DESIGN OF CORROSION AND WEAR RESISTANT Fe-Cr-Nb-B COATINGS

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ABSTRACT

Corrosion and wear of alloys is a costly and hidden safety risk for components in petrochemical, agroindustry, and mining industries, 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 Fe-Cr-Nb-B coatings can be produced from commercial grade precursors and industrially available thermal spraying routes. The development 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 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: Bulk Metallic Glass; Steel; Coating; Thermal Spraying; Corrosion; Wear; Crystallization.

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 sector. In this scenario, the metallic components are exposed to environments characterized by: 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.

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. 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, and is the ninth largest oil producer in the world, with about 3.3 million barrels per day. 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 ducts, 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 provided 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. 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. 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) and the ninth largest producer of crude steel in the world (34.4 million tons in 2017) . 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

RESULTS AND DISCUSSION

The Fe-Cr-Nb-B system is interesting because it meets several requirements: i) relatively simple system, with only four main elements with an affordable associated cost, ii) alloys can be produced from industrially grade precursors, iii) alloys that promise to be corrosion resistant given the presence of Cr and Nb, iv) Fe-Cr-Nb-B alloys are likely to be strong, hard and wear resistant, as most of Fe-based BMGs are. Alloys on the Fe-Cr-Nb-B are not intended to be regarded as the first tier in each isolated property or characteristic. However, they satisfy an exquisite balance of requisites instead, aiming to reduce the tremendous preliminary barriers for the entrance and acceptance of new alloys for commercial purposes. In this regard, pursuing even superior individual properties alone may be an insufficient motivation to tackle the consolidation of these systems in real applications. Thus, alloys in the Fe-Cr-Nb-B system do not rely on a single property or characteristic but in their conjunction, as summarized in **Figure 1**.

