

Microstructural investigation of Fe—Cr—Nb—B amorphous/nanocrystalline coating produced by HVOF



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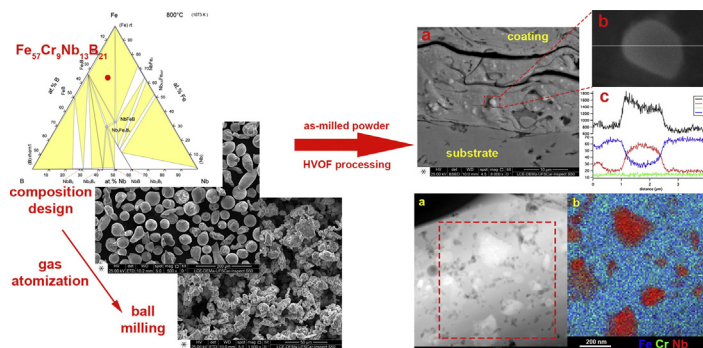
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HIGHLIGHTS

- A new Fe₅₇Cr₉Nb₁₃B₂₁ amorphous/nanocrystalline coating was designed and obtained by HVOF thermal spray.
- The microstructure of the HVOF coating was investigated in details to identify the crystalline phases.
- Orientation image mapping was performed by TEM coupled with an ASTAR system to index the nanocrystalline phases.
- The coating exhibits high microhardness and good wear resistance due to the composite structure of amorphous and nanocrystalline phases.

GRAPHICAL ABSTRACT



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ABSTRACT

Protective coatings of the steel tubes used in the oil and petrochemical industry require good corrosion and wear resistance. Our previous research shows that the Fe—Cr—Nb—B quaternary system is a promising candidate for the above application. In the current work, a new Fe—Cr—Nb—B glassy alloy, with nominal composition Fe₅₇Cr₉Nb₁₃B₂₁, was used to produce amorphous/nanocrystalline coatings by High-Velocity Oxygen Fuel (HVOF) thermal spray process onto 410 stainless steel substrate. The composition was designed to induce, during coating production, preferential formation of fine Nb-rich phases embedded within an amorphous matrix. Amorphous broad halo as well as crystalline (Fe,Cr)NbB and (Fe,Cr,Nb)₃B₂ peaks were confirmed by X-Ray diffraction (XRD) patterns and fine micrometric Nb-rich phases with the size ranging from about 1 μm to 100 nm were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Large fraction of Nb-rich nanocrystals was revealed by high-angle annular dark field (HAADF) and elemental mapping. Some α-Fe, FeB and Fe₂B nanoparticles were also detected by XRD and TEM analyses. Due to the composite structure, the coating was found to exhibit much better wear resistance and higher hardness than the 410 stainless steel substrate.

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1. Introduction

In the past decades, the global market of protective coatings has witnessed a striking growth. Among all fields requiring protective coatings, the city infrastructure accounts for the largest demand followed by the oil and gas industry [1]. Failure of structural and petrochemical

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Table 1
Commercial raw materials, in wt.%, used to obtain the desired Fe–Cr–Nb–B alloy.

Alloy/wt.%	C	Si	Mn	Cr	Ni	S	P	Nb	Co	N	B	Fe
AISI 430	0.06	0.20	0.74	17.62	0.37	0.17	0.02	0.03	0.03	0.03	–	Bal.
Fe–B	0.30	0.57	–	–	–	–	–	–	–	–	16.50	Bal.
Fe–Nb	0.10	1.10	–	–	–	0.10	0.10	66.40	–	–	–	Bal.
Cr	–	–	–	100	–	–	–	–	–	–	–	Bal.
Fe–Cr–Nb–B	0.19	1.79	0.12	9.60	2.94	4.07	5.63	34.21	0.24	0.005	3.80	Bal.

engineering materials due to wear/abrasion, corrosion and fatigue originates usually from the surface [2]. Amorphous Fe-based coatings have been attracting great attention as an effective way to protect structures thanks to their excellent corrosion and wear properties combined with their relatively low costs [3–7]. Moreover, application of amorphous Fe-based alloys as coatings is interesting compared to the use of bulk amorphous glasses (BMG) because of the brittle behavior and poor room temperature plasticity of BMG [8,9]. Coating application is also a viable way to overcome the volume restrictions imposed by the critical cooling rates of BMG and, therefore, large and complex substrates can be coated by wear and corrosion resistant Fe-based amorphous coatings [4,9–11].

