


Development of Fe-based glass former alloys for thermal spray coatings with optimized corrosion and wear properties

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Abstract

Corrosion and wear of alloys is a costly and hidden safety risk for components in petrochemical, agroindustry, and mining activities, which are key segments in Brazil and in many countries. Accelerating the development of high-performance and durable ferrous alloys and their insertion into engineering structural applications has never been more important. Glass former steels have drawn considerable attention in recent years, due to the remarkable combinations of strength and degradation control that can be achieved by tailoring corrosion and wear resistances, which places these alloys amongst the durable ferrous alloy ever developed. Recent results from our group indicate that coatings using these alloys can be produced from commercial grade precursors and industrially available thermal spraying routes. The development of Fe-based bulk metallic glass (BMG) alloys for degradation control will open the door to next-generation coatings with unprecedented combinations of corrosion and wear resistances. This work summarizes the development of Fe-based glassy coatings for corrosion and wear control performed in our research group in the last 17 years covering: i) glass forming ability of alloys, ii) development of Fe-based glass former alloys, iii) thermal spraying of Fe-based glass former alloys, and iv) scientific and technological impacts of this research.

Keywords: Amorphous alloys; Metallic glass; Glass forming steel; Surface engineering; Corrosion; Wear.

1 Introduction

Most deterioration processes that result in failure of metallic materials originate at their surface. Besides fatigue main causes are corrosion and wear, especially when components operate in harsh conditions and environments such as those commonly found in the sugar-alcohol and petrochemical sectors. In this scenario, the metallic components are exposed to environments characterized by [1]: presence of hydrogen sulfide; high concentration of chloride ions; high temperatures and pressures; presence of abrasive particles such as sand; constant contact with other moving metallic components. The consequences of corrosion involve economic, safety and conservation aspects. The annual cost directly associated with corrosion was estimated at 3% of the Gross World Product (GMP) in 2012, i.e., about 2.2 trillion dollars [2].

Components wear is also associated with considerable economic losses. For example, annual wear-related costs are estimated to be approximately 1% of the gross domestic product (GDP) of developed countries such as Germany and the United States of America [3,4]. To contextualize the magnitude and importance of the development of metallic alloys with high resistance to corrosion and wear for Brazil, we present in the following paragraphs the cases of the petrochemical and sugar-alcohol industry.

Brazilian has a reserve of crude oil of approximately 12.8 billion barrels [5,6], and is the ninth largest oil producer in the world, with about 3.3 million barrels per day [7]. It is noteworthy that most Brazilian oil reserves are offshore, which increases the aggressiveness of the environment in relation to degenerative processes by wear and corrosion. The components used in the petrochemical industry such as pipes, risers, valves and handles are generally produced in carbon steel for economic and practical reasons. The useful life of these components can be considerably extended through the use of coatings, produced by thermal spraying, using wear and corrosion resistant alloys. This process allows carbon steel components, which have satisfactory structural properties at low cost, to be protected by coatings of nobler alloys, whose quantity to be deposited is controlled to allow protection combined with relatively savings of more expensive material. Stainless steels provide high resistance against corrosion; however, wear is of concern even for the martensitic series of stainless steel.

Brazil is the world leader in sugarcane production and is responsible for more than 40% of global production, having produced 760 million tons of sugarcane in 2017, compared to a world production of 1.85 billion tons [8].

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During the process of preparation and extraction of sugarcane juice, interactions and relative movement between surfaces happen, inevitably involving friction and wear, resulting in loss of surface mass, and, when more pronounced, formation of cracks. Replacement and maintenance of deteriorated components during the harvest period are constant, reflecting the increase in costs [9]. Examples of components are feed table and conveyor, chippers and shredders and mills; coating processes with wear-resistant and corrosion-resistant alloys are used in manufacturing processes and in recovery processes for these components.

In addition, Brazil stands out as the second largest producer of iron ore (397 million tons in 2015 [10]) and the ninth largest producer of crude steel in the world (34.4 million tons in 2017) [11]. Ferrous materials are essential to produce affordable multipurpose structural elements which are exposed to harsh environments. In this context, scientific and technological research with the objective of designing alloys compositions and processes that lead to microstructures containing specific phases that can optimally meet the requirements of high corrosion and wear resistance of ferrous alloys has great importance and innovation potential for Brazil. As such, the present work describes the development of Fe-based alloys with good glass forming ability and their use in thermal spray processing to result in coatings with optimized corrosion and wear properties.

