcements, because this process holds the advantage in easiness of mixing and blending. Additionally, this process holds the effectiveness of densification. Targeted ceramic and metal powders are first mixed which is followed by isostatic cold compaction and hot pressing. Novel low-cost approaches, such as sinter-forging, are also part of solid state processing [10].

Processes like pressure infiltration, squeeze casting, compo casting, stir casting, spray deposit method, centrifugal casting deal with liquid metal. Advantages of liquid state method over solid state techniques lie in capability of rapid production. Complex shape parts can be easily fabricated by this method. But capillary forces hinder the combination of molten metal with particles. Ceramic reinforcements are generally 'metal repellent' and metal does not easily bond with something which is 'non-metal.' External forces/energies are required to overcome this energy barrier. In infiltration technique, molten metal is pushed into reinforcement. Some modifications are being practiced to overcome the issue of wettability and ease of mixing. Processing at elevated temperature is one of the modifications which help to increase wettability. In liquid state method, matrix phase solidifies with size constraints as they are placed between reinforcement particles which do not move at the time of solidification. If particles move, matrix metal pushes them into the area solidified in the last. But this results in undesirable shrinkage cavity.

For fabrication of aluminum-based nano-composites in recent times, friction stir processing (FSP) and accumulative roll bonding (ARB) are attempted. During FSP, a tool consisting of a shoulder and a pin rotates and dives into the base matrix surface. Simultaneously, by the pin, grooves are filled with the desired volume fraction of nano-particles. Al [38] and Mg-based nano-composites have been produced by FSP by incorporating ceramic or carbon-based nano-reinforcement. Accumulative roll bonding is a solid state method. Severe plastic deformation processes majorly occur in this process. ARB process develops roll bonding stacked sheets (about 50% of thickness reduction) first, then cuts the roll-bonded material and rolls it again after stacking the pieces over each other [4].

8 Tribological Properties of AMCS

One of the important reasons behind popularity of AMCs is better tribological behavior over base Al matrix at dry condition as well as other operating conditions. Antoniou and Subramanian [5], Balasubramaniam and Maheswaran [6], Lim and Ashby [37], Rao et al. [60], Wilson and Alpas [80], Wilson and Alpas [81] and other researchers reported wear and friction behavior of AMCs and suggested varying mechanisms (adhesive, abrasive, delamination, plowing, etc.) being active on the composite surface at the time of sliding. Some researchers studied effect of mechanical parameters on tribological behavior while some studied influence of material parameters on wear and friction of AMCs.

Like mechanical properties, common observation in wear behavior of AMCs is that wear resistance of composites increases linearly with increase in the amount of particles. Some study reveals that such increase in wear resistance occurs only up to a certain amount of reinforcements after which particles play detrimental role in wear behavior of composites. Wear of composites depends on the reinforcement particle size and increases with increase in size. Wear rate generally increases with increase in the applied load. Wear of composites is also a function of sliding distance and it is observed that volume/weight loss increases with increasing sliding distance. However, wear rate may also increase with increase in sliding velocity. Several studies are also available which show wear rate decreases with increase in sliding velocity of composites. For in situ composites, in situ reaction holding time is an important parameter for influencing the wear rate. It is generally observed that longer reaction time results in reduction in grain size of matrix. Such reduction in grain size directly influences the wear resistance of composite.

Identifying suitable wear mechanism through wear debris and worn surface analysis is a common practice in study of tribological behavior of AMCs. Active wear mechanisms majorly depend on the hardness of reinforced particles and applied contact load. Several tribo-chemical reactions occur on the contact surfaces. Wear mechanisms are modified accordingly. Those reactions are influenced by the presence of lubricant or corrosive solution. Operational environment also influences tribo-chemical reactions. Not only hard particles, soft particles are also incorporated

into Al matrix which enhance wear behavior in a different way. Soft particles either absorb moisture or provide protective layer against hard asperities. So to understand wear behavior of an AMC, it should be studied under varying operating conditions.

Generally, friction of AMCs depends on applied normal load, amount of particles, temperature, sliding distance, sliding velocity, in situ reaction holding time (for in situ composites), processing temperature and existence of protective layer on the surface, etc. In case of in situ Al-TiB₂ composites, it is seen that for a given temperature, friction decreases with increasing wt% of TiB₂ and increases with increase in temperature [49]. Reaction holding time also affects COF and it has been observed that COF increases with increasing reaction holding time [43]. Study shows friction of composites increase with sliding distance and sliding velocity for a fixed amount of reinforcement [58].