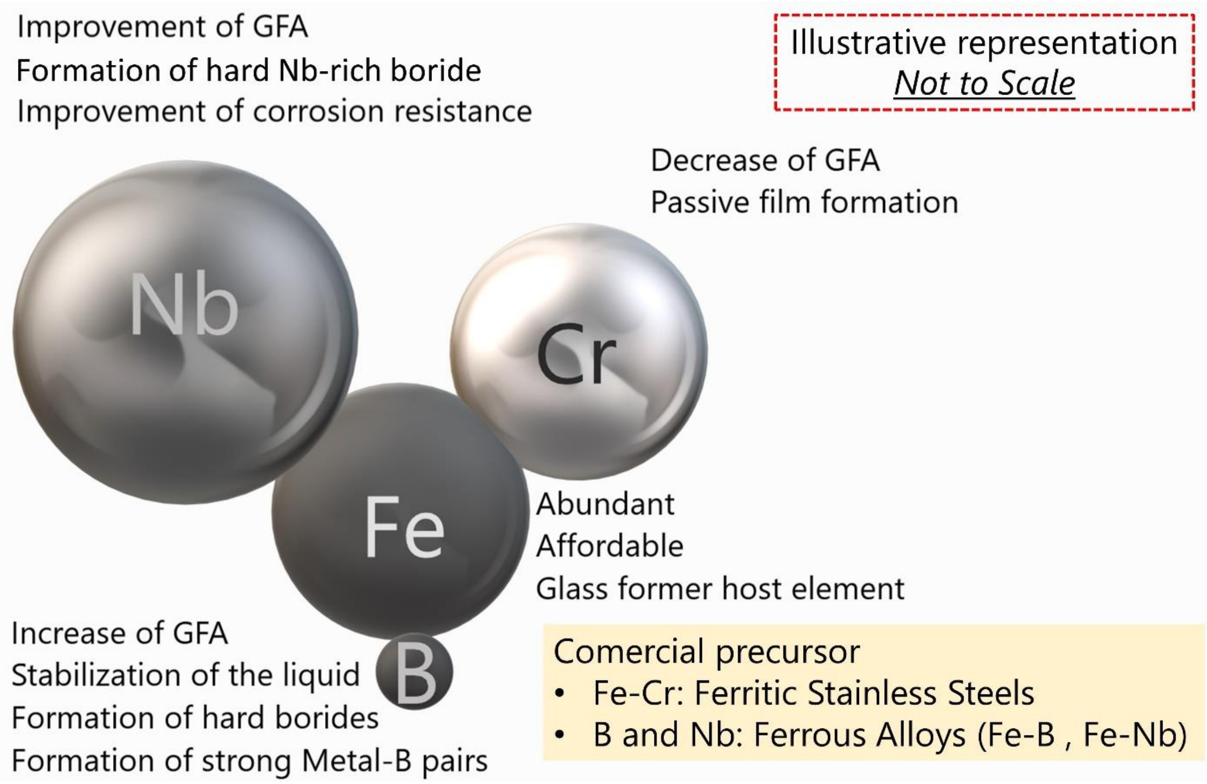

Figure 1 *Summary of the importance of each element on the Fe-Cr-Nb-B system for assisting the alloy design: compositions with high GFA that promise to be resistant to corrosion and wear.* [1]

Figure 2 compares the cross-sectional micrographs of Fe-Cr-Nb-B coatings and deposits from scanning electron microscopy (SEM), using backscattered electron signals (BSE). For HVOF and FS, the effect of the feedstock powder morphology on the coatings' properties was studied, employing particles from two routes, **Figure 2a**: direct from gas-atomization (named gas-atomized) and after high energy ball milling of coarse gas-atomized particles (denoted milled).

DS coatings in **Figure 2b** display a dense microstructure with reduced oxides. The featureless appearance of the microstructure indicates that most particles achieve the substrate at sufficient temperature and velocity to allow effective spreading and densification of droplets. By confining the combustion within the barrel in which the feedstock powders are introduced, the DS process ensures high thermal and kinetic energy jets, improving the deformation of high-velocity particles upon coatings' buildup. Compared to the DS coatings, the HVOF ones in **Figure 2c** exhibit larger pores and some fine bright contrast ascribed to crystals. Besides the typical lamellar structure of thermally sprayed coatings, part of the microstructure of the HVOF coating is composed of particles that were barely deformed upon deposition, compromising the spreading, and causing preferential porosity in their surroundings. Among the particles of the 20 – 53 μm range, the increase of temperature of large ones is slower, so they are more prone to reach the substrate in the solid or semi-solid state. Flame sprayed coatings in **Figure 2e** are more porous, present coarser crystals, and display detached intersplats compared to coatings produced by DS and HVOF. The lower velocity of impacting particles compromises densification, especially for coarser particles that may not be well melted. Regarding jet velocities, the thermal spray processes evaluated has typically the following values: 50 to 100 m/s (FS) < 500 to 1200 m/s (HVOF) < above 1000 m/s (DS) (Ref 170).

The morphology of feedstock powders impacts the microstructure of the coatings. HVOF coatings from gas-atomized, **Figure 2c**, and from milled, **Figure 2d**, feedstock powders, are different, with coatings from milled powders apparently denser and without indication of unmelted particles as a micro constituent. Heat exchange is more efficient for a higher surface-to-volume ratio; hence, considering coarse particles around 50 μm, the temperature of irregular powders from milling increases at a higher rate than the spherical ones produced directly from gas-atomization. Thus, the arrival of molten and semi-molten particles is favored using milled feedstock powders, ensuring better densification and a complete lamellae structure. Similar trends have been found comparing FS coatings from milled, **Figure 2f**, and gas-atomized, **Figure 2e**, feedstock powders. Although denser, the FS coatings using milled powders seem to be more oxidized compared to FS coatings from gas-atomized precursors. Given the better heat exchange, the milled powder may be overheated, favoring oxygen pick-up from the atmosphere. Even if not fully melted, in-flight solid or semi-solid irregular particles have a superior specific exposed surface for oxidation compared to spherical equivalents. Interesting, besides the lamellae constituents, the microstructure of the coating produced from milled powders, **Figure 2f**, is composed of round particles. Some irregular milled particles have their edges preferentially melted before deposition, while the core remains solid. As such, the in-flight particles tend to a spherical shape and, if solidified prior to reach the substrate, result in round constituents within the coatings, similar to what has been seen for HVOF coatings using gas-atomized feedstock, **Figure 2c**.

