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Metallic Glasses for Triboelectrochemistry Systems

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Abstract

A fundamental quest of modern triboelectrochemistry is to unravel the prevailing failure mechanisms when surface interactions are operated in corrosive environments and to study how these influence the performance of materials and tools. Both system and materials oriented approaches are thus required to deal with the electrochemical and physico-chemical changes of matter due to the influence of a mechanical sliding energy between the two contacting surfaces (i.e. tribocorrosion damage). In this chapter, metallic glass material concepts used in environments where tribocorrosion occurs are described. Concepts to act in opposition to wear and corrosion are briefly reported. In particular, a description is given of different groups of metallic glasses designed to withstand the effects of combined and uncoupled wear and corrosion. Metallic glass composition, structural effect, crystallization level, passive film formation, microhardness are often viewed as the most critical elements in the performance of tribocorrosion of metallic glasses. Interactions between wear and corrosion mechanisms are identified along with some models that aim to inform metallic glass selection and predict performance.

Keywords: wear-resistant bulk metallic glasses, corrosion-resistant bulk metallic glasses, wear-corrosion synergy, tribocorrosion, triboelectrochemistry

1. Introduction

Metals and their alloys of quasi-crystalline structures have been widely used for thousands of years, commencing with the Bronze Age, which took place approximately 3000 down to 100 years, and passing through the Iron Age [1]. Although, the utilization of these common engineering materials, namely ferrous and nonferrous, are still in current use nowadays, however, they are experiencing much concurrence with a range of novel materials and a bewildering array of solid products due to the engineering progress, which essentially depends on the availability and the intelligent use of materials.

At the present time, there are available for use in excess of 45,000 different metallic alloys [1]. Albeit, the steels and cast irons make up the largest use on a weight basis, the number of different nonferrous alloys exceed the number of ferrous alloys. The primary nonferrous alloys are those in which the base metal consists of either aluminum, copper, nickel, magnesium, titanium, zirconium or zinc [1].

With the introduction of new metallic alloys and the breakthrough in the production of the so-called glassy metals, what was the best choice several years ago may no longer be so. Over the years, considerable efforts and great progress have been made in the field of materials selection, in particular through the improvement of the specific properties of different sorts of alloys. These growing developments, inter alia, include processes for enhancing their metallurgical, mechanical, physical, chemical, and especially their tribocorrosion properties. Alternatives in the composition have also been formulated to improve the workability (e.g., glass-forming ability) of many metallic glass alloys through, commonly, monitoring the quenching rate. Critical cooling rate and maximum attainable size, known as critical casting thickness, are both direct indicators of glass-forming ability (GFA). The smaller the critical cooling rate and/or the larger maximum attainable size, the higher is the GFA.

In order to conduct a meaningful evaluation of a design alloy, all essential data required to fit with the most appropriate material must be disposable. It is the purpose of this chapter to supply as much of this information as possible for commercially available metallic glass materials, and for use in systems where mechanical and chemical surface interactions take place and leading to deterioration effects. The main strategies known to meet these requirements are outlined. Since mechanical wear and corrosion are broad fields, where the interplay between several mechanisms can occur, different approaches to prevent them have been contracted. Some of the most common ways are discussed. Examples from different classes of metallic glass material are given.

2. A short overview of mechanical properties of metallic glasses

A close relationship exists between properties of materials whose magnitude is usually determined by their bond strength. The choice of a material is the result of several compromises. For instance, the technical appraisal of an alloy will generally be a compromise between mechanical resistance, such as fracture toughness and some other properties such as yield strength, Young's modulus, density etc. A convenient way of bringing out these relationships is by a series of figures or charts, in which one parameter is plotted as a function of another.

An important relationship is that between fracture toughness and the yield strength, a typical characteristic of the damage tolerance of materials. Values of most engineering materials, including monolithic metallic glasses, and ductile-phase-reinforced metallic glass composites [2] are shown in **Figure 1**.

Generally, ductile metals have very high fracture toughness and fairly low yield strength. Metallic glasses, however, show limited plastic yielding and have toughness-strength (K_c - σ_y) relationships that lie between brittle ceramics and marginally tough materials. The lack of

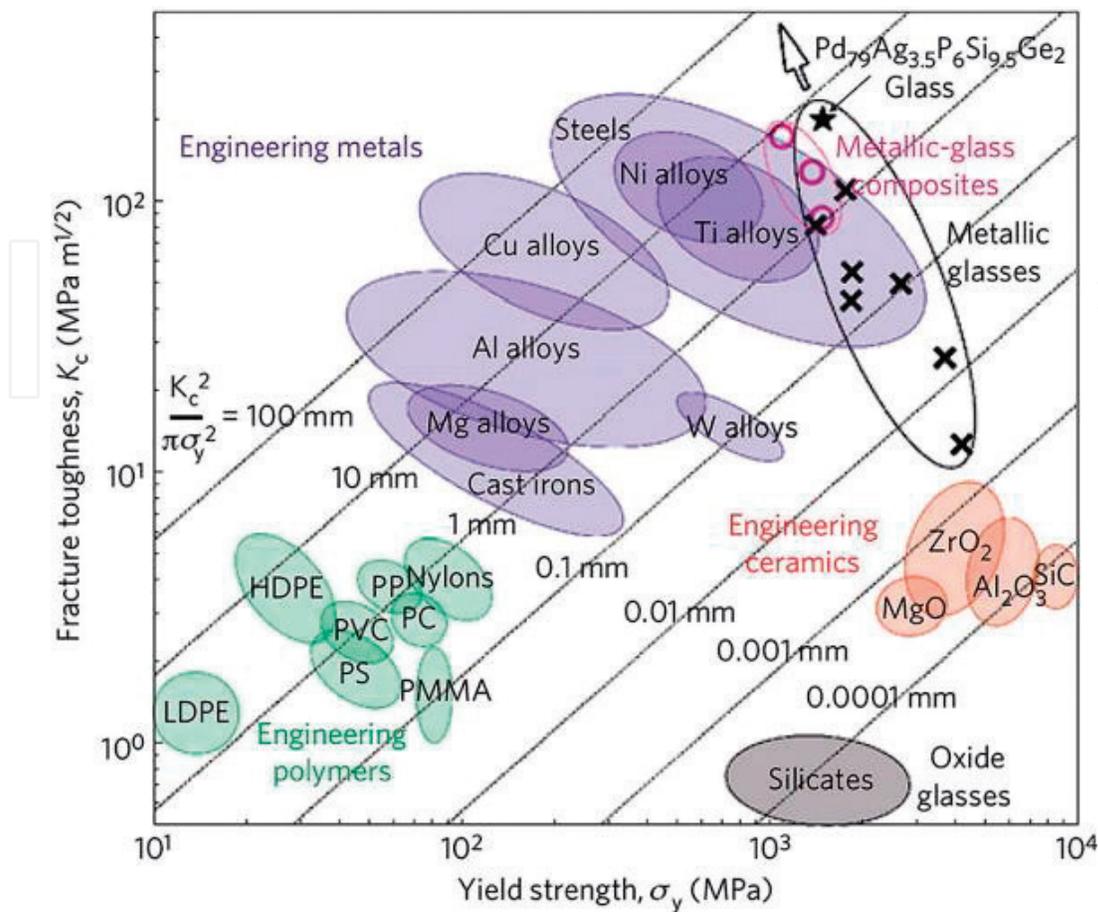


Figure 1. Ashby map of the damage tolerance of materials (fracture toughness *vs.* yield strength) including oxide glasses, ceramics, polymers, metals, monolithic metallic glasses (Fe-based glasses, Zr-based glasses, Ti-based glass, Pt-based glass) designated by crosses, Pd-based glass designated by a filled star, and ductile-phase-reinforced metallic glass composites designated by circles. (reproduced from Demetriou et al. [2] with permission from copyrighted ©Nature, 2011).

plasticity hinders the application of bulk metallic glasses (BMGs) as structural materials, and prevent their usage for instance in load-bearing structures. The need for the development of new efficient and resistant materials is thus essential in order to ensure this objective.

In this regard, great improvements in fracture toughness have been made as new alloy compositions were discovered and optimized to extend the fracture toughness limit for BMGs. The occupation of a new region of property space for BMG composites (BMGCs), designated by circles, is shown in the Ashby's map (**Figure 1**) [2]. Contours correspond to values for the plastic-zone radius, $K^2/\pi\sigma_y^2$. In this zone area, plastic deformation predominantly occurs at the crack tip because of the high stresses generated by the sharp stress concentration [3]. It is mostly this enhanced plasticity scale in BMGCs, which is at the origin of their superiority over other technical candidate materials. It is argued to be due to the fact that all the shear bands initiated in plastically soft regions with lower yield stress (or lower shear modulus) are prevented in the surrounding regions of higher yield stress or stiffness. This enhancement in both ductility and toughness is analogous to the tempering of plastics by inclusion of rubber particles [4]. As indicated by the arrow, the conjunction of toughness to the strength,

potentially accessible to metallic glasses extends beyond traditional benchmarks towards levels formerly inaccessible to any material (e.g., Pd-based alloys in [2]). One direct result of the unique microstructure is the high toughness-to-yield strength ratio, mainly accessible to BMGCs. Their strength exceeds that of the strength limit of known crystalline pure metals or alloys and approaches that of engineering ceramics, whereas their toughness is markedly high, among metallic alloys.

Some recent significant developments have been made towards the design of this kind of BMGC materials. This was achieved through the successful implementation of effective composite microstructures, which typically combine a strong glassy matrix with ductile crystalline reinforcements that suppress fracture while sustaining high strength. This variety of composite materials can only be obtained through the commitment of a nanocrystallization process [5] or *via* the reinforcement with ceramic particles [6]. Current studies on BMGCs performance are still at the development stage and concern the evaluation of either their mechanical properties or their corrosion resistance, but the perspective is very promising.

In recent years, a wide variety of industries including food, medical and pharmaceutical, aircraft components, electronics, building materials, and automobile industries have been promoting the technological development of newly composite materials including the vitreous-based composites to achieve suitable strength/density, and toughness/stiffness ratios.

3. Tribocorrosion fundamentals

An important problem in tribology concerns the interaction between friction processes and electrochemical reactions (corrosion) occurring in reactive environments such as aqueous media or hot aggressive gases. The effect of mechanical stimuli on chemical degradation of materials and, *vice-versa*, the influence of corrosion on the mechanical response of contacting materials are of great concern in many areas of tribology. A new research area, "tribocorrosion", emerged in recent years, mainly driven by the increasing demand from the biomedical implant, power generation, marine, and offshore industries. Since tribocorrosion is ubiquitous in many technical applications, it is necessary to employ material means capable of withstanding its damage effects.