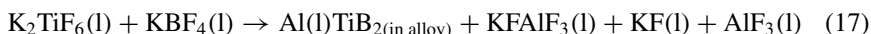
9 Al-TiB₂ Metal Matrix Composites

Improvement of properties in AMCs mostly depends on the selection of materials, reinforcement phase and process of synthesis. TiB₂ as reinforcement over Al alloy matrix is a specific area of attention among AMCs for last few years due to some specific advantages of TiB₂ in aluminum alloy matrix as well as varying scopes for fabrication (liquid phase, solid phase, two phase), apart from excellent combination of the properties of final composite [34].

Advantages of titanium diboride (TiB₂) as reinforcement are its high Young's modulus (345–409 GPa), high hardness (3400 HV), low density, high wear resistance [71, 72]. TiB₂ has tendency to not react with molten aluminum/aluminum alloy which results in less reaction product at particle matrix boundary and TiB₂ is also known as the hardest material that can be reinforced in aluminum matrix alloy [74]. It is well documented that mechanical properties, viz., elongation, fracture behavior, tensile strength and tribological properties, viz., wear resistance in dry sliding condition at ambient temperature as well as at high temperature, abrasive wear resistance, friction behavior of aluminum matrix composites enhance qualitatively when TiB₂ particles have been reinforced [3, 41, 49, 75]. According to the literature and several industrial report, major volume of the commercially produced AMCs is held by SiC incorporated AMCs. For incorporation of SiC, casting or powder metallurgy techniques are major choice for fabrication. Still, major drawback of Al-SiC composites exists in formation of aluminum carbide (Al₄C₃) which reduces physical, mechanical and chemical properties of the composites [30]. Literatures reveal that, instead of SiC if reinforcement like TiC, TiB₂ are used, then composites will be free from such drawback of Al-SiC [44]. Moreover, TiB₂ particles act as nucleating agent for aluminum and α -Al matrix grains are refined due to TiB₂ which provide various ways of fabrication compared to any other ceramic particulate reinforced AMCs [63].

10 Fabrication of Al–TiB₂ MMC

Regarding fabrication of Al–TiB₂ metal matrix composites, it can be said that most of the fabrications have been done through in situ methods. In in situ method, TiB₂ has been formed inside molten aluminum ingots through different chemical reactions. Total reactions during in situ fabrication can be divided into three parts [34]. The first one is decomposition of K₂TiF₆ and KBF₄ to KF liquid, TiF₄ and BF₃ gases. Second one is reaction between TiF₄ and BF₃ gases inside the molten ingots to form TiB₂ and AlF₃. The third one is the formation of 3KFAIF₃ and KF mixture. The overall reaction regarding the formation of TiB₂ can be written as:



The maximum amount of TiB₂ formed in situ is determined by the viscosity of the subsequent melt. Values of up to 12% have been reported till now [41]. During in situ fabrication, there are a lot of factors which can influence the distribution of particle over the base alloy along with the final properties of the fabricated composite. Several studies are also there regarding influence of the overall reaction time on the properties of Al–TiB₂ composites. Lu et al. [41] have reported that grain size of the TiB₂ is a clear function of the reaction duration. Grain size decreases with increase in reaction time at the starting of reaction. Grain refinement decreases at a later stage.

Other than in situ technique, there are also a lot of methods through which researchers have been tried to fabricate Al–TiB₂ metal matrix composites. From several reports, different fabrication techniques for fabrication of Al–TiB₂ composites have been noted in Table 2.