2 Glass forming ability and Fe-based glasses

The glass forming ability, GFA, of a metal alloy is expressed by the minimum rate required for the molten metal to be cooled so that nucleation and growth phenomena are suppressed (critical rate of cooling, R_c) or by the maximum thickness (Z_c) or maximum diameter (D_c) that a sample of the alloy can be produced with 100% glassy structure.

Several methods or criteria have been developed for predicting or evaluating the GFA in metal alloys. The first correlations were those based on qualifying the GFA with the alloy's thermal characteristics, relating the different characteristics of the transformations that the alloy undergoes from the glassy state when heated: i) the reduced glass transition temperature, T_{rg} (T_g/T_l ratio, where T_g is the glass transition temperature, and T_l is the liquidus temperature; alloys with high GFA have T_{rg} values from 0.66 to 0.69) [12], ii) the supercooled liquid region, ΔT_x , ($T_x - T_g$, where T_x is the onset temperature for crystallization; the higher the ΔT_x value, the greater the GFA) [13]; iii) gamma parameter, T_γ ($T_g + T_l$) [14]. However, these criteria have limitations, such as, T_{rg} generally has a weak dependence on the composition of the alloy, being difficult, for example, to be associated with alloys with easy glass formation with compositions outside the eutectic.

Historically, the first to address this issue from the point of view of the development of new alloys was Inoue

and co-authors [15], in 1996, who proposed the following three empirical rules to define alloys with easy GFA: the systems must have more than three elements; the difference in atomic radii between the three main alloying elements must be above 12%, and the enthalpy of mixing between the three main alloying elements must be quite negative.

A criterion that correlates the GFA with the atomic size of the constituent atoms of a binary alloy is the topological instability parameter, λ_0 , proposed by Egami and Waseda [16]. This criterion satisfactorily describes the minimum solute concentration (C_{min}^B , in at. %) for fast solidification vitrification ("melt-spinning") in binary systems. The model analyzes the local microscopic deformation induced by the incorporation of a solute atom of different size in the solvent (matrix). Vitrification occurs when the local atomic deformation generated by the difference in atomic radii reaches a critical level, leading to a topological instability of the crystal lattice, thus changing the coordination number. This topological instability can increase the material density resulting in significant internal stress relaxation. Thus, after reaching a critical solute level, glass formation is favored. Previous work from our group at DEMa UFSCar [17] concluded that the model is supported in more than 60 glassy alloys, where the ratio of the metallic radius of solute (B) to solvent (A) empirically related to C_{min}^B through the topological instability parameter, λ_0 , is found as $\lambda_0 \approx 0.1$ [16], being represented by Equation 1:

$$\lambda_0 = C_{min}^B \left| \left(r_B / r_A \right)^3 - 1 \right| \quad (1)$$

The concept associated with the topological instability parameter was thus extended to multicomponent Al-based alloys of generic composition $AlB_{cB}C_{cC}D_{cD}...Z_{cZ}$, where B through Z are solute elements (TM and/or RE), with the corresponding atomic concentrations, c_i , and radii, r_i . By analogy to the condition of binary alloys, a new parameter is obtained for multicomponent alloys of the Al-TM-RE group, called lambda criterion " λ ", represented by Equation 2:

$$\lambda = \sum_{i=B}^Z c_i \left| \left(r_i / r_{Al} \right)^3 - 1 \right| \quad (2)$$

The " λ " criterion was successful to predict the following behaviors for fast quench Al-based systems [17]: vitreous structure for alloys with $\lambda > 0.1$, nanocrystalline for $\lambda < 0.1$, and nano-glassy for alloys with $\lambda \sim 0.1$. Regarding GFA, this criterion proved to be useful for the selection of new compositions using the strategy of avoiding the field of compositions associated with $\lambda < 0.1$.

The topological instability criterion was also combined with the average electronegativity difference of an alloy to predict the GFA [18]. The electronegativity difference between the elements of an alloy is directly related to their

enthalpy of formation and the stability vitreous phase [19] justifying that the higher this difference, the greater the GFA.