The microstructures of the EBC, **Figure 2g**, and SF, **Figure 2h**, deposits are quite similar and considerably different from those of thermally sprayed routes (DS, FS, and HVOF). The EBC process in the study relies on the consolidation of powders dispersed within the substrate surface assisted by an electron beam in a regular air atmosphere to produce a coating. The powders were submitted to a high-power electron beam sufficient to melt them completely, resulting in an almost pore- and crack-free coating with refined crystals dispersed homogeneously within a ferritic matrix, **Figure 2g**. In SF, the alloy is melted, and then the molten is slowly poured through a conical tundish into a small-bore ceramic nozzle. The exiting molten fall as a thin stream being broken up into droplets by an annular array of nitrogen gas jets. These droplets then proceed downwards, accelerated by the gas jets to impact a substrate to be protected. The atypical solidification sequence of SF alloy (Ref 171) ensures high levels of microstructural homogeneity and low levels of macrosegregation, as seen in **Figure 2h**.

The thickness of thermally sprayed coatings determines the through-porosity that forms channels for electrolyte entrance towards the substrate. A threshold value exists beyond which percolation of porosity is significantly prevented. A study of HVAF coatings using the $Fe_{49.7}Cr_{18}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ alloy found a threshold value around 240 μm (Ref 172). The thickness of the thermally sprayed coatings in **Figure 2** was around these values, between 200 and 280 μm, with EBC coating and SF deposit as thicker as 1300 and 5000 μm, respectively.