Among ex situ methods, simple stir casting and modified stir casting methods are becoming popular. Simple stir casting is a liquid state method. Schematic diagram of simple stir casting method is presented in Fig. 2. This method is different from infiltration because particles are introduced into molten metal by mechanical forces. Molten metal is agitated by mechanical energy and particles are forcefully distributed in the matrix phase. Stirring is kept on until random but uniform distribution of reinforcements is ensured. Stir casting process is patented by Skibo and Schuster [66] for fabrication of Al–SiC composites. There are several researchers who specifically fabricated Al–TiB₂ composites through these ex situ methods and tested tribological properties of it under different conditions [24, 54, 71, 72]. Some modifications like two-stage stirring, ultrasonic vibration assisted stirring are being used nowadays

Table 2 Processing routes for Al–TiB₂ metal matrix composites

Fabrication methods	References
Exothermic dispersion (solid–liquid state), reactive hot pressing (solid–liquid state), stir casting (liquid state), flux assisted synthesis (liquid state), mechanical alloying (solid state), hot isostatic pressing (solid state)	[7, 14, 42, 52, 73, 74, 76]

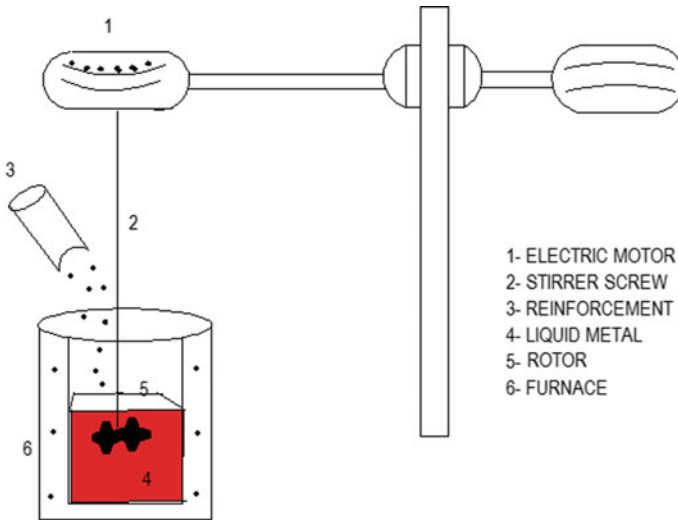


Fig. 2 Schematic diagram of stir casting process

by several researchers. Figure 3 presents schematic diagram of ultrasonic vibration assisted stir casting process. It clearly shows what modifications have been incorporated in the furnace to achieve cluster free cast metal matrix composites.

11 Tribological Properties of Al-TiB₂ MMCs

Al-TiB₂ metal matrix composites show better tribological properties than base aluminum alloy. Accordingly, Al-TiB₂ composites have been used as tribological parts in various applications. Before studying tribological properties of Al-TiB₂ composites, mechanical properties have been thoroughly studied by researchers.

In general, tribological properties of any materials/components denote the wear and friction behavior of it under different operating conditions, i.e., dry sliding, lubricated sliding, elevated temperature sliding. Maximum report on tribological properties of Al-TiB₂ composites has been performed on dry sliding condition. Tribological behavior of T6 treated A356-TiB₂ in situ composites under dry sliding conditions has been reported by Mandal et al. [44]. Tests have been carried out in a pin on disk set up. The wear resistance of Al-TiB₂ composites is significantly improved with increase in the TiB₂ amount in the composites. Regarding friction, no clear trend with respect to the weight percentage of the reinforcement has been observed. Increase in the wear resistance of the composites with respect to the amount of TiB₂ is the contribution of mechanical mixed layer formed on the surface of the pin. This layer is a mixture of the O₂, Fe from counter surface and Al from the base matrix. Niranjan and Lakshminarayanan [50] have studied wear rate of Al-TiB₂