Tribocorrosion can be defined as "...the process leading to a material degradation (i.e., material loss) which results from simultaneous mechanical (materials properties, surface and sub-surface transformations, cracking, etc.), chemical, electrochemical (corrosion attack) and/or biological material removal mechanisms (i.e., bio-tribocorrosion)..." [7]. It is basically an integration of two major areas of significance and application in mechanical systems, namely Tribology and Corrosion [8, 9]:

Tribocorrosion involves the inter-play between friction, wear (tribological), and corrosion (electrochemical) phenomena in a complex way. This includes such diverse phenomena as wear-accelerated corrosion, fretting-corrosion, erosion-corrosion, oxidational wear, chemical or corrosive wear often described in the literature. Therefore, tribocorrosion (or tribological) processes are intricate and not intrinsically fundamental, in the sense that Young's modulus

for example is fundamental, but rather that they depend on the triboelectrochemical system approach. In particular they are determined by a combination of a number of more fundamental properties of the contacting materials, testing parameters, and test conditions, especially the nature of the environment in which the tests take place. An important aim of research in tribocorrosion field is precisely that of determining the nature of this dependence, so that the triboelectrochemical behavior may be predicted from a knowledge of a system approach and the more fundamental properties of interacting surfaces. Although, this aim has not been achieved yet, a fair progress has been made, and still more work is required to have a good comprehension of just which are the important distinctive features determining the surface interaction behavior in a triboelectrochemical system.

3.1. Elements of tribocorrosion (instrumentation)

Tribocorrosion of two contacting solids in relative motion is, just as friction, a system parameter. A triboelectrochemical system consists of implementing electrochemical techniques to a tribological designed system (i.e., tribometer type, and complete material system). That mechanical designed system is of a great importance since this will enable to simulate as much as possible the entire material system used in the field, and the constraints that have associated with it (e.g., similarity of the wear mechanisms active in the laboratory test and in the field, such as abrasion, adhesion, fatigue, penetration hardness, bending, existence or not of a third body, erosion, corrosion, their combinations, etc.).

Generally, the tribological configuration involves:

- The choice of a tribometer type with respect to its characteristics (e.g., contact noise, vibrations, residual stress ...);
- The choice of a body (material specimen under test), and a counter-body (material antagonist, usually a ball, a pin, a plate or a disk), which constitutes the contact system geometry (e.g., sphere-on-flat, sphere-on-sphere, cylinder-on-flat, flat-on-flat...). This choice has to consider the metallurgical and chemical features of the two solid bodies (e.g., inertness, composition of contacting materials, microstructure, surface film composition, etc.);
- The choice of a lubricant or other matter between the two bodies (e.g., composition of the medium, viscosity, solid particles in suspension, stagnant or stirred, etc.);
- The choice of surrounding media and temperature (e.g., relative humidity, vacuum, composition of the corrosive environment, pH, aggressiveness, ionic conductivity, etc.);
- The loading conditions (pressure or force, relative velocity, acceleration, or frequency, a working distance, or number of contacts);
- And finally, the choice of the type of relative movement (uni- or bidirectional, continuous or reciprocating).

The measuring instruments in tribocorrosion tests allow to monitor in real-time and on-line the foregoing system parameters (e.g., contact conditions: normal or tangential force, relative displacement, velocity, etc.). The main focus is to promptly control any variation or change

associated with these parameters or settings *in-situ*. They need also to be instrumented with electrochemical techniques, which enables the management and the recording of applied electrochemical parameters and/or their responses (e.g., polarization of the contacting materials, charge density, etc.). The ultimate goal is to obtain promptly any information on the evolution of the input and output chemical-mechanical measurements during the test. These *in-situ* data outcome combined with *ex-situ* surface characterization techniques (e.g., high resolution SEM imaging, TEM, XRD, EDAX, FIB, XPS, Auger spectroscopy, FT-IR, roughness surface profilometry, micro- or nanoindentation hardness, etc.) and chemical analyses of post-test solutions (e.g., ICP-AES, ICP-MS) allow for the disclosure of the wear-corrosion mode, and thereby contributing to a better understanding of the tribocorrosion mechanisms involved (corrosion mechanism, wear regime, friction process, etc.).

The typical configuration of a triboelectrochemical cell experiment involves an inert material (e.g., corundum counter-body) sliding against the investigated material (i.e., working electrode) under mechanochemical well-controlled conditions. Although metal-on-metal contact configurations are possible, but the use of an inert counter-body simplifies the interpretation of the electrochemical results of the corrosion-wear process. In addition, it is most advising to perform the electrochemical measurements under stationary regime conditions, at least prior to starting up of the measurements. The development of relevant models for the interpretation of the tribocorrosion mechanism concurrently depends, essentially, on the choice of electrochemical techniques to be implemented in a tribocorrosion test and the mechanical contact conditions (e.g., relative motion). The state-of-the art and reviews on triboelectrochemical techniques and experiments are available elsewhere [8–13].

3.2. The use of electrochemical techniques in the study of *in-situ* tribocorrosion processes

Corrosion processes are of electrochemical nature and therefore electrochemistry likely interferes with the tribological behavior of tribocorrosion systems. Attempts were made in recent years to control wear by electrochemical methods in engineering and biomedical systems. These electrochemical techniques provide a very convenient way to measure the rate of corrosion processes in either the laboratory or the field. Such methods can also be used in many different ways to assess either their efficiency of monitoring corrosion material degradation (e.g., concrete steels, and marine alloy structures) or their capability for material protection (e.g., inhibitors, protective layers, coatings, and appropriate metals and alloys). The theoretical bases and the practical implementation of the electrochemical techniques have been published in books and review articles [8, 9, 11, 14] and this material is compendiously repeated here only to the extent that it is needed to define the terminology as well as the utility of the topic for the chapter.

In mechanical lubricated contact systems where surface interactions do occur, these techniques offer the possibility to simulate different corrosion conditions under well-controlled electrochemical environments. This can be done for instance by the measurements of open-circuit potential (E_{oc} or E_{cor}) during a corrosion-wear test, measurements of cyclic potentiodynamic polarization curves under wear and pure corrosion conditions, records of the current-induced

applied potential resulting in an infinitesimal disturbance of the surface (potentiostatic control), measurements of current-induced single step anodic potential pulse (for the study of film repair, or repassivation), measurements of electrochemical noise for on-line tribocorrosion monitoring, measurements of electrochemical impedance, measurement of the linear polarization resistance (LPR), etc.

Since most of the undertaken studies on chemical degradation of glassy materials involve the use of cyclic potentiodynamic polarization method, it would be interesting to outline the conditions and limitations of this electrochemical technique for its use in tribocorrosion.

3.2.1. Measurements of cyclic potentiodynamic polarization curves

The susceptibility of metals to localized corrosion is usually expressed by the breakdown potential, E_b , or designated to, as the pitting potential, E_{pit} , and the repassivation potential, E_r , or termed the protection potential, E_p . At the breakdown potential, localized corrosion starts. The E_{pit} of a metal is often associated with the potential at which the current density suddenly increases and with the breakdown of its passive surface film. The higher the potential (more noble), the less likely the alloy is to cause the initiation of localized corrosion. At the repassivation potential, pitting stops.

A cyclic potentiodynamic polarization technique can be employed to determine both E_b and E_r of a corrosion system under wear (i.e., tribocorrosion) and pure corrosion conditions.

Many researchers [15–21] have successfully used the potentiodynamic anodic polarization technique to study the corrosion, the wear-corrosion synergism, and the tribocorrosion behavior of metallic alloy systems including the BMGs in various electrolytes [17–21].

ASTM G61-86 provides a procedure for conducting cyclic potentiodynamic polarization measurements [22]. By convention a cathodic current is negative whereas an anodic current is positive [23].

This technique uses a typical three-electrode system (WE working electrode or metal being investigated, RE (SHE, reference electrode), and CE (Platinum or Graphite, counter-electrode)) controlled by a potentiostat as shown in **Figure 2**. The potential, which applies to the WE, is usually swept from the active (cathodic) direction to the noble (anodic) one, while tracking the current density continuously until it reaches a selected value of current density, where after, the scan is inverted in the active direction, until the hysteresis loop closes or until the corrosion potential is reached. The potential of the WE can be considered as the “driving force” of the corrosion system, while, the anodic current density can be regarded as proportional to the corrosion rate of the WE.

A typical plot of polarization curve generated by this method as E - $\log(i)$ is shown in **Figure 3**. If a specified material is susceptible to localized corrosion, a hysteresis loop as shown in **Figure 3** will be observed as the potential scan is reversed. Otherwise, a uniform corrosion takes place in the transpassive or oxygen evolution region. Note that the larger the area of the hysteresis loop, the lower the ability of the metal to repassivate.

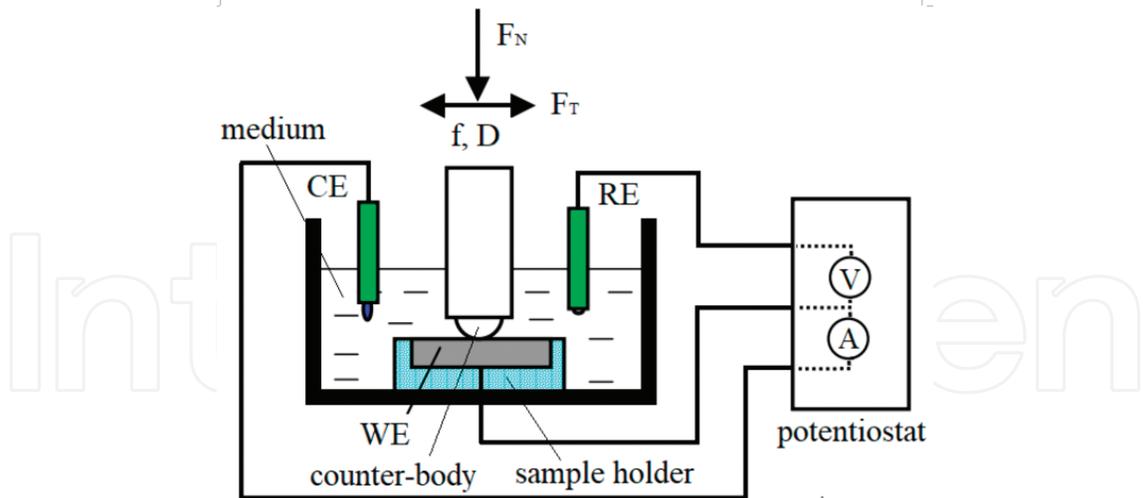


Figure 2. Schematic view of a tribocorrosion experimental set-up under potentiodynamic polarization conditions. Potential (E), and current density (i) measurements are performed on a working electrode (WE) sliding against a counterbody ball (unidirectional reciprocating sliding, sphere-on-flat) with respect to a RE reference electrode (e.g. Ag/AgCl (3 M KCl)) via a V voltmeter and CE counter-electrode (platinum or graphite) via an A ammeter respectively. F_N normal force, F_T tangential force, f sliding frequency, D displacement amplitude.