Glassy Fe-based alloys produced by rapid solidification processes are traditionally classified into metal-metal and metal-nonmetal (metalloid) types. In the metal-metalloid type, the alloy composition is typically 80 wt% Fe and 20 wt% non-metal. The metal can be just one element or a combination of more than one element, and similarly, the metalloid element can also be just one or a combination of more than one element, typically B, C, P, and Si. Typical examples of Fe-based glassy alloys of the metalloid type are: $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{78}\text{B}_{12}\text{Si}_{10}$, $\text{Fe}_{80}\text{P}_{13}\text{C}_7$, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, $\text{Fe}_{71.3}\text{Cr}_{10}\text{Mo}_9\text{P}_8\text{C}_{1.7}$ and $\text{Fe}_{73.4}\text{Cu}_1\text{Nb}_{3.1}\text{B}_{9.1}\text{Si}_{13.4}$. On the other hand, in metal-metal vitreous alloys, there is no such strict composition requirement. Metallic elements can be present in any proportion, and some typical compositions studied include $\text{Fe}_{90}\text{Zr}_{10}$ and $\text{Fe}_{60}\text{Zr}_{40}$ [20].

In principle, vitreous alloys can be produced in metal-metalloid and metal-metal variants. Most alloying elements are typically elements of the Fe group, i.e., Fe, Co and/or Ni. Occasionally, other metallic elements such as Cr, Mn, Al, Ga, Mo, Zr, Nb and Ta are also added, with their concentrations ranging from a few % to high levels, 15-20% of the total. Rare earth elements such as Y, Er, Gd and TM (transition metals) are also occasionally added with beneficial effects of increasing the formability of the alloy [20].

The first synthesis of bulk Fe-based glassy alloys was reported in 1995 for the system Fe-(Al,Ga)-(P,Si)-(B,C) [21]. After such event, a large number of “bulk metallic glass” (BMG, massive samples in dimensions of millimeters or even centimeters, much thicker than the “conventional glassy alloys”) were developed showing glass transition and wide temperature range of the supercooled liquid.

Many efforts toward development of new compositions of alloys with a high tendency to form a glassy structure included propositions of semi-empirical models based on a combination of thermodynamics, topological instability, and electronegativity of the constituent elements of the alloy to predict new good glass former alloys [22-24]. Using these models, many international groups have discovered new alloys including Zr-based, Fe-based, Al-based, Ni-based, Ti-based and Mg-based systems.

Contributions in Fe-based alloys are in references [25-38], which include those of Fe-B-Nb, Fe-Nb-Al-Si-B, Fe-Cr-Nb-B, Fe-Co-B-Si-Nb, Fe-Co-Cr-M-Si-B-Y (M = Mo, Nb) and Fe-Nb-Zr-Ti-B-Cu, being evaluated their thermal stabilities and properties such as corrosion resistance; and more recently in the references [25,26,28,39-41] dealing with the development of corrosion and wear resistant systems for coating applications.

The use of the computational thermodynamic method tool for mapping the phases of interest, using the CALPHAD method via Pandat® and Thermo-Calc® software, has been extensively used too. For example, on Fe alloys Thermo-Calc® was used to calculate the equilibrium diagram of the $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ alloy, whose application in coating was

investigated by processes such as spray forming [29], LVOF (Low Velocity Oxygen Fuel) [29] and HVOF (High Velocity Oxygen Fuel) [42]. HVOF coatings resulted in more than 66% of glassy phase, with excellent resistance to wear and corrosion. For this alloy design Thermo-Calc® calculations indicated compositions located very close to the eutectic point of the system, which is associated with high GFA [41], and final composition was chosen by the subsequent microstructural characterization of glassy and heat-treated samples. Thermodynamic calculations were also useful in the study of the microstructural evolution of the $\text{Fe}_{51}\text{Cr}_{10}\text{Nb}_{20}\text{B}_{19}$ alloy, confirmed by experimental observations [26].

3 Wear and corrosion properties of glassy alloys and partially crystallized structures

The lack of long-range atomic ordering and absence of the typical defects, such as grain boundaries and dislocations line, have very important consequences for the mechanical and electrochemical behavior of the vitreous alloys. For instance, the classic mechanisms of plastic deformation of metallic alloys by movement of dislocations and interaction of these with the grain boundaries, precipitates and among themselves, do not happen. In the glassy alloys plastic deformation occurs by shear bands, which can provide slip in a reduced number of planes, after reaching a high level of stress (high yield strength of the order of up to 1 GPa), but no ductility [43]. The hardness can also be very high but because of the unusual mechanism for deformation, the wear behavior, for instance, does not follow the same tendency as the hardness.