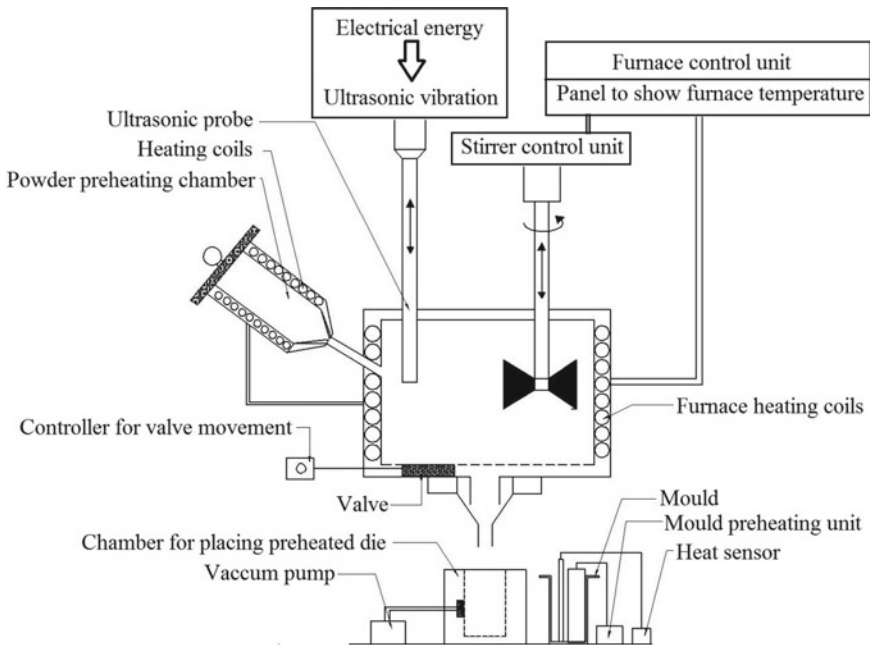


Fig. 3 Schematic diagram of ultrasonic vibration assisted stir casting process

composites with respect to load and weight percentages of TiB_2 . They have prepared composites at different melt temperatures with different reaction time. Decrease in wear rate with increase in weight percentage of TiB_2 has been also observed in their study at low load. Al– TiB_2 composites with 6 wt% reinforcement processed at melt temperature 900 °C and reaction time 30 min have shown best wear resistance compared to the other composites processed through different conditions. Natarajan et al. [49] have studied wear resistance of Al– TiB_2 composites at ambient as well as elevated temperature with different operating load. Effect of grain refinement, surface roughness and in situ reaction parameters on wear behavior of Al– TiB_2 composites is also studied by Mallikarjuna et al. (2014). Niranjana and Lakshminarayanan [50] have shown that 6% Al– TiB_2 composite yields maximum wear resistance. Lorusso et al. [40] have reported that 10% micro- TiB_2 reinforced AMC shows worst results when compared with base Al–Si 10 Mg alloy and higher wt% of TiB_2 leads to agglomeration resulting in detrimental effect on properties. Vivekananda and Prabu [78] have studied wear behavior of Al–5 wt% TiB_2 composite by varying the wear test parameters such as operating temperature (in the range of 25–200 °C), applied load (in the range of 10–40 N), sliding velocity (in the range of 0.4–1.3 m/s). They have concluded that at room temperature, the maximum reduction of wear rate of composite is 75% less than Al alloy. Poria et al. [54] have reported the variation of wear depth as a function of applied load for various weight percentages of TiB_2 present in stir cast Al– TiB_2 metal matrix composites. Figure 4 presents that variation

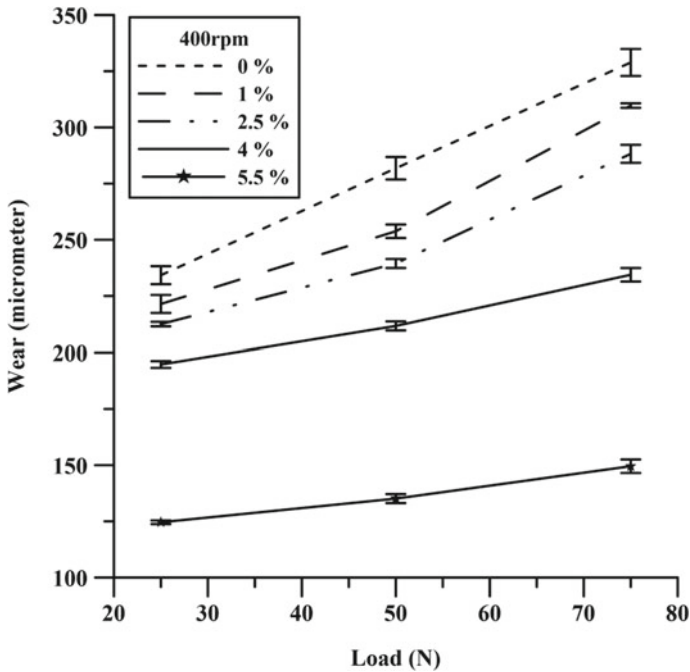


Fig. 4 Wear as function of applied load for different wt% of reinforcement

and it is clearly observed that wear resistance of Al-TiB₂ composites increases with increase of TiB₂ weight percentage.