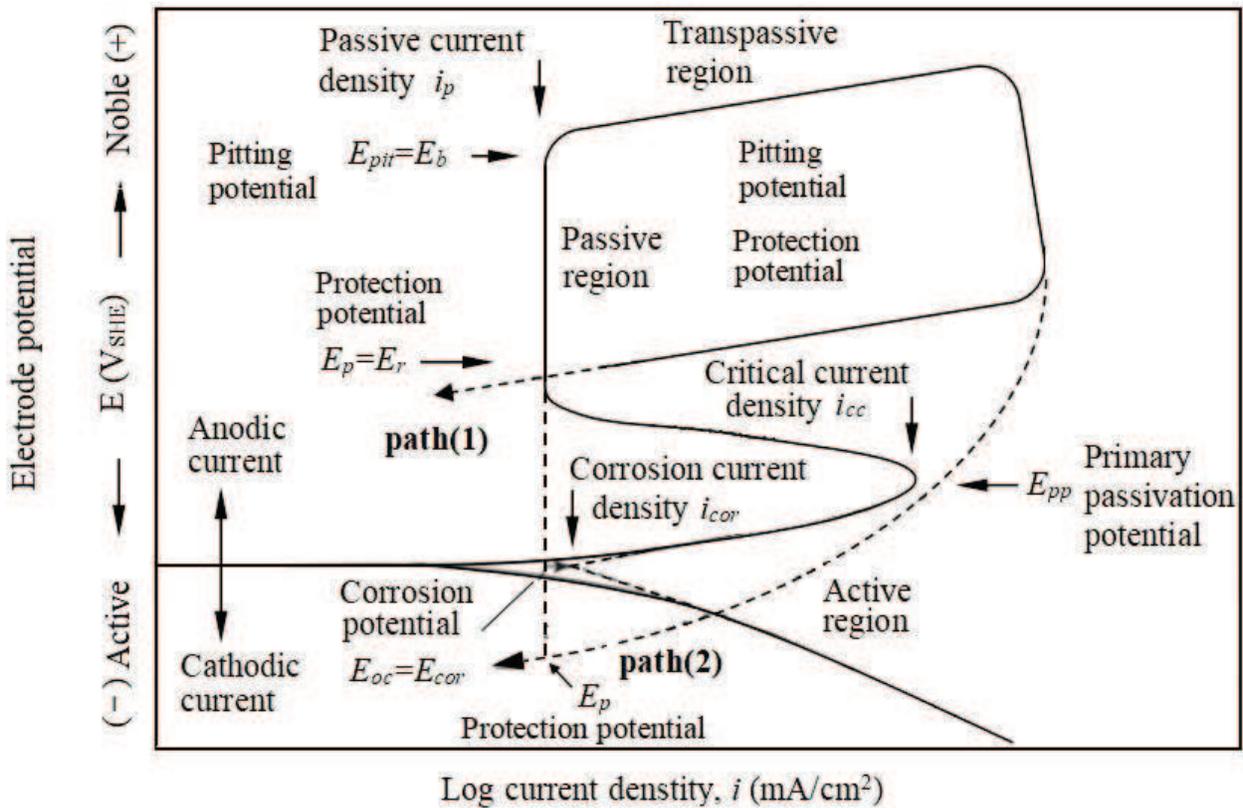


Figure 3. Schematic view of a hypothetical cyclic potentiodynamic polarization (cathodic and anodic) plot for determining localized corrosion parameters.

The approach to be considered for getting a quick picture of the electrochemical behavior of a metal under polarization is to identify some of the key corrosion parameters directly from the cyclic potentiodynamic scan mode (**Figure 3**), mainly:

- The corrosion behavior of a metal is assessed at E_{cor} (or E_{oc}) and other potentials.
- The process is designated as anodic polarization when the potential is above the E_{cor} and cathodic polarization when the potential is below the E_{cor} .
- The corrosion potential, E_{cor} , corresponds to the potential at which the current density approaches or theoretically equal zero ($i \approx 0$).
- At cathodic potentials lower than E_{cor} , the cathodic reactions takes place (H_2 evolution or O_2 reduction prevails).
- The extrapolation of the experimental anodic and cathodic branches of the polarization curves, as shown in **Figure 3**, indicate the corrosion current density, i_{cor} .
- The primary passivation potential (E_{pp}) corresponds to a potential positive to which passive surface layers are formed, and at which a maximum corrosion current density is reached coinciding with the critical current density (i_{cc} current requisite prior to the formation of surface layers).
- The region, where the current density remains approximately 10 mA.m^{-2} (i.e., passive current density, i_{p} of the electrode at E_{r}) as the potential increased, is called the passive region. This corresponds to the stabilization of a passive film. A material that exhibits a high resistance to localized corrosion in a specified environment form an adherent, and dense, nonporous, thin passive oxide/hydroxide film, which protects it from high corrosion rates.
- The protection potential E_{r} (or E_{p}) is the potential at which passive layers are stable and protective.
- At the potential interval, ($E_{\text{b}} - E_{\text{r}}$), pits are initiated and propagated. In fact, the material may suffer from localized corrosion when the potential is higher than E_{r} .
- High values of both pitting overpotential ($\eta_{\text{pit}} = E_{\text{b}} - E_{\text{oc}}$), and protection overpotential, ($\eta_{\text{p}} = E_{\text{r}} - E_{\text{oc}}$) may indicate a strong resistance of the metal to pitting at E_{oc} . High values of both (η_{pit} and η_{p}) are desirable to reflect high values of E_{b} and E_{r} relative to the E_{oc} .
- At potential above E_{b} , transpassive region starts. The local breakdown of the passive film continued driven by a rapid active dissolution (e.g., case of some stainless steels immersed in chloride solutions), and usually at more elevated potentials, oxygen evolution may occur (*cfr.* Pourbaix diagram, E -pH).
- In the reverse scan, as in case of path (1), the localized corrosion will not be triggered at E_{oc} ; in this case, the working electrode will not suffer pitting under free E_{oc} conditions. If the path (2) is observed, where E_{pp} is below E_{oc} , the working electrode will undergo pitting corrosion on the surface defects or after E_{oc} incubation periods.

Many of the foregoing determined corrosion key parameters are based on empirical observations. As with any empirical method, it is perplex with many questions about the extent of its validity. The power of this technique should not be over-estimated, since the values of E_b and E_r are subject to change by a number of factors. Typically, for instance, environmental changes (e.g., temperature, pH, reagent as chloride ions) will influence these values drastically. Moreover, this method can be function of scan rate, pit size or depth, polarization curve shape, and specimen geometry, which can affect the accuracy of these electrochemical parameters (E_b and E_r) [24]. For example, if the scanning rate is too high, the E_b usually has a higher value than the correct value. This is due to the potential dependence of the induction period (time required for localized corrosion to initiate) which is long at low potentials and short at high potentials. To overcome this issue, the E_b can be measured by using a stationary potentiostatic method, in which the electrode is polarized at a constant potential and the time dependence of the current is measured. If the current starts to increase with time at a particular potential, then this potential is the correct E_b . Due to these uncertainties, this technique should be considered as qualitative and should never be used alone. In fact, it is often desirable to use at least two different types of corrosion monitoring devices whenever possible to weed out spurious or inaccurate readings.

A complete discussion regarding DC and AC electrochemical techniques for the measurement of corrosion rates is beyond the scope of this chapter. A more comprehensive treatment of this subject area may be found elsewhere [9, 11, 22, 65].

3.3. Aspects of tribocorrosion

Wear is an unavoidable and a potentially serious problem in all areas of engineering. In particular, wear due to tribocorrosion is reflected by a loss of material from the exposure to corrosion of contacting solid surfaces and in relative motion. Designers and engineers who have to make optimal decisions in situations where tribocorrosion considerations are significant, need to know "how long will a component last?" To solve this question, numerous models have been developed so far to distinguish this material loss due to tribocorrosion. These models usually correlate a wear volume or a wear rate with physical and geometrical quantities. Various expressions have since been attributed to this material loss, of which the material loss can be defined in terms of weight, volume, surface, depth, width or even charge density or current density, per unit hardness, per unit frictional dissipated energy (work due to the tangential force), per unit input energy (work due to the normal force), or even per unit sliding distance, or sliding time, sliding frequency, contact frequency, etc. It becomes readily understandable of the complexity of comparing results between the various wear data published so far. It is expected then that the terminology in this field is rather uncertain, and it will remain so for a certain time, hence the need for a specific standardization, despite some recent progress made in this area [25].

One of the earlier attempts to predict the wear rate or wear volume loss of a material in sliding contact is the commonly Archard wear criterion [26] used during the second half of the twentieth century. That criterion is usually expressed as follows,

$$W_v = k \frac{F_N}{H} \quad \text{or} \quad W_r = kA_r \quad (1)$$

where, W_v and W_r represent the volumetric loss (assigned as total volume of wear debris produced), and the wear rate (usually expressed per unit sliding distance) respectively. k is the dimensionless Archard wear coefficient, A_r the real area of contact, F_N the applied normal load, and H the hardness of the worn material.