However, superior mechanical properties can be obtained with partial crystallization of the glassy alloys, which can result in a composite structure with a distribution of nanometric crystalline phase in the glassy matrix. Such composite nanostructure can hold or restrict the fast spread of the shear bands, inducing the formation of bridges between the shear bands and movement of dislocation lines in the crystals, which represents a greater mechanical work until fracture and, therefore, greater mechanical strength and also ductility. For example, in Al alloys containing a dispersion of nanometric crystals (with a volumetric fraction of 10 to 30%) the mechanical strength values are on the order of 30% higher than those of totally vitreous alloys and 150% higher than those of conventional high-strength alloys [44]. As it will be discussed later, formation of a composite nanostructure has also important consequences for the wear behavior of the original glassy alloys.

Glassy alloys with compositions containing strongly passivating elements such as Cr present superior corrosion resistance in comparison with the crystalline alloys of the same composition. This behavior has been attributed to two factors: (i) the high microstructural and chemical homogeneity, with absence of the typical crystalline defects or elemental partitioning that prevent the formation of a

uniform, adherent and compact passive film and (ii) the fast superficial enrichment of corrosion resistant alloying elements that promotes the rapid and spontaneous formation of the passive film [45].

The higher corrosion resistance of the glassy alloy has also been related to the uniform distribution of the alloying elements on the passive film [46]. In fully glassy alloys of the Fe-Cr-Mo-C-B system [46] chemical homogeneity with a uniform distribution of the elements have been observed while the totally crystalline alloy contained the presence of phases rich in Mo and in Cr. In this system, the uniform distribution of alloying elements in the glassy structure allows the formation of a homogeneous passive film significantly rich in Cr. In the crystalline structure, the presence of Mo-rich phases and Cr-depleted phases resulted in selective dissolution sites competing with the passive film growth, resulting in severe surface roughness and less protective film. Regarding pitting corrosion, Gostin et al. [47] observed for $(\text{Fe}_{44.3}\text{Cr}_5\text{Co}_5\text{Mo}_{12.8}\text{Mn}_{11.2}\text{C}_{15.8}\text{B}_{5.9})_{98.5}\text{Y}_{1.5}$ a critical role of C that forms a loose permeable C-rich layer.

Contrary to the mentioned positive effect on mechanical properties, the presence of crystalline phases in a glassy matrix results in a decrease in the corrosion resistance of the alloy [48], since the formation of the crystalline phase affects the uniformity of the passive film, thus reducing its protectiveness. Furthermore, in a partially crystalline alloy, regions with different susceptibility to corrosion occur, thus causing galvanic corrosion. It has been found that the partial crystallization of the glassy alloys based on Fe-Cr results in the formation of crystalline phases with nanometric dimensions such as, $(\text{Fe,Cr})_{23}(\text{C,B})_6$ and $(\text{Fe,Cr})_3\text{B}$ in the $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6$ alloy and $(\text{Fe,Cr})_{23}\text{C}_6$ and $(\text{Fe,Cr})_7\text{C}_3$ in the $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ alloy [49]. The presence of these phases results in regions with Cr depletion responsible for the decrease in corrosion resistance.

To minimize corrosion resistance vanishing caused by crystallization, crystal composition control is key. Crystal formation tuning with composition close to the primordial alloy composition inhibit pronounced chemical partitioning, such as the crystallization of multi-principal FCC and/or BCC phases whose composition is close to the remaining glassy matrix, as recently verified for Fe-based pseudo high-entropy glass forming alloys [50-54].

4 Fe-based glassy alloys and their applications in coatings

The use of $\text{Fe}_{50}\text{Cr}_{15}\text{Mo}_{15}\text{C}_{14}\text{B}_6$ vitreous alloy to produce a HVOF coating on stainless steel substrate was reported in 2007 [55]. The coating was produced with an average thickness of 0.2 mm and high content of 99% and 100% of glassy structure. The glassy coating proved to be superior in both corrosion and wear resistance in comparison with a 304 stainless steel coating. This alloy has been successfully

used in lining containers with a diameter of 50 cm and a height of 34-40 cm [55].

In several studies, glassy Fe-Cr-based coatings were found to present a higher corrosion resistance than austenitic stainless steel 316 and 317 [56-58]. Furthermore, it was observed that these coatings have a high resistance to abrasion wear [59]. Still considering wear resistance, glassy coatings of the Fe-Cr-Mo-C-B system resulted in satisfactory adhesion to 304 stainless steel substrates and higher abrasion wear resistance than the hard chrome coating [60]. These characteristics make the use of Fe-Cr-based glassy coatings promising in applications where resistance to erosion corrosion is important. In these applications, material deterioration occurs due to the combined action of corrosive processes and mechanical wear.