Reason behind such trend has been mentioned as higher amount of hard TiB₂ particles yields higher hardness of the composite. It is also observed that wear depth increases with increase in applied load for all percentages of reinforcements in the composites. Poria et al. [54] have also reported the friction behavior of Al-TiB₂ composites against weight percentage of reinforcement at different sliding speed for different applied load. Figure 5 is presented here from that report. It is clearly seen that friction is highest for un-reinforced Al alloy and friction has been decreased with increase in weight percentage of reinforcement.

To summarize in nut shell, it can be said that whatever be the fabrication route of the Al-TiB₂ composites, wear resistance improves with addition of the reinforcement. But such improvement persists only up to a certain weight percentage of TiB₂ in base matrix. Further addition of reinforcement generates detrimental effect due to agglomeration of particles inside base matrix. Along with reinforcement, operating load significantly influences the wear and friction behavior of composites. At low load, composites show better tribological behavior which is quite relatable with Archard's wear theory.

Tribological properties of Al-TiB₂ composites under elevated temperature sliding condition also have been reported in several work. Actually in many applications of

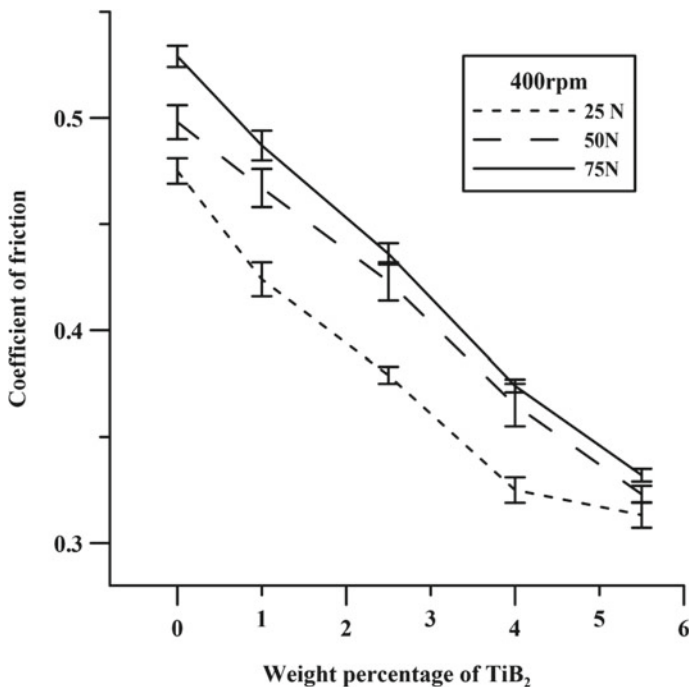


Fig. 5 Friction behavior as function of weight percentages of TiB₂

composite materials, components have to undergo the operating temperature which is nearly 40–50% of the melting point of aluminum alloys/AMCs. That is why tribological performance of composites should be clearly adopted before applying those composites in making industrial components. Kumar et al. [33] have studied Al–TiB₂ composites effect of sliding temperature and load on the wear behavior of Al–4Cu alloy and in situ Al–TiB₂ composites. They have observed that irrespective of the increase in operating temperature, wear resistance increase with weight percentage of TiB₂ composites. When operating temperature has been increased, mild wear has been transformed into severe wear. Temperature at which such transition occurs actually depends on the amount of TiB₂ present inside the composite. General observation of them is that normalized wear rate decreases with increase in temperature for the given amount of TiB₂. Poria et al. [55] have also reported high-temperature tribological performance of Al–TiB₂ composites under five different operating temperatures (50, 100, 150, 200 and 250 °C). From that report, Fig. 6 has been taken to show how wear rate varies at a fixed load with respect to operating temperature and weight percentage of reinforcement. It is seen that wear rate of composites does not change much with increase in operating temperature in the range from 50 to 150 °C, after which it increases sharply in the range from 150 to 200 °C.