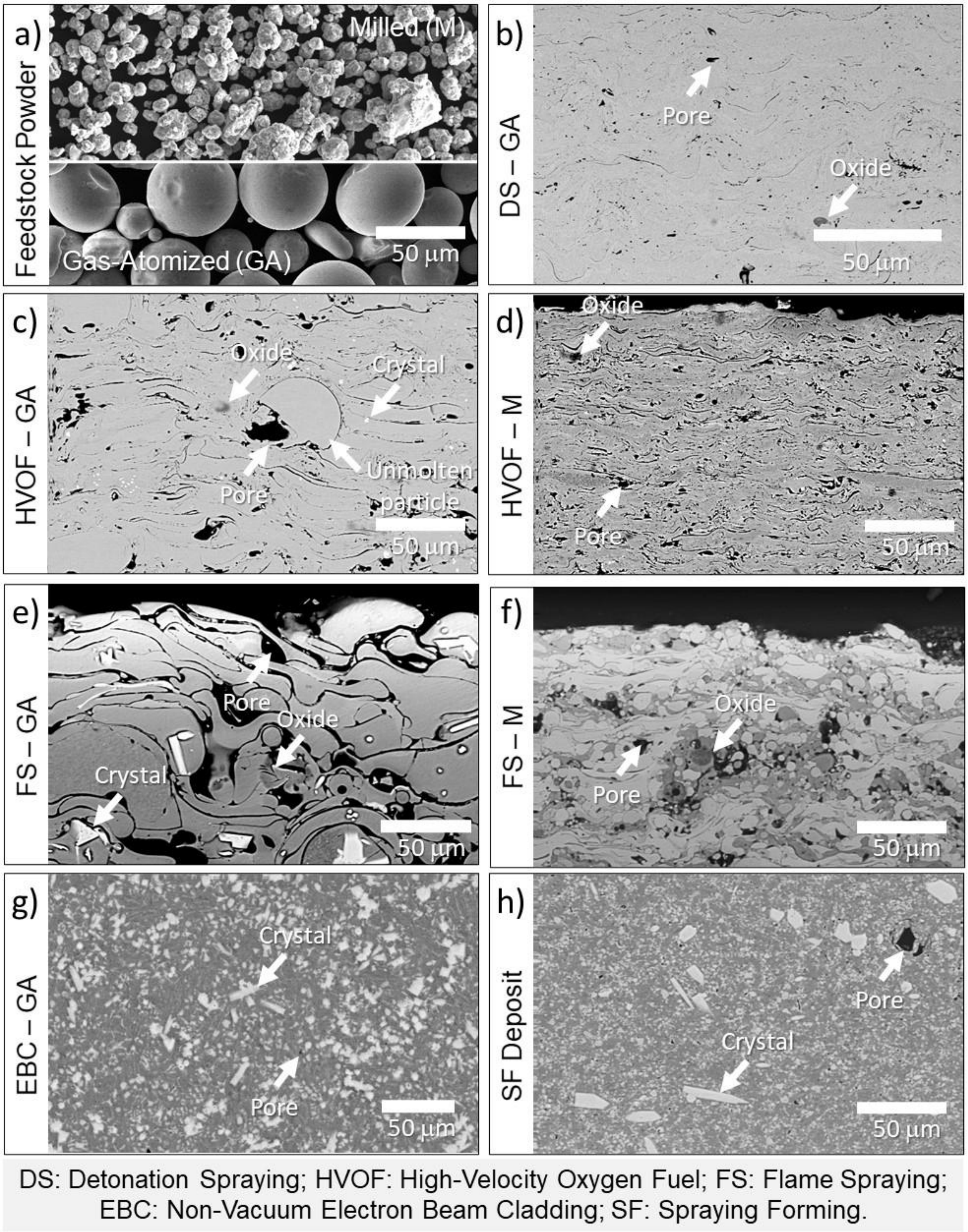

***Figure 2** a) Secondary electron (SE) scanning electron (SEM) micrographs of gas-atomized, GA, and milled, M, feedstock powders. Cross-sectional backscattered electron (BSE) SEM imaging of coatings: b) ~220-µm-thick from detonation spraying from gas-atomized feedstock* (Ref 166), *c) ~280-µm-thick HVOF from gas-atomized feedstock, d) ~200-µm-thick HVOF from milled feedstock, e) ~200-µm flame spraying from gas-atomized feedstock, f) ~220-µm flame spraying from milled feedstock, g) ~1300-µm non-vacuum electron beam cladding from gas-atomized feedstock, and h) spray formed ~5000-µm-thick deposit formed from the liquid. All images for the $Fe_{60}Cr_{8}Nb_{8}B_{24}$ alloy, except (b) $Fe_{66}Cr_{10}Nb_{5}B_{19}$ alloy and (g) $Fe_{62}Cr_{10}Nb_{12}B_{16}$ alloy. Bright phases identified as (Fe,Cr)NbB.* [1]

CONCLUSIONS

Fe-based glassy-containing coatings have more potential than has yet been revealed as suggested the notorious and fast progress in the field. Crystallization upon Fe-based coatings' production is hard to avoid if only commercially grade precursors and processing in conventional atmosphere must be considered. The minimum crystal content observed was ~1% for the DS $Fe_{66}Cr_{10}Nb_5B_{19}$ coatings in optimized conditions. Alloys' performance relying upon a fully glassy structure is clearly not the best strategy. Instead, taking the benefit of crystals seems paramount for enabling feasible corrosion- and wear-resistant Fe-based glassy/nanocrystalline coatings. Also, The current stage of development of Fe-based BMGs and thermally sprayed coatings gives a glimpse of application possibilities that must be validated through in-service testing, which demands interest and collaboration of industrial partners. The durability of critical structural components demands strict requirements established by consolidated standards and recommendations codes. The entrance of new materials or solutions is expensive due to the many tests and committee meetings required for validation and approval. Starting from usage in non-critical components still exposed to a moderated aggressive environment seems more appropriate; however, it is evident that concert among industry and scientific community is highly appreciated in this endeavor.

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