Among several suggested applications for Fe-Cr-based glassy coatings are the coating of cut-off wheels for tunnel boring machines and ship deck coatings [61]. The use of these alloys in the coating of pump rotors, ship propellers and in the lining of containers for the storage of nuclear fuel waste has been also considered.

Coatings produced with the glassy alloy $\text{Fe}_{54.2}\text{Cr}_{18.3}\text{Mo}_{13.7}\text{Mn}_{2.0}\text{W}_{6.0}\text{B}_{3.3}\text{C}_{1.1}\text{Si}_{1.4}$ in marine pump impellers resulted in an erosion corrosion rate ($\text{mg}/\text{cm}^2\text{h}$) significantly lower than that of 304 stainless steel for different flow rates [62].

Coatings produced from alloys of the FeNiCrBSiNbW system [63], consisting of a glassy matrix containing crystalline phases of α -(Fe,Cr) with nanometric dimensions, presented superior resistance to corrosion by cavitation than the 316 stainless steel due to the presence of the glassy / nanocrystalline structure. Resistance to cavitation corrosion is important in various equipment such as pumps, water turbines and ship propellers.

In a recent article from 2021 [64] the base composition $\text{Fe}_{76}\text{Nb}_5\text{B}_{19}$ was modified to the composition $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ in order to optimize corrosion and wear resistance, considering 100% glassy, glassy/nanocrystalline and crystalline conditions. Figure 1a indicates the use of thermodynamic calculations via the CALPHAD methodology to identify good glass former compositions close to the eutectic, as indicated by the DSC curve (Figure 2b), XRD pattern (Figure 2c) and TEM analyses (Figure 2d).

5 The development of corrosion and wear resistant Fe-based glassy alloys

Two families of commercial alloys with compositional modifications have been systematically studied by our group in the last 5 years; one based on superduplex stainless steels, for example, $\text{Fe}_{56}\text{Cr}_{23}\text{Ni}_5\text{B}_{16}$, $\text{Fe}_{53}\text{Cr}_{22}\text{Ni}_6\text{B}_{19}$ or $\text{Fe}_{50}\text{Cr}_{22}\text{Ni}_5\text{B}_{23}$ [39,65] and the other on ferritic stainless steels, such as $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ [41,42,61] or $\text{Fe}_{51}\text{Cr}_{10}\text{Nb}_{20}\text{B}_{19}$ [26]. A major motivation for this strategy is the ease of preparation of the alloys as it is based on commercial precursors. In both families of alloys we are evaluating the total content of