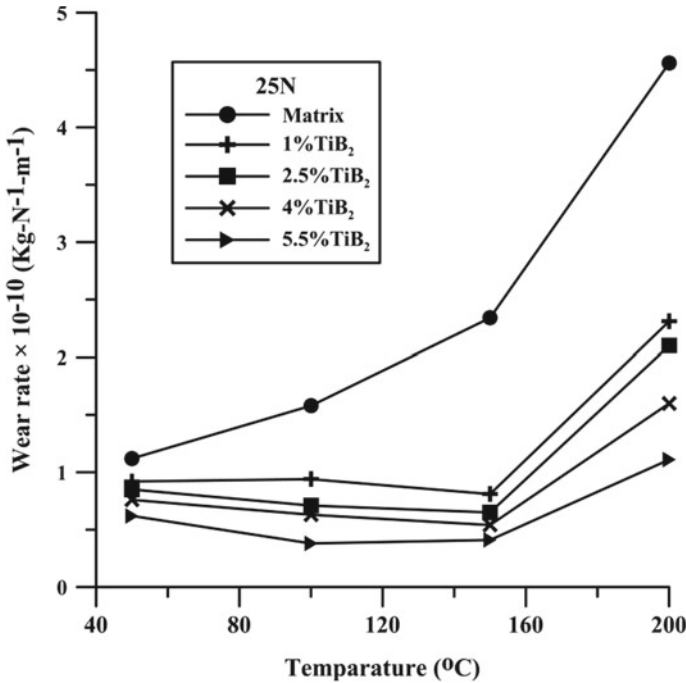


Fig. 6 Wear rate for different temperatures at 25 N load [55]

Some work is also available in lubricated condition tribological behavior of Al-TiB₂ composites. Because the outcome is obvious which is role lubricant is more influential than reinforcement effect on properties.

12 Corrosion Behavior of Al-TiB₂ MMCs

Corrosion of Al-TiB₂ composites also has been reported as the composite has already shown positive outcomes in terms of dry, lubricated and high-temperature tribological behavior. Previously, in steel-TiB₂ composites, it is observed that corrosion resistance of composites increases up to 4 wt% of the reinforcing phase after which corrosion resistance starts to decrease [68]. This phenomenon may happen due to the fact that with increase in the reinforcement phase in composites, fraction of the interface also increases and areas with significant difference in the electrochemical potential also enlarge. Thorough literature survey reveals that if reinforcement phase of AMCs/MMCs is not pure, then galvanic corrosion may increase through dropping in resistivities [25]. Major reinforcements actually do not possess resistivities enough to avoid galvanic corrosion. Sun et al. [69] have established that presence of TiB₂ as reinforcement develops higher corrosion sensitivity of the composites due to the

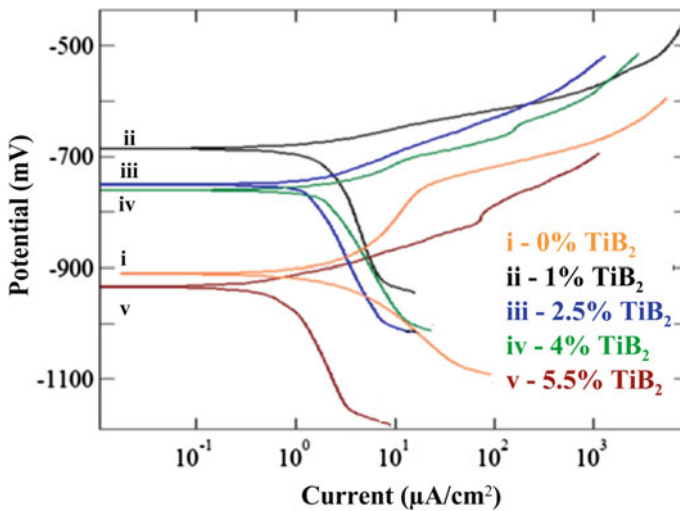


Fig. 7 Tafel plot for base alloy and different wt% of Al-TiB₂ composites

galvanic coupling effect between noble reinforcements (TiB₂) and much more active matrix (Al or Al alloy). Still, Poria et al. [56] have reported corrosion sensitivity of Al-TiB₂ composites through potentiodynamic corrosion test and electrochemical impedance spectroscopy. From their report, Tafel plot and Nyquist plot of base alloy and four different wt% composites have been presented in Figs. 7 and 8. From these two figures, it is clear that corrosion resistance of base alloy sufficiently increases with addition of 1 wt% TiB₂. Further increase in amount of reinforcement leads to decrease in corrosion resistance in terms of corrosion potential though they are better than base alloy until wt% becomes 5.5%. Highest wt% composites exhibit lowest corrosion resistance even lower than base alloy.