This equation was originally used for the case of adhesive wear [27, 28], then it was extended to more cases including that of tribocorrosion. This is because the k parameter in the Eq. (1) exclusively remained the only flexible parameter consistent with the case to which the wear may originate. For example, unidirectional sliding of mild steel against mild steel without any lubricant has a k of 10^{-2} , whereas, for stellite sliding against tool steel, k is 10^{-5} [29]. Even more confusing is that, according to literature, the Archard wear coefficient can vary by two orders of magnitude for the same couple of materials just due to a slight change in load or speed [30]. These findings should be taken with precautions in view of the number of empirical error cases reported with respect to the wear reproducibility and validation of test methods. Friction and wear properties are often considered as subjects of poor accuracy in comparison with materials intrinsic properties. Indeed, comparative round robin studies on the topic have shown that the reproducibility of wear derived from different inter-laboratories with the same material pairing was often very poor [31]. Using the wear track width, the scattering was roughly 50% whereas the scatter in the wear coefficient was over three orders of magnitude. No clear correlation was found between a single and constant parameter (type of tribometer, normal force, and sliding velocity) and the wear rates measured in inter-laboratories. Interestingly, a good convergence was found between the wear volume loss and the energy dissipated in the tribocontact zone [32–36]. This can readily be explained by the fact that the dissipation of frictional energy is one, among others, of the main causes of triboelectrochemistry, playing an essential contributing role in wear mechanism, in this case entailing an acceleration (e.g. chemical wear rates) or modification of tribochemical reactions. The yielded frictional heat between interacting surfaces leads to a stationary rise in temperature at surface contact asperities and flashes. Furthermore, such frictional energy can take the form of high quantum excitations with short lifetime of surface and bulk sites due to the mechanochemical forces involved during the sliding process. Those excitations are also responsible for the occurrence of triboluminescence and triboelectricity.

Tribologists nowadays are seeking for an agreement due to the fact that there is an unavoidably need to address more fundamental research towards the establishment of an original formulation or a universal methodology to define a “wear criterion” in order to better understand the complexity of the wear process in a tribocorrosion test. Although, this aim has not yet been achieved, a fair amount of progress has been made on this matter-oriented approach. This remains so far valid only as part of the case-by-case study.

To conclude, research must focus on establishing an approach that emphasizes the nature of the dependence of the mechanochemical wear rate (output) on the energetic aspect of sliding friction, the electrochemical aspect of the exposure of bare metal surface, and the transformation of the subsurface material (input). This usually should incorporate materials properties, and behavior. If it does, this could be very useful to solve most the issues and difficulties encountered in the specific field (e.g., cases involving the failure of mechanical systems related matter at any given time), and thereby leading to a better improvement of the reliability life of

selected material and design technologies when adopted in mechanical articulations. Further, this could predict materials performance in an environment where tribocorrosion plays a significant role.

In tribocorrosion phenomena, where tribological contacts are exposed to corrosive environments, such as aqueous lubricants, the contact materials are subject to both mechanical, and chemical/electrochemical solicitations, which contribute to material removal from sliding surfaces. The rate of material degradation/removal cannot be predicted simply by adding the wear rate in absence of corrosion to the corrosion rate in absence of wear. The reason is that corrosion and wear do not proceed independently and synergistic effects usually (but not always) result in accelerated material degradation (tribocorrosion). In that respect, theoretical models have been developed so far with respect to mechanical, chemical, and electrochemical factors and their mutual interactions, and which can be tested under well-controlled experimental conditions. In general, modeling has followed either an empirical or a mechanistic approach. The empirical approach is based on the independent measurement of material loss due to wear and corrosion. These parameters are summed up and compared to the material loss due to tribocorrosion. The difference between the two is termed synergy (ΔW_{syn}). A general equation for this approach is of the form [37–39],

$$W_{\text{tot}} = W_{\text{mec}} + W_{\text{cor}} + \Delta W_{\text{syn}} \quad (2)$$

where, W_{mec} represents the material loss due to wear measured in the absence of corrosion, and W_{cor} is the material loss due to corrosion only without any influence of mechanical wear.

Although, the empirical approach is technically feasible which allows for the ranking and the performance of materials based on their resistance to tribocorrosion in engineering systems, it is still time-consuming, quite economically not justifiable in the long-term, and furthermore, it integrates a synergy term, which has no physical meaning.

The advantage of a mechanistic approach is that it leads for a better understanding of the physical processes involved in tribocorrosion by incorporating the notion of synergism into the mechanical and electrochemical terms. Many factors can be responsible for the mutual dependence of mechanical and chemical material removal in a tribocorrosion system. For example, local abrasion of the passive film can lead to wear accelerated corrosion due to rapid dissolution of the locally depassivated metal surface, followed by repassivation [40]. The abrasive action of hard oxide particles formed by corrosion can accelerate the mechanical metal removal by wear [41]. The plastic deformation of the surface layer of a rubbing metal can lead to a transfer of material to the opposite body resulting in a reduction of the corrosive wear rate [42].

Therefore, it is important to distinguish material loss due to chemical or electrochemical oxidation (i.e., wear accelerated corrosion) from material removed due to mechanical wear (i.e., mechanical material removal from the sliding contact). The former arises from the fact that an asperity sliding on a material surface produces a fresh wear track zone of clean bare material (i.e. metal), which is usually more susceptible to corrosion than the same surface subjected to free corrosion under no mechanical plastic contact or sliding conditions. The

effect of repeated sliding may cause the removal of metal particles by asperities burrowing beneath the surface [12, 42, 43].

Therefore, the overall wear volume due to tribocorrosion, W_{tot} , can be defined as follow:

$$W_{\text{tot}} = W_{\text{che(wac)}} + W_{\text{mec}} \quad (3)$$

where, $W_{\text{che(wac)}}$ is the electrochemical contribution to wear; it is termed wear accelerated corrosion and it reflects the material loss due to corrosion in the presence of wear. W_{mec} is the mechanical wear, and it reveals the material loss due to wear in the presence of corrosion, and which can be related to processes as that for the formation-ejection of oxide debris, oxide layers or any corrosion products, and plastically detached metal.

W_{tot} can be determined by measuring the volume of the wear scar post-experiment using, for instance, a laser non-contact profilometry or by on-line measurement of the rate of moving down of the counter-body (e.g., a pin) on the surface wear track during sliding. The latter method has the advantage of recording an instantaneous wear rate, but it would only be applicable if no significant amount of solid reaction products (such as third body particles) accumulate in the contact zone during the tribocorrosion experiment. Under potentiostatic control, the electrochemical term ($W_{\text{che(wac)}}$) can barely be related to the anodic corrosion current ($I_{\text{a,tribocor}}$) measured under mechanical sliding wear (occasionally by subtracting the background current) using Faraday's law. The amount of anodically oxidized metal under such conditions is calculated as follows [12]:

$$W_{\text{che(wac)}} = \frac{M \cdot q}{\rho \cdot z \cdot F} \quad (4)$$

where, $W_{\text{che(wac)}}$ is the volume of the metal transformed by anodic oxidation in a triboelectrochemical test. $q(t) = \int I_{\text{a,tribocor}} \cdot dt$, is the electric charge generated during that transformation process, which is obtained by integrating the measured current $I_{\text{a,tribocor}}$ over the time of the triboelectrochemical experiment, M is the atomic mass of the metal, z is the valence for oxidation reaction, F is the Faraday constant (96,480 C/mol) and ρ is the density of the metal.

This equation is credible and independent of whether the anodic oxidation leads to the formation of dissolved metal ions or solid reaction products, such as oxide films.

It is worthwhile to note that few assumptions must be met in order for the Eq. (4) to be used [12, 40], namely:

- The measured current must be equal to the anodic partial current for metal oxidation, which means that cathodic partial currents due to the reaction of oxidizing agents must be negligible. This can be performed by anodic polarization into the passive potential region.
- The charge number z for the oxidation reaction must be known [12, 40, 42].

The mechanical wear (W_{mec}) is taken as the difference between the total wear volume W_{tot} and the chemical wear volume $W_{\text{che(wac)}}$ determined from the electric charge.

3.4. The causality of wear-corrosion synergism

The synergy between wear and corrosion has recently attracted increasing attention to improve materials used in systems where tribocorrosion plays a role. However, wear-corrosion synergy still seems to be a developing topic of discussion as no convincing expression is available yet.

A positive or a negative (antagonism) synergistic effect can occur in most cases where surface interactions interfere with tribocorrosion phenomena. It intervenes especially (in a positive way) by increasing the wear (volume) when the mechanical process affects the electrochemical process and *vice versa*. In these situations, the total wear (volume loss) will be very different and greater than the sum of the mechanical wear in the absence of corrosive environment and the loss of material by corrosion in the absence of any mechanical stress. A negative effect of synergy, however, will occur when the total wear is less than the sum of the two protagonists taken individually and independently, namely wear and corrosion.

Madsen et al. [37, 38] critically reviewed the measurement of wear-corrosion synergism, and proposed a group of penetration rate equations to quantify the wear and corrosion processes and the wear-corrosion synergism. Their results showed that the wear-corrosion synergism is of great extent for alloys, such as AISI 316 stainless steels, which depends on the formation of a film of passive layers for their corrosion resistance, sometimes only a few atom layers thick, resulting from an interaction between the material and the surrounding environment [37, 38]. On the contrary, the synergism was limited for alloys, such as low alloy steels (e.g. amorphous steels), which do not depend on the presence of a passive film for their resistance to a corrosive environment. The causality of this synergistic effect has been explained in part for some passive materials. The presence on their surface of passivation layers and the ability of their surface, even in a deformed or partially damaged state, due to the sliding contact by the counter-body or a third-body, to be rehabilitated (by forming reaction layers with a thickness of a few nm, such as oxides, solid precipitates, adsorbed layers or passive surface films) is at the origin of the increment of that synergy. Dense oxide layers, precipitates, or passive films may play a protective role in isolating the underlying metal from a direct contact with the surrounding corrosive environment, thereby protecting the metal from a corrosion increment, but not necessarily their mechanical wear. In particular, one of the possible explanations could be related to the mechanical or chemical shear strength of these formed layers. This can likely be one of the causes of the incremental or decline effect of the wear-corrosion synergism of passivating metals. This is mainly true in the case of stainless steels and other alloys containing chromium. Their passive surface film formed in the ambient air or in contact with an aqueous solution has a thickness of a few nanometers but gives them a high resistance to corrosion. The sliding of a hard counterbody material on such a surface is likely to damage that passive film what is known as a “depassivation” process by which the bare material is exposed to the corrosive environment [8, 10, 13, 32, 44]. Various but essentially electrochemical processes can then compete on these bare surfaces [8, 10, 13, 32, 44], namely:

- The dissolution of the metal in the corrosive medium;
- The formation of a new compound that may contribute to the breakdown process;
- And the restoration of the protective film known as “repassivation” process.

Most amorphous alloys, such as bulk metallic glasses (BMGs), usually do not depend on the presence of a protective surface film to exert a corrosion resistance. Therefore they can be expected to claim showing a negative synergistic effect, hence their opportunity to be selected as potential candidates over other passive alloys (such as stainless steels) in systems where tribocorrosion plays a role.