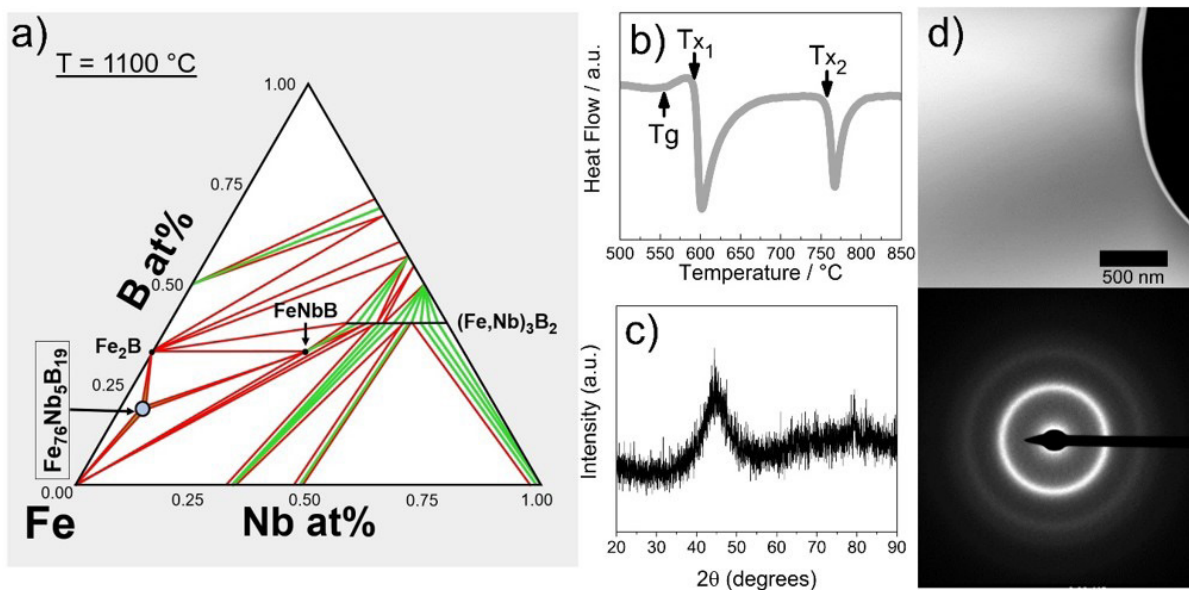


Figure 1. (a) The calculated Fe-Nb-B ternary isotherm at 1100 °C, indicating the $Fe_{76}Nb_5B_{19}$ composition as the ternary eutectic. Replacing a fraction of Fe by 10 at% of Cr result in the $Fe_{66}Cr_{10}Nb_5B_{19}$ alloy, with the assumption that Cr replace the Fe atoms and therefore the alloy can still be evaluated by the ternary diagram. The fully glassy structure of the melt-spun $Fe_{66}Cr_{10}Nb_5B_{19}$ ribbon as indicated by: (b) differential scanning calorimetry (DSC) curve with extended supercooled liquid region ($T_{x1} - T_g$); (c) x-ray diffraction (XRD) pattern dominated by a broad halo, and (d) dark-field transmission electron microscopy image with no contrast of crystals and the selected-area electron diffraction pattern with diffuse halos [64]. Cited images has been reproduced with due permission from the publisher.

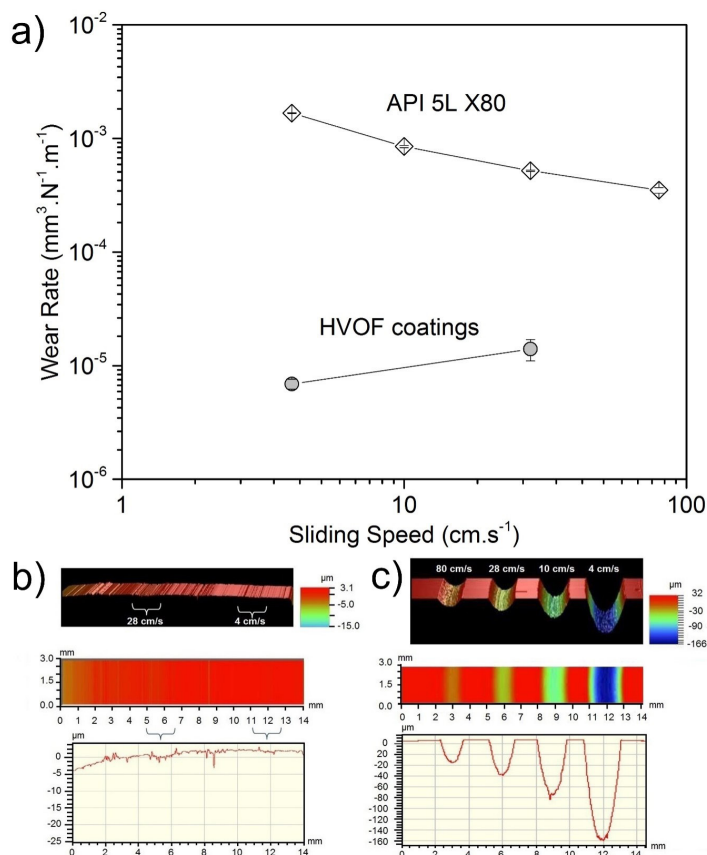


Figure 2. a) Specific wear rate from pin-on-disk sliding wear test of the $Fe_{60}Cr_8Nb_8B_{24}$ HVOF coatings in comparison to that of the API 5L X80 substrate. Surface-profilometer images from worn surface after pin-on-disk measurement for: b) HVOF coating, and c) API 5L X80 steel [25]. Cited image has been reproduced with due permission from the publisher.

metalloids (typically B) and its importance in forming a glassy alloy; for example, the content of B is in most alloys in the range of 20 at%, although there is a general tendency that the minimum content of B for the formation of a glassy phase may decrease with increasing content of transition elements. The need for the metalloid element to exceed a threshold is normally associated with the formation of atomic configurations with medium-range ordering, which requires a certain amount of this element [66,67]. However, the dissolution of large amounts of the metalloid brings some disadvantages, such as, for example, a greater tendency to embrittlement, an increase in the cost of materials and a greater possibility of borides precipitation during, for example, the technological processing to produce coatings, such as HVOF [29].