Surface microstructure and composition play essential roles if a coating is to be resistant to both corrosion and wear. The production of fully amorphous coatings through conventional thermal spray processes by using only low cost precursors is rare. On the other hand, for partially amorphous coatings, the properties of both crystalline and amorphous phases should be taken into account. Fully amorphous Fe-based alloys containing small addition of corrosion resistant elements, such as chromium, niobium, and molybdenum, show outstanding corrosion resistance due to the rapid dissolution of iron followed by the enrichment of the surface with corrosion resistant elements thus forming a highly stable passive film [12–17]. On the other hand, crystallization of hard borides, such as Fe_xB ($x = 1, 2$) and $(\text{Fe,Cr})\text{NbB}$, is an effective way to improve the wear resistance of Fe-based amorphous alloys [8,18,19]. However, the presence of crystalline phases embedded within an

amorphous matrix may create contacts between phases of different compositions which generate galvanic cells and, consequently, selective dissolutions [12–15].

Recently, several Fe-based multi-component systems with high glass forming ability (GFA) and corrosion and wear resistance have been developed, such as Fe–Cr–Mo–C–B [20], Fe–Co–Cr–Mo–C–B–Y [21], and Fe–Co–Si–B–Nb–Cr [22]. Usually, the achievement of high GFA combined with good surface properties is obtained by using large amounts of noble element additions. For large scale structural applications, an optimization of GFA and surface properties through alloy and microstructure design is essential.

Fe–Cr–Nb–B alloys have potential industrial applications because of the relatively low cost of alloying elements and their high GFA [14,15,23,24]. Recent work has shown that it is possible to obtain amorphous alloys in the Fe–Cr–Nb–B system by using commercial precursors [24]. The corrosion resistance of these amorphous alloys is higher than that of 316L stainless steel in alkaline and acid environment containing chlorides [14]. Although the crystallization of Fe_xB ($x = 1, 2$) in this system would be interesting to improve the wear resistance, this phase is likely to corrode due to the absence of corrosion resistant elements. Additionally, Fe_xB and amorphous Fe–Cr–Nb–B have significantly different chemical potentials which may intensify the selective dissolution of the less noble phase. Since chromium is a relatively expensive alloying element that tends to decrease the GFA of Fe-based

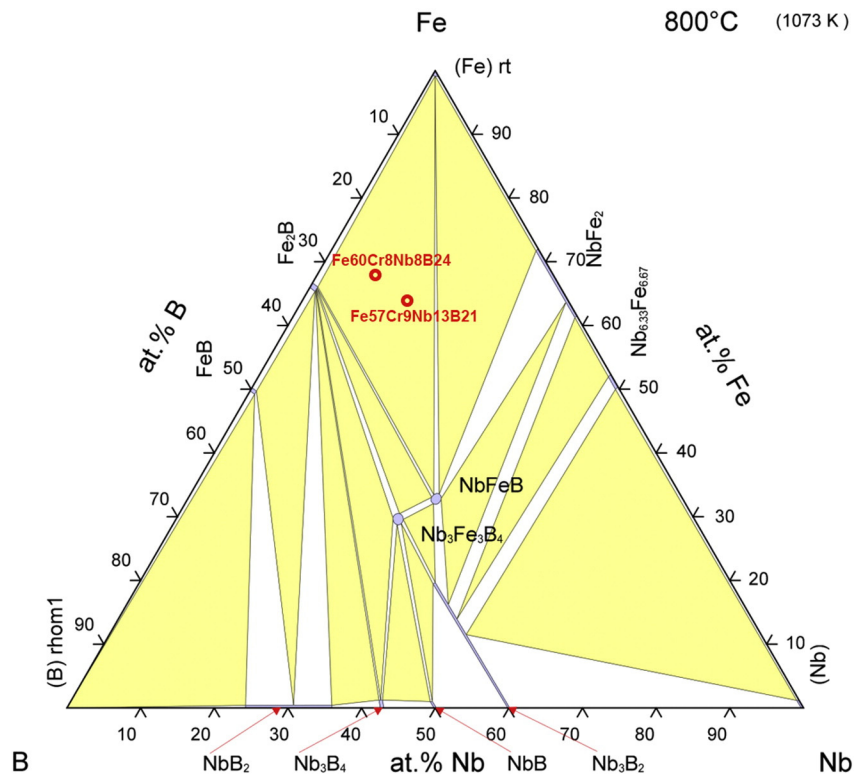


Fig. 1. Isothermal section at 800 °C of the Fe–Nb–B ternary system [32,33]. $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ alloy exhibits high GFA [14] and the shift of this composition towards the $\text{Fe}_{57}\text{Cr}_9\text{Nb}_{13}\text{B}_{21}$ composition is interesting in order to favor the $(\text{Fe,Cr})\text{NbB}$ formation without impairing the GFA.

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