Celis et al. [10, 13] identified five mechanisms in tribocorrosion, which could explain the synergism noticed between mechanical and chemical factors acting on contacting materials, mainly:

1. The debris can speed up or reduce wear compared to what happens in the same environment where debris does not exist like e.g., in sliding contacts polarized at a large cathodic potential;
2. A galvanic coupling is established between the worn (active) and unworn areas (passive). It accelerates the anodic dissolution in the area where the metal is depassivated;
3. A galvanic coupling may be established between the two contacting counterparts;
4. An accumulation of dissolved species may take place in the liquid surrounding the contact. This may render the medium chemically or electrochemically more aggressive;
5. The mechanical loading in the contact area and its nearby zone may cause a work hardening of the materials. This work hardening can alter the kinetics of corrosion and/or repassivation processes.

3.5. Passivity breakdown

Most of engineering and biomedical metals and alloys oxidize and frequently passivate “spontaneously” in contact with the ambient air, and with suitable aqueous media to form “natural” thin passive surface oxide films. Alternatively, alloying is also considered to be, *inter alia*, the most extensively used method for enhancing the passivity of base metals [45]. Passive films that grow on most surface alloys are found to be of two types: discontinuous, and continuous [46]. Discontinuous films are porous and are formed at the metal/solution interface from the reaction of metal cations with species in solution. They have a thickness of up to 1 mm and are less protective. Continuous films, on the other hand, are tenacious and thin (nm’s to μm ’s thickness range). They have high resistances ($\geq 10^6 \text{ ohm.cm}^{-2}$) and support a high electrical field. They are called barrier protective layers, which serve to prevent current flow, and corrosion (i.e., dissolution). Commonly, the passive film on most metals and alloys consist both continuous, and discontinuous layers, with discontinuous film forming the outer layer, and the continuous film forming the inner barrier protective layer. A typical example of a bi-layer passive film formed on Fe-based amorphous alloy and interacting with anions adsorption in various aqueous solutions [47] is depicted in **Figure 4**.

The approach that links the improved resistance of amorphous alloys to their ability to promote amorphous passive oxide formation is well accepted by the scientific community. In high-temperature gas working conditions, vitreous or amorphous oxides offer improved

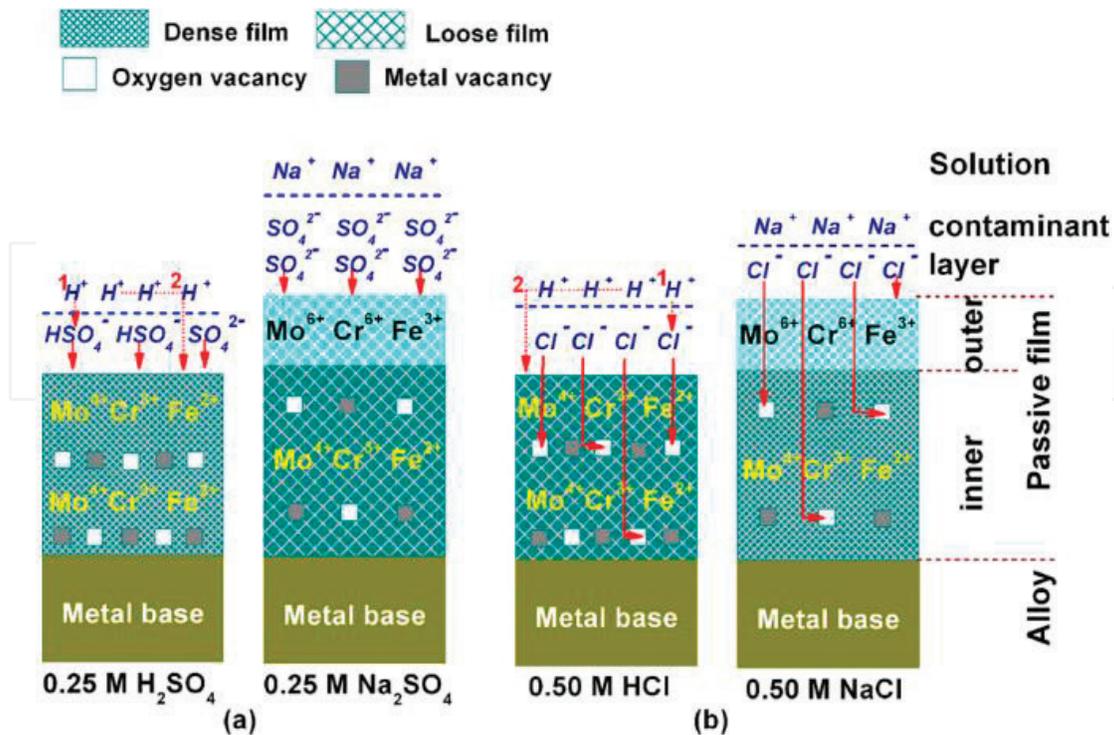


Figure 4. Schematic diagrams of anions adsorption and characteristics of passive films (bi-layer structure) formed on Fe-based amorphous alloy in (a) sulfate and (b) chloride solutions. (reproduced from Wang et al. [47] with permission from Elsevier Science).

oxidation resistance due to the absence of oxide grain boundaries, which provide a rapid diffusion path for concentration gradient-driven ion movement [46]. In aqueous solutions, ion transport is mostly driven by the electric field across the oxide film. The lack of oxide grain boundaries may lower ion migration rates, rendering the passive film more protective [46, 48].

It is worthwhile to mention that if the passive films on metals, like iron, nickel, and chromium, remained intact, then the corrosion current flowing across the interface under most industrial conditions would be of the order of $0.01\text{--}1.0 \mu\text{A}\cdot\text{cm}^{-2}$, corresponding to corrosion rates of approximately $0.15\text{--}15 \mu\text{m}$ per year [49]. For most practical situations, metal loss rates of this order are of no concern, so that our automobiles, bridges, aeroplanes, and industrial systems would last for periods extending well beyond the current design lifetime. Unfortunately, passive films do not remain intact, and corrosion rates of many orders of magnitude greater than those indicated above for fully passive substrates are commonly observed, particularly if the attack occurs locally.

Passivity breakdown can occur for a variety of reasons, including mechanical straining of the substrate metallic alloy, the frictional dissipated energy in tribological contacts required for micro-cracking, the presence of thermal stresses within the oxide due to differences in thermal expansivity, compressive stresses in the oxide growth (Pilling–Bedworth ratio), fluid flow and cavitation, transpassivity polarization, and chemically-induced phenomena. In particular, the rapid transport and accumulation of cation vacancies at the oxide/metal

glass interface is one theory accounting for oxide breakdown [50]. Moreover, vitreous oxides on amorphous alloys perform well due to the enhanced bond flexibility, because the vitreous or amorphous material can rearrange to accommodate lattice mismatch and strain between the oxide and the metal [48, 51]. As a result of this flexibility, almost all surface atoms can bond with oxygen or OH without requiring an optimal epitaxial relationship between the ordered metal substrate and oxide. Intolerable changes in oxide/metal misfit strain with halide incorporation is another theory accounting for the rupture of protective oxide films on metals [52].

In the case of crystalline alloys, such as the highly passivated stainless steels, it should be noted that the improved corrosion resistance associated with the addition of 18% Cr to crystalline iron is attributed, in part, to a change in the protective oxide structure from a well-oriented spinel structure at 0–12% Cr to a non-crystalline structure at 18% Cr [48]. This disordering has been demonstrated by low-energy electron diffraction [53] and scanning tunneling microscopy [54]. A retardation in ionic transport may occur, because non-crystalline films have fewer defects or grain boundaries to enhance ionic movement. In summary, desirable amorphous oxide/amorphous alloy properties include defect minimization, film ductility, bond flexibility, and efficient, rapid film repassivation, which all contribute to improved corrosion resistance [48, 51].

4. Consensus on the need of materials for triboelectrochemistry systems

The development of tribocorrosion resistance requirements has resulted in the development of a much larger number of materials that did not exist before, especially metallic alloys. In turn, such a development of materials has multiplied case studies, and increased the number and the diversity of corrosion-wear problems. Accordingly, the resolution and the nature of corrosion-wear problems are intimately related to the choice of materials. This does not mean that the tribocorrosion resistance is necessarily the determining parameter in the choice of a given material. Such a choice must, in fact, make it possible to fulfill at best one or more technological functions, and it is quite obvious that, under such conditions, the mechanical properties of the materials, their properties of implementation, their price or their availability are in many cases, parameters are just as decisive in the choice as their only resistance to tribocorrosion.

5. Evolution of the solutions to triboelectrochemical problems

The choice of metals and their alloys seems to be more relevant for designing materials over plastics, foams, polymers, and natural materials if the intended application requires a limiting risk factor of deformation and flexibility, hence interest on their application to load-bearing structures. Alternatively, the development of novel metallic-glass-matrix composite materials

has open up the opportunity for alloy design and innovations in new bulk metallic glass (BMG) materials to withstand deformation and flexibility that cannot be achieved by traditional metals, or casual BMGs making them attractive for various tribological systems (e.g., journal bearings), and mechanical engineering applications.

The ultimate resolution combining selection and material design is a consensus between economical parameters and technical qualification. Generally, this requires three essential steps, namely:

1. Identification of the requirements (e.g., design considerations);
2. The choice of materials assigned for the function of interest, including, inter alia, mechanical and chemical risk factors;
3. The election of the least expensive material.

This third step in the choice of a material emphasizes the problem of economic compromise. It is thus brought to compare investment costs (resistant but expensive material) and operating costs (costs of failures, replacements, and stops they may cause). The relative weight of these two types of cost has slowly changed. The current trend is often to prefer high but predictable investment costs and to minimize operating costs when these are too difficult to predict. In addition, in a competitive economy, short-term cash optimization is increasingly being replaced by optimizing long-term profitability. In turn, this may well favor investment, especially in metallic glass alloys whose resistance to mechanical and chemical constraints (i.e., to tribocorrosion) is optimal.

In what follows, we will particularly focus on the second step above, namely the behavioral of BMG materials with regard to their wear and corrosion testing, and in particular to their mutual coupling effect (tribocorrosion).