Reference [68] reports the microstructure and mechanical properties of a coating obtained by HVOF with a new composition, $\text{Fe}_{57}\text{Cr}_9\text{Nb}_{13}\text{B}_{21}$, deposited on a 410 stainless steel substrate. The microstructure of a glassy matrix with crystalline phases $(\text{Fe,Cr})\text{NbB}$, $(\text{Fe,Cr,Nb})_3\text{B}_2$ and Nb-rich phases with sizes in the range of 1 μm to 100 nm observed in the coating led to the coating having high average microhardness (890 ± 75 HV), superior to the substrate (240 ± 12 HV), and good wear resistance. The coefficient of friction of the coating was less than that of the 410SS substrate by about a factor of two at a sliding speed of 0.1 m/s, while the weight loss was on the order of 1 mg in the coating during the 1000 m sliding distance, much lower than the substrate that showed a loss of 4 mg during the first 200 m of slide and 2 mg of loss during the following 800 m.

Reference [29] reports the corrosion properties of $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ alloy produced using pure and commercial materials under the following conditions: ribbons processed by the melt spinning process, partially crystallized ribbons and coatings produced by spray deposition and powder flame spraying process, in this case LVOF. The ribbons showed a 100% glassy structure while the partially crystallized ribbons and the two coatings also showed α -Fe, FeB and Fe_3B crystalline phases. The as-spun ribbon showed excellent corrosion resistance with the formation of a stable passive film that ensured a very large passivation plateau. The coatings (LVOF) showed a high fraction of glassy phase and the crystalline phases, with a layered structure, high porosity (16.2%) and low oxidation level. The coatings formed by spray deposition showed a totally crystalline structure with low porosity (1.9%) and low level of oxidation (about 0.1%). The results showed that in both acid and alkaline media, glassy ribbons have better corrosion resistance than partially crystallized ribbon, coatings, and FSS 430. The fully glassy alloy also showed corrosion performance equivalent to 316L SS. The spray deposition and LVOF coatings did not show high corrosion resistance, and the deterioration of this characteristic in relation to the glassy ribbon was attributed to the presence of crystalline phases as observed for the partially crystallized ribbons. Although boride precipitation can have a deleterious effect related

to corrosion properties, it can also have a beneficial effect related to wear properties. Therefore, alloys with optimized properties can, in principle, be designed to control boride compositions and remaining glassy phases (desirable for corrosion properties) and to control the type and kinetics of boride formation (desirable for wear properties).

$\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ HVOF coatings produced from an AISI 430 stainless steel modified with Fe-B and Fe-Nb resulted in glassy matrix reinforced with borides. The coatings were effective to protect the surface of an API 5L X80 steel against sliding wear [25], with the coating specific wear rate significantly inferior to that of the substrate, Figure 2a, with shallow scars (Figure 2b) compared to the pronounced and deep wear experienced by the uncoated substrate (Figure 2c). Besides the wear resistance, $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ HVOF coatings are effective to protect the surface of API 5L X80 against chloride induced corrosion in acidic medium [69]. Polarization curves in Figure 3 indicate nobler corrosion potential, E_{corr} , inferior corrosion current density, i_{corr} , of the $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ HVOF coatings compared to the API 5L X80 substrate. Also, $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ HVOF coatings displayed a restricted current density increase upon anodic polarization limited at low values, indication of efficiency to restrict the corrosion rate at reduced levels. When the pitting potential is reached, the intersplat surroundings have been identified as the locations more prone to trigger localized corrosion, given a Cr-depleted zone near the intersplat due to the oxidation effect [47].

Associated with this technological challenge of designing alloys with specific microstructures, there are also fundamental scientific aspects that are of relevance for the development of these alloys. For example, Fe-B non-crystalline alloys typically do not show a glass transition [70,71], but this transition has been observed in Fe-based alloys with B contents below 18 at%. Therefore, the development of Fe-based glass alloys with lower B content is important