13 Conclusion and Future Scope

Starting from laboratory-scale research activities, right now MMCs have established its position in industry level and product level. For example, in applications like exit guide vanes of aircrafts, materials should possess high stiffness along with suitable strength, resistance to erosive wear and aluminum-based MMCs are obvious choice there. Al-TiB₂ composites reported in this chapter have been discussed in terms of their tribological properties and corrosion behavior. Importance of MMCs, why particulate reinforced MMCs are better than other type of composite materials, existing models and theories regarding mechanical properties of particulate reinforced metal matrix composites have been discussed in detail in this chapter. Discussion is also on how MMCs are fabricated and why ex situ techniques for

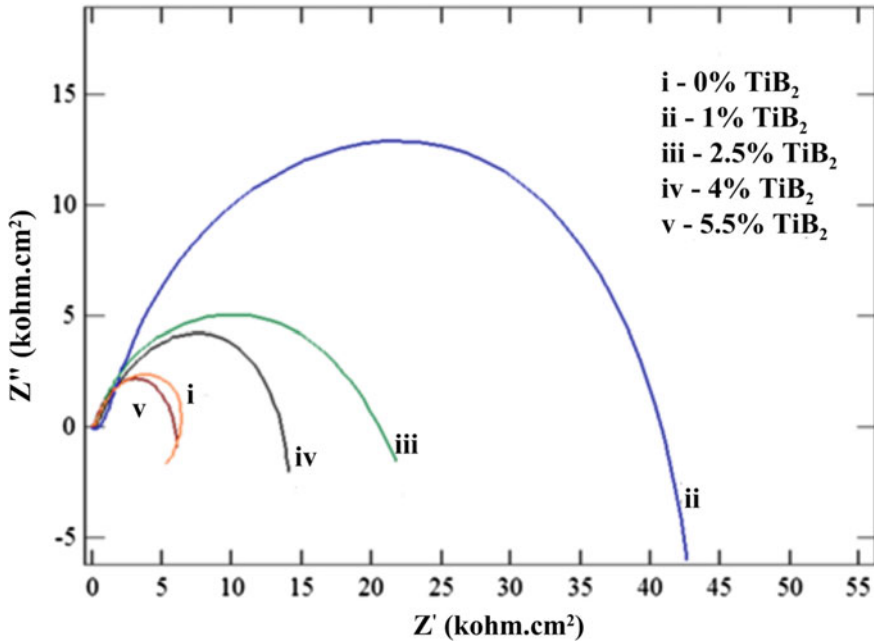


Fig. 8 Nyquist plot for different wt% composites

fabrication of Al-TiB₂ composites are better than in situ techniques. Tribological behavior of Al-TiB₂ composites is very much promising as per discussion. With increase in wt% of TiB₂, wear resistance of composites increases accordingly. It is also discussed how higher amount of TiB₂ phase can effect negatively on the tribological performance of composites. Unlike tribological behavior, corrosion resistance of Al-TiB₂ composites is not so well, though up to 1 wt% reinforcement (TiB₂) it behaves properly.

Future lies in the present. Invention and progression of composites are totally driven by the need of material in adverse and newer working conditions. Applications are modified on daily basis with development of knowledge domain. Researches on materials are also expanding day by day to catch up the newer domains. Al base matrix has been discussed in this study. Magnesium base matrix is now in focus for making new MMCs. Change in fabrication methods is also tried by several researchers. Very recently, Song et al. [67] have published a paper in nature on processing of bulk natural wood and claim that their processed wood is superior than many widely used structural materials as plastics, steels, alloys and composites. Rekha et al. [64] have reported high entropy alloy nano-particle decorated graphene as new age material in very recent time. So it is clearly seen that materials already have been shifted from composite materials. Functionally graded materials are the shifted version of composite materials. But they are also not sufficient to meet the requirements. Now

focus is on 'self-healing materials' [77]. Composites being multi-phase can play role in that domain. Research on self-healing composites has been started.

Currently, it is observed that transportation sectors are shifting towards electrical drive vehicles. Electric drive is the new age technology and it requires huge modification in technology involved with battery cells. But materials are not ready to be adopted for electric drive cars. From the materials of batteries to materials of engines, all are different in electric drive cars from existing one. This is a challenge from a material point of view. It is expected that future of materials research is awaiting a major shift.

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