6. Towards the needs in tribological and electrochemical testing to meet the requirements of effective usage of metallic glass materials

Actually, despite the cost for developing new BMGs of desirable types and compositions, the examination of their appealing properties remains a persistent issue. Although, wear and corrosion are an important topic, they have never received the attention they deserve. Many tribological and electrochemical aspects of BMGs have not been characterized yet or are not well assumed, and the actual deformation and failure mechanisms are not fully understood. Albeit, localized corrosion, fatigue, wear, and fracture all have been reported in almost every BMG corrosion or mechanical study published to date (see next chapter). Though, theoretically speaking, this fact is unexpected for an ideally homogeneous material. Therefore, an overview of the material-oriented approach to resist the mutual and opposite interactions between the main actors of tribocorrosion involving both mechanical (friction, wear), and electrochemical (corrosion) phenomena is given below.

7. Material properties, which influence surface interactions in a triboelectrochemical contact

Fundamentally, tribocorrosion depends on the dominating deterioration mechanism of interacting surfaces in chemical environment and under relative motion conditions [10, 55]: *viz.* wear, corrosion, and their mutual interaction (synergism).

Modern research has established a consensus on four main forms of wear, namely, chemical wear (i.e., corrosion and corrosive wear), adhesive wear, abrasive wear or surface fatigue wear [56]. Each process of wear obeys its own laws and, to confuse things, repeatedly one of the modes of wear acts in such a way as to affect the others, hence of the complexity of wear. Typically, there is a combination of wear mechanisms in a mechanochemical dynamic contact. In that respect, the classification of wear mechanisms remains a matter of debate among the scientific community of researchers and authors. Albeit, the terminology used by Burwell in 1957 [56] to describe wear is simple and rational, that of seeking out the primary cause of each form of wear. To avoid any further issue regarding the nomenclature in this field study, all wear mechanisms should be referenced to the ASM standards [57, 58].

Other forms of wear can be found in the literature depending upon the contact configuration (e.g. unidirectional and reciprocal sliding and/or rolling, rolling with slip, etc.). Wear in these contact geometries is reported to as erosion wear, fretting wear, sliding or rolling wear, impact or slurry wear, etc. This is one of the approaches that judges wear by the consequences of the conditions of a tribological contact *vis-a-vis* its environment (e.g., reactivity of tribosurfaces with the environment, the contact system configuration, etc.). Such wear descriptions are all-technical and do not represent wear mechanisms in a scientific manner.

According to the recent critical review on the quantification of wear made by Meng and Ludema [55], several models have been proposed to explain various phenomena of wear. The authors have clearly enumerated 182 equations with 625 variables for explaining wear processes. This clearly shows that wear is not a material property, but rather a material system response. Wear can change drastically even as a result of a relatively small change in dynamical, environmental or material parameters forming the tribosystem. Indeed, wear rates change promptly (10^{-15} up to 10^{-1} $\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$) depending upon the conditions in which the materials are exposed to (tribological system, corrosive medium, loading contact parameters, etc.) and the choice of these materials [26, 59–61]. The combination of these two main factors, namely the operating conditions and the choice of materials, are the primary keys for monitoring the wear of materials (modes and rates) exposed to normal working conditions. Optimal solutions have been recommended as a means of meeting these requirements, are the wear maps that predict both modes and rates of wear of materials [8, 62]. A wear map or chart can be considered as one of the best descriptions of tribological/tribocorrosion conditions and as useful strategy in the design of mechanical systems (tribosystems) and for the selection of materials to be used in a wide range of operating conditions.

The wear volume loss measured during or after the end of an operating tribological test provides useful information in characterizing wear. Generally, there are three typical types of

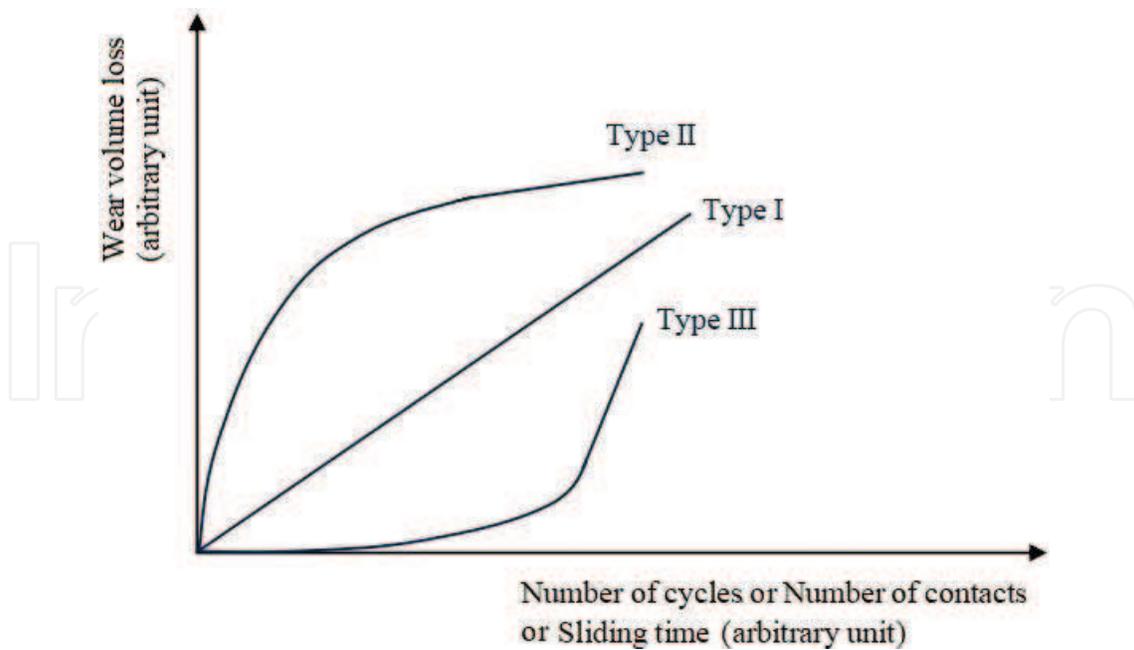


Figure 5. Three typical wear curves in repeated sliding contacts.

wear volume curves as shown in **Figure 5**. Type I shows a constant rate of wear throughout the process (likely one ideally mechanism monitoring wear). Type II shows the transition from an initially high wear rate to a steady-state low wear rate. This type of wear behavior is often observed in metals and metallic alloys [63]. Type III shows a fatal transition taking place from an initial low wear rate up to a high wear rate (e.g. fatigue wear by fracture mode). This is frequently encountered when using ceramic materials [64]. The total number of sliding contacts, before any catastrophic wear can occur, reflects the period for which the crack initiation takes place, and this latter depends on a number of material and system parameters, mainly surface roughness, material properties, and sliding conditions.

When considering the tribocontact system as a whole, including the entire design configuration and components, and specific for a given application either in laboratory or in the field, it is not possible to increase the strength of the solid material *vis-a-vis* one of the wear mechanisms in general. Nevertheless, the selection of suitable materials should always be established based on a more knowledge and a better understanding of the conditions in which the solid material is subjected to (e.g., surface interactions in aggressive medium, and loadings).

In the following sections, an overview of the desired material properties and trends towards how wear and corrosion resistance can be achieved is given.

7.1. Materials oriented approach to act in opposition to corrosion and corrosive wear

7.1.1. Corrosion

Corrosion may be defined as "...an irreversible reaction of a material with the environment, which usually (but not always) results in a degradation of the material or its properties..."

Therefore, there are several aspects of corrosion: the material, the environment, and the material properties. Considerable information is available in textbooks [9, 45, 65]. This general definition of corrosion includes the physicochemical (oxidation/reduction) reaction processes taking place at the surface of widely varying material classes (metallic, ceramic and organic), such as localized corrosion cells in some Fe-based metallic glass ribbons used in waste water treatment, the degradation of dental amalgams or metallic restorations by galvanic corrosion, polymers by ultraviolet radiation, and the chemical attack of refractory bricks during steel-making.

The severity of a corrosive medium depends on a variety of parameters. Nevertheless, the following four main parameters can generally be selected, namely the pH of the medium, the presence of chlorides (and other alkyl halides), the oxidizing power, and the temperature. The corrosion resistance properties can then be characterized directly by the limits of use of the materials, which can be expressed, for example, in terms of maximum temperature in-service or maximum concentration of use. In real service and under normal conditions, the understanding and control of corrosion are based on the electrochemical interpretation of corrosion phenomena and the consideration of the relative ranking scales of materials in order to select, by successive approaches, the materials best suited to each application of interest.

Since these materials may interact in a complex way with the environment that they are used for, the assessment of the reactivity of their surfaces with respect to their environment, and the evolution of that reactivity with time greatly accounts for their corrosion performance. Usually, certain metallic materials gain their resistance from the formation of a thin, yet dense and adhesive oxide layer, which protects the underlying substrate from further oxidation (a passive layer). Thus, the potential at which this layer is growth and the rate at which it is built (passivity) and rebuilt after being mechanically or chemically damaged (repassivation) are decisive for its corrosion resistance.

On a theoretical level, passivity concerns, a priori, most metals (and alloys). However, only a small number of those metals actually allows a systematic usage of this property. Conversely, some metals resist to corrosion without any appealing to passivity. Some of them are chemically inert, or not very reactive; this is the case for example for noble metals, such as gold, platinum and iridium, which are not prone to oxidation due to their high standard electrode potential, and are hardly used in technical applications because of their excessive price and often poor mechanical properties, or even copper and nickel in non-oxidizing acids. Other metals are roughly covered with a protective layer of corrosion products; this is the case of steels exposed to atmospheric weather, copper alloys in natural waters, lead in sulfuric acid, or even, occasionally, the most ordinary steel in the presence of acidic gas medium, CO_2 , or H_2S .

In total, metals and engineering alloys, including metallic glasses, actually used for their passivity are limited to Fe, Co, Nb, and Ta, stainless steels, alloys of Al, of Ni, of Ti, and of Zr, etc. It should be noted that some metals are less passivable than others are; especially this is the case of Fe, and Co, which do not reveal any sufficient passivation or oxidation. Not all oxide layers that form on metals are protective. If the oxide does not form a continuous layer on the surface of the metal, it will not be able to reduce the amount of oxygen reaching the metal

surface, and thereby increasing the brittleness of the layer leading to further corrosion (*cf.* Section 3.5).

7.1.2. Corrosive wear

A more obvious mechanism of triboelectrochemistry is the periodic exposure of fresh bare surfaces when sliding friction between surfaces occurs in corrosive liquids or gases. This results in reaction products mainly driven by chemical and electrochemical interactions. The surfaces of the materials are quickly covered by a scale of the reaction product, the oxide in the case of metals and metallic alloys, acting as a protective barrier layer. The thinner the scale, the faster the reaction, and the weaker the protectiveness.