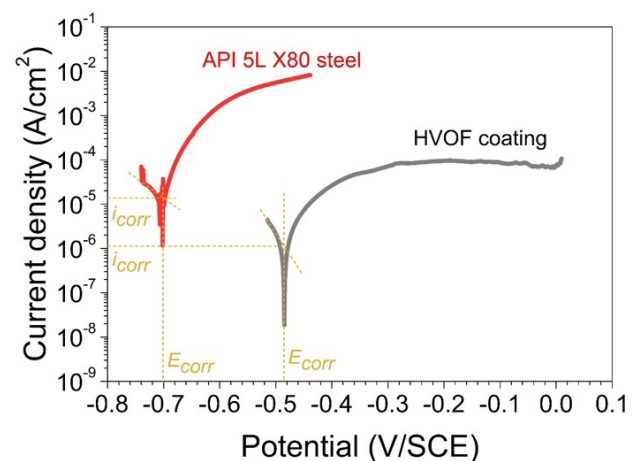


Figure 3. Potentiodynamic polarization curves $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ HVOF coatings in comparison to that of the API 5L X80 substrate in chloride-rich acidic media (pH 3 and 3.5 wt% NaCl) [69]. Cited image has been reproduced with due permission from the publisher.

both from an engineering point of view, due to the probable increase in ductility, and from a fundamental point of view, because of the opportunity to clarify the origin of the glass transition phenomenon in these alloys, which is typically associated with an increase in the ability to form a glassy phase. Certainly, the expected decrease in brittleness should also expand the fields of application of these alloys.

Inoue and Takeuchi [67] reported that Fe-based vitreous alloys can be formed in the range of 16 at% and 18 at% of B in the multicomponent Fe-Co-Ni-Cr-Mo-B system. This system was classified by these authors as the pseudo-high entropy type, and the improvement in ductility observed in relation to almost all glass alloys containing B contents above 20 at% was associated with a lower metalloid content. Glass alloys with high B contents easily form body-centered cubic (BCC) clusters, due to the strong chemical bonds between their constituent elements, which probably become responsible for the brittleness typically associated with these alloys. In addition to this expectation of increased ductility, Fe-based multi-component alloys with low B content should also have useful engineering properties, even in partially and fully crystallized states, because some multi-component borides with nanometer dimensions can have high hardness values, wear-, corrosion- and high temperature-resistances. In fact, these multicomponent (or pseudo-high glass former) alloys present characteristics of great interest, since their partial or total crystallization results in a nanoscale composite structure, due to the ease of nucleation and, therefore, high nucleation rates, and extremely low growth rates of the crystalline phases.

Therefore, the study of the formation, structure, thermal stability, crystallization behavior, mechanical properties and chemical properties of Fe-Cr-Mo-Nb-B alloys containing low B contents, and of high or pseudo-high entropy Fe-based vitreous alloys, for example, (FeCoNi)-(CrMoNb)-B will help to clarify important fundamental characteristics of low-metalloid Fe-based vitreous alloys, also aiding in the development of new glassy / nanostructured alloys.

It is important emphasize that the correct choice of systems and specific compositions can simultaneously result in alloys with high capacity for glassy phase formation and with extremely slow crystallization reactions. As already indicated, these characteristics are associated with the increase in the stability of the supercooled liquid through the high entropy effect and with the low growth rate of the crystalline nuclei, due to the difficulties of long-range atomic rearrangements between the multicomponent elements [51,67,72-74].

Finally, several studies [35,36,50], report that multicomponent alloys containing Cr have excellent corrosion resistance characteristics in different environments, justifying the relevance of electrochemical evaluating, under different conditions, and mechanical study, of glassy and partially crystallized alloys that will be developed in next future.

Also, recent reviews of Fe-based glassy coatings have been published [75-77] and the number of publications and citations have grown remarkably, reaching over

4,000 cumulative citations for specific Fe-based thermally sprayed metallic glass coating. Indeed, the topic is also present in patents, as indicated in recent studies that demonstrate the applied potential of Fe-based metallic glass alloys [78] and coatings [79].

6 Conclusion

Fe-based glass former alloys and coatings are still attracting the academic and technological interest, as pointed by the high pace of publications and patents in the field in recent years. The continuous finding of good glass former Fe-based alloys allows to ensure increasing content of glassy structure even using commercial stainless steels and inexpensive ferrous-alloy additions as precursors. Technological progress is represented by the successful use of such alloys to produce thermally sprayed coatings with retained glassy content, enabling to achieve unprecedented corrosion resistance in chloride media and resistance against sliding and abrasive wear. Novel Fe-containing glass former alloys also proved to surpass the conflicting role of partial crystallization on the corrosion and wear resistance by tuning crystal / glass chemical interface from the formation of multi-principal element crystal with composition similar to remaining glass matrix. Given the abundance of iron ore and steel makers in Brazil, devoted research in advanced ferrous alloys is valuable in the context of environmental applications where corrosion and wear are major risks such as in petrochemical, agroindustry, and mining activities, key national sectors.

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