In the case where these reaction products strongly adhere to the surface and behave as the bulk material, the wear mechanism should be almost the same as that of the bulk material. Otherwise, as observed in many cases in practice, the reaction products behave rather differently compared to that of the bulk material. The resulting wear is therefore very different from that of the bulk material, and it is thus controlled by the scales of reaction products (i.e. tribochemical reactions). In corrosive media, the tribochemical reaction at the contact interface is accelerated by the friction processes (*viz.* elastoplastic deformation, heating, micro-fracture, and successive removal of these scales of reaction products). In the case of metals, friction can cause extensive plastic deformation of a subsurface layer in the material; whereas in the case of ceramics, microfracture predominantly occurs. These strains lead to structural defects (microcracks, grain boundaries, vacancies, dislocations, etc.), thereby accelerating the diffusion of reagents through the protective scale. This results in the acceleration of the chemical reactions, which leads to a material removal from the contact interface. The resultant wear is called “corrosive wear”. In air, oxygen prevails as a corrosive medium, and tribochemical wear of metals in air is usually called “oxidational wear”. More detail about this type of wear can be found elsewhere [29]. The material removal rate in corrosive wear is governed by the balance between the relative growth rate and the removal rate, which determines the wear rate of the reaction layers.

It is worthwhile to note that in the absence of chemical reactions, the sliding surfaces experience mechanical wear, while in the case of the absence of sliding friction, the surfaces experience corrosion degradation.

7.2. Materials oriented approach to act in opposition to adhesive wear

Adhesive wear is the most common form of wear that exists when one solid surface material is slid over the surface of another (e.g. tribological/tribocorrosion contacts) or is pressed against it (e.g. loaded surfaces under bending conditions, fretting mode II, etc.). The removal of material takes the form of small particles which are usually transferred to the other surface, but which may come off in loose form [27].

In loaded or pressed tools, the tendency of contacting surfaces to adhere arises from the attraction forces, which exist, between the surface atoms of the two materials in intimate contact. In a presumed elastic contact, elastoplastic deformation of the asperities in contact

takes place, which often results in a growth of the real contact area as the load increases [32]. This, in turn, leads to increasing the area for which the distribution of bonding and attraction forces may occur by forming an interfacial junction area along the contact, thus resulting in a strong adherence and promoting surface welding at a solid-state (*viz.* adhesion). The removal of the load breaks off most of the junctions, as a result of elastic spring-back. At this point, the chemical, plastic deformation and wear become clear in light of the formation of a series of grain-sized microwelds, microcracks, and material transfer.

The presence of adsorbed films containing water and other molecules derived from the air serves measurably to reduce the surface interaction of contacting materials. The effect of grease films, if present, however, is even more marked, and reduces, often by one or more orders of magnitude, the severity of surface interaction, and thus friction too. Clean and smooth contacting metallic surfaces are more prone to promote higher attraction than contaminated surfaces (e.g., oxides, corrosion products) and thereby increasing both the adhesion and the static frictional strength of interfaces (i.e. a certain minimum tangential force is required to produce motion).

Most non-metals essentially have the same chemical composition at the surfaces as they do within the interior. A handful of metals and alloys will form surface oxide films in air, however, and in other environments they are likely to do, for other films (e.g., nitrides, sulfides, and chlorides).

Under sliding conditions, the first stage involves the removal of the thin surface film (e.g. oxide layer) covering the surface of the material through a mechanical wear process. As the oxide layer is degraded after the first few sliding cycles, the distance between the two surfaces becomes in the order of the interatomic distance of the metal lattice, and metallic bonds are thus established (*viz.* direct adhesive bonding contact) between the two interacting surfaces (e.g., counter-body and underlying bare surfaces), thereby leading the contact surfaces to starting adherence by forming “microwelds” or “cold welds”. When the adhesive bonding strength resists the relative sliding motion, large plastic deformation caused by dislocation is produced in the contact zone under the effect of compression and tangential shearing. The generation of slips along slip planes in the contact zone entails the formation of flake-like shear tongues and/or wedge-like shape, and are followed by a crack initiation and propagation in the combined fracture mode of tensile and shear in the contact zone area. Currently, the real actual contact area is made up of all areas of asperities welded to the surfaces and upon tangential sliding/shearing, the crack reached in the contact interface causes a mass separation of the asperities in the underlying softer material rather than in the interface, and therefore a wear particle from the bulk material is formed and eventually transferred to other surface.

The adhesive wear process is responsible for the initial accumulation of wear debris between the contact surfaces. Additional sliding cycles bring near-surface plastic deformation, new bonds often prevail and fracture occurs at some distance to the surface, additional wear and the potential formation of new oxide [7, 8, 10–13, 16, 32].

Under tribocorrosion conditions, the surface roughness, as well as the oxide film growth or chemical corrosion layers adsorbed on top of the surfaces, normally hinder the direct metal

contact. However, the plastic deformation of the surface can result in the flattening of the roughness as well as the cleavage of the oxide layers. Preventing plastic deformation or solid-state attraction is therefore a feasible concept to avoid adhesive wear.

The role of the environment on the adhesive wear is of a great importance in tribological contacts. Under dry friction conditions, for example, often part of the energy is dissipated in the form of thermal heat, which boosts the surface reactivity and results in an increase of the temperature of the interacting surfaces. This, in turn, affects both the oxidation and the friction of the two surfaces in contact and entails material transformations (e.g. phase transformation, depletion zone, hardening, welding process, material transfer, etc.). Little part of the frictional work is done to overcome surface roughness, but most of the work being done in inducing shear displacement of the junction interface as well as the removal of bulk underlying previously welded material.

One of the interesting approaches used to explain the friction behavior of metallic oxides just below and above their melting temperature is the polarizability approach, initially introduced by Vesselin et al. [66], and later extended by Prakash et al. [67]. Thus, based on that approach, the lubricity of a wide variety of solid oxides at high temperature could be explained.

A correlation may exist between the dissipated energy due friction and the wear rate. Often a low friction induces a low dissipated energy, which may result in a low wear rate. However, this is not a universal law, and there are numerous examples showing high wear rate regardless of low friction.

Despite its omnipresence in almost all modes of degradation by sliding wear, adhesive wear is not necessarily preventable form of wear, nor is it the most dangerous since adhesive wear rates are usually fairly low. The mechanism behind this type of failure wear process is quite expected.

In general no equation can fully describe the adhesive wear process but the most widely used is the Archard equation (Eq. (1), see Section 3.3).

Adhesive wear can be addressed effectively by deliberate and intelligent choice of materials. Solid materials with high hardness or having undergone strain or work hardening (e.g. metals) lead to a reduction of plasticity of the surface. Alternatively, metals or alloys with a hexagonal or body centered cubic (bcc) crystal lattice are thus preferred to those with a face centered cubic (fcc) structure, since these show a high number of slip systems making them very ductile. Solid materials with covalent bonds are less prone to adhesion than those with metallic bonding. Adhesion, thus, can be effectively reduced by ceramic layers that can be produced by coating technologies or surface treatments. Nitriding of steels, for example, can lead to the formation of a nitride layer that reduces adhesion. If these layers, however, are damaged or removed by superimposed abrasive or cyclic loading, the underlying material become unprotected, and may favor adhesion. This often happens during tribological and tribocorrosion processes.

In case of metallic glasses, surface treatment or coating with material composites can be very useful to improving their hardness, and thus reducing their plastic deformation. A fine dispersion of hard phases into metal glass matrix for instance can effectively reduce adhesion.

After mechanical processing, they slightly protrude from the surrounding matrix and impede metallic contact.

7.3. Materials oriented approach to act in opposition to abrasion wear

Abrasive wear is defined as wear by displacement of material caused by hard particles or hard protuberances, which results in a significant plastic deformation of the softer surface material. Actually, this is the form, which occurs when a rough hard surface, or a soft surface containing hard particles, slides on a softer surface, and ploughs a series of grooves in it. The material from the grooves is displaced in the form of wear particles (debris) generally loose ones. When these wear particles are attached to one of the surfaces in contact, the phenomenon is called as two-body abrasion. Otherwise, it is known as three-body abrasion. The severity of abrasive wear depends on size and angularity of abrasive wear particles and the ratio between hardness of metal and the abrasive particles too [68, 69]. To be effective, either the hard particles or the harder surface must be 1.3 times harder than the softer surface material undergoing abrasion, which Hutchings [68], and Ludema [69] note is the difference of one unit on Mohs scale of mineral hardness.

In a tribocorrosion process, abrasion usually occurs when interlocking of inclined or curved asperity contacts at the contact interface takes place or when harder particles are introduced into the tribosystem between the interacting solid surfaces at the contact interface (e.g., through erosion (abrasive particles) or fretting (trapped in contact), etc.). These sharp and hard particles or asperities are then pressed onto the softer surface (usually being the investigated material), causing a plastic flow of the surface. During sliding-corrosion, the softer surface undergoes ploughing, entailing the formation of scratches, and abrasive grooves, which leads to a significant material removal (e.g. as volume).

It is likely that diverse modes of action contribute to the mechanisms by which abrasive wear occurs and proposed models include micro-cutting, micro-chipping, and micro-fatigue (e.g., due to cyclic loading-sliding). Other models have also been emphasized. Hutchings [68] quotes three common models for the occurrence of abrasive wear *via* plastic deformation, which can be categorized as cutting, ploughing and wedge-forming.

Note that the contact geometry in a tribological/tribocorrosion system remains, inter alia, a parameter either favoring or discouraging the manifestation of abrasion phenomena when a hard surface slides on another softer one or remained in intimate contact with it. In fretting or unidirectional reciprocating sliding conditions, for example, the use of a sphere-on-flat configuration can promote both trapping and ejection of the abrasive particles brought into contact between the two slid protagonist surfaces, whereas, in a flat-on-flat contact geometry, such abrasive particles may remain regularly trapped in the contact zone, driving various possible mechanisms as plastic flow, welding, scratches, grooves, etc. It is therefore recommended that the project designer or engineer consider the incidence that the choice of the geometrical contact system may have on the wear of the contacting materials.

The abrasive wear rate is defined in the same way as for the adhesive wear. Indeed, the Archard equation (Eq. (1), see Section 3.3), which was originally formulated to model adhesive wear,

is commonly used for abrasive wear, although this is derived from a completely different set of material removal mechanisms. However, the validity of the Archard wear criterion is still questioned by the scientific community (see Section 3.3).

According to the Archard equation, a timely way to avoid abrasion is to increase the surface hardness of the component [70]. However, it should be pointed out that for a number of metallic glass composites and bulk glassy alloys, the wear rate may deviate and even do not follow the Archard equation [26]. Only a good combination of the hardness and the toughness taken together can allow the metallic glass to be wear resistant. A convenient way of bringing out this choice is by a series of figures or charts, in which one parameter of interest is plotted against another. The Ashby chart [71] plotted in **Figure 6** compares the normalized wear rate and the hardness for most of the common engineering materials including metals, technical ceramics, and polymers. In that figure, the wear-rate constant, k_a (MPa^{-1}) is defined as the ratio of the volume of material removed (m^3) to the distance slid (m) multiplied by the normal load (N). That quantity represents a measure of the propensity of a sliding couple for wear: if k_a is high this would correspond to a rapid or severe wear at a given bearing pressure.

The wear rate of metals are markedly hardness dependent, however, technical ceramics show nearly the lowest wear rate and the largest hardness over metals, polymers, and elastomers. Note how certain engineering materials lie roughly on a diagonal (dotted lines). Interestingly, the wear rate is strongly correlated to the hardness.

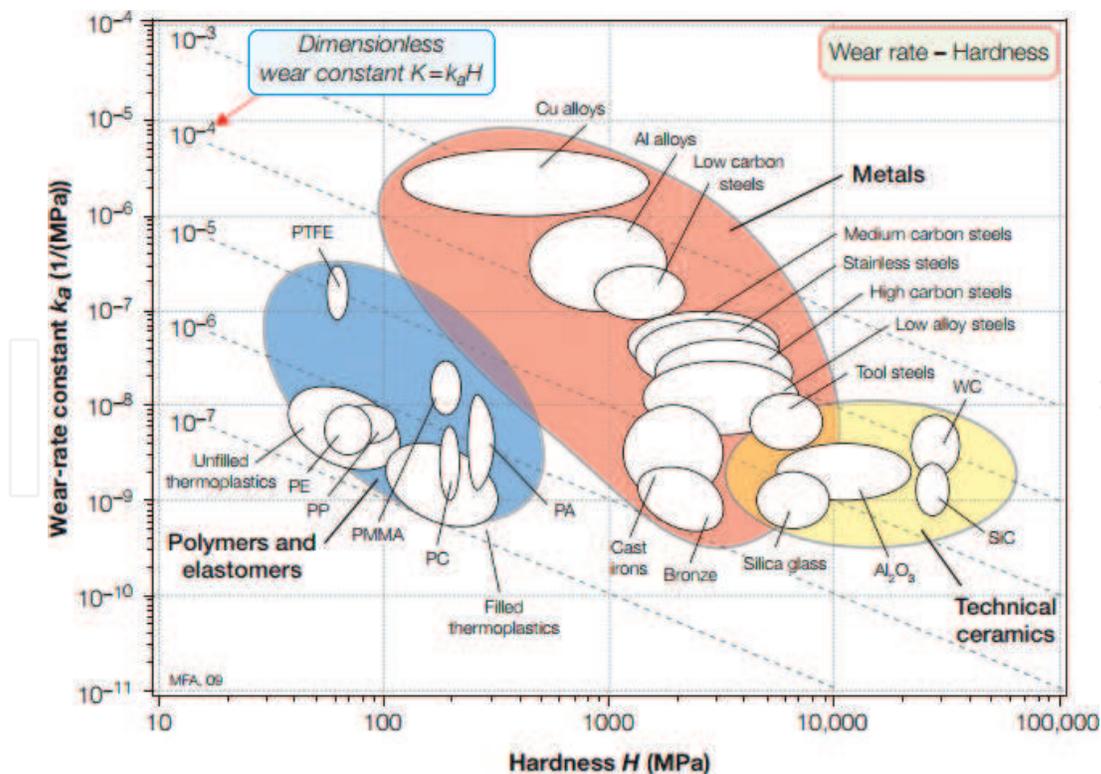


Figure 6. Ashby plot comparing the normalized wear rate k_a to the hardness H , here expressed in MPa rather than Vickers (H in MPa = 10 H_v). The chart gives an overview of the way in which common engineering materials behave. (reproduced from Ashby [71] with permission from Elsevier).

The hardness of a metal is more likely structure dependent, so that the hardness of an annealed metal may be lower than that of a work-hardened metal. The state of a metal in fully work-hardened condition corresponds to the state, which a metal surface might achieve after repeated sliding over it had occurred. Steels, for example, when hardened by quenching may be less prone to abrasive wear than soft-annealed. The application of this concept is, however, limited especially against mineral abrasives: metallic materials cannot reach the required hardness. Ceramics, on the other hand, are sufficiently hard but owing to their lack of toughness (**Figure 1**, see Section 2) and ductility they cannot claim to be eligible candidates as basic materials in many specialized fields. In addition, they are prone to micro-cracking during abrasive loading, which reduces their wear resistance. To counteract this issue, metallic materials are reinforced with hard phases. The tough/hard metallic matrix provides high ductility and strength, while the hard phases prevent indentation and grooving of the surface [72]. They are most effective if they are harder than the abrasive, and larger than the groove width. The hardness of precipitated-hard phases is raised by hard phase forming alloying elements. Their size usually decreases with the temperature of precipitation, i.e., primary, eutectic and secondary carbides. Tool steels and white cast irons belong to this group. Another group comprises metal matrix composites, e.g., Al-, Fe- or Co-based with a mixed hard phases, such as carbides (fused tungsten carbide, TiC), oxides (Al_2O_3 , ZrO_2), cubic boron nitride or diamond. The matrix hardness needs to be sufficient to back up the hard phases and to minimize the indentation depth of the abrasive.

7.4. Materials oriented approach to act in opposition to fatigue wear

Fatigue (delamination) wear is defined as, “the removal of particles detached by fatigue arising from cyclic stress variations”. The delamination or fatigue theory of wear was proposed by Suh [73], as an attempt to explain weaknesses in the Archard theory of adhesive wear [26].

Repeated cycles of contact are not necessary in adhesive and abrasive wear for the generation of wear particles. There are other cases of wear where a critical number of repeated contacts are essential for the generation of wear particles. Wear generated after such contact cycles is called “fatigue wear”. When the number of contact cycles is high, the high-cycle fatigue mechanism is expected to be the wear mechanism. When it is low, the low-cycle fatigue mechanism is expected.

To better guide the choice of materials in the field, where surface interactions interferes with fatigue wear, it is necessary to understand the mechanisms and processes that govern the wear by contact fatigue with or without sliding. Detailed explanations can be found elsewhere [73, 74]. Nevertheless, in the following, a summary of this material is recalled concisely.

This form of contact fatigue-induced wear is often observed in systems where cyclic contact stresses (e.g., loaded tools) take place, but in most cases during sliding or rolling contacts.

In loaded mechanical parts, the contact surface undergoes compression stresses and shear stresses are developed beneath the surface. The repeated loading and unloading cycles to which the materials are exposed may induce the formation of surface and/or sub-surface nano- and microcracks, at critical zones where, for example, imperfections, inclusions or second phases are located. This eventually will result in the growth of fatigue cracks as further

load stresses become apparent, and ultimately driving to the breaking-up of the surface with the formation and detachment of large fragments (i.e. sheet-like particles or spalling process), leaving large pits in the surface. This mechanism can be predominant, for example, in periodically loaded dies and tools, in roller bearings or in pumps that are exposed to cavitation.

Under tribological/tribocorrosion conditions, the location of maximum shear stress moves towards the near-surface during tangential sliding and micro-cracking occurs at the locations of surface defects. The transition from sliding wear to fatigue wear is evidenced by the initiation and propagation of one or more surface micro-cracks into the bulk material. The analysis of crack initiation in sliding (e.g., fretting) is far more challenging than that of propagation. A wide range of factors affects the number of cycles required for damage to accumulate but they can be conveniently be grouped into three categories [74]: (a) Material factor (grain size, morphology, fracture toughness, flow stress, etc.), (b) Environmental factors (temperature, humidity, etc.), and (c) Mechanical factors (surface tractions, slip amplitude, frictional dissipated energy etc.). A full understanding of the problem will only be gained when all these factors are brought under consideration. However, the range of expertise necessary to master these three areas is considerable. At present, few effects are particularly well understood (*viz.* contact stress field and surface slip amplitude) and approaches are developed accordingly. Two main approaches are available to develop an understanding of crack formation, either a “bulk” or macroscopic approach or a “local” or micromechanics approach. The actual crack initiation process occurring on the scale of a few grains in non-homogenous, anisotropic material riddled with defects, inclusions, and imperfections. There is some discrepancy in the literature as to what fraction of the total fatigue life is consumed by the crack initiation process.

Another challenge under hot working conditions has caught attention in mechanical loaded contacts: an unexpected heat may induce surface or volume expansion and the development of stresses between the surface and the bulk material. Between two loaded contact events, the surface cooling once more generates stresses, and “thermal fatigue” may occur resulting in a network of cracks resembling a mosaic.

Generally, contact fatigue can be mitigated by all usual measures that reduce the susceptibility to cracks, i.e., a high strength to impede crack initiation and a high toughness to retard crack growth (*cfr.* **Figure 1** in Section 2).

The relationship between these two material properties, namely toughness and strength, have been introduced in Section 2 (**Figure 1**). It is shown that, generally, ductile metals exhibit virtually the greatest fracture toughness; however, they may display weak strength. Metallic glasses, on the other hand, often have toughness and strength that lie between brittle ceramics and marginally tough materials. Nevertheless, following the development of very recent bulk metallic glasses, the introduction of newly metal glass composites on the market has led to overcome the early success of metals by acquiring a very high resistance to deformation, and toughness, which imparts them a good resistance to cyclic stresses and solicitations. A strong interface between the glassy matrix and second phase particles is to be guaranteed. Therefore, these glassy composites can substitute metals in application areas not achieved yet so far. Among these novel alloys, there are Pd-based glasses, and ductile-phase-reinforced metallic glass composites [2].

8. Future trends

All the metallic glass materials described in this chapter are subject to further development. Therefore, the attempt to sketch out all possible developments does not seem appropriate. In the design of materials, however, there is a general tendency to form graduated structures and multiphase models, i.e., materials that exhibit a property gradient from the surface to the core, and which can conceive a composite pattern.

With a better understanding of the mechanisms of tribocorrosion, knowledge-based development can lead to new microstructures capable of counteracting specific mechanochemical loads.

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