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Multi-component boron and niobium coating on M2 high speed steel processed by powder metallurgy

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ABSTRACT

A multi-component boron and niobium coating can improve properties compared to conventional boron coating. A thicker layer of boron diffusion could be formed, providing a support layer of higher mechanical strength for the hard layer. The objective of this research is to develop a boron and niobium-based coating on the high-speed steel M2 produced by powder metallurgy (P/M). Firstly, calculations by ThermoCalc[®] were made to estimate parameters of niobium boronizing. Secondly, thermochemical treatments by pack cementation were carried out, in stages and also simultaneously. Microstructures, phases, hardness, roughness, wear resistance and coefficient of friction of the coatings were investigated. Finally, coatings composed of niobium carbides or niobium borides and iron borides, measuring more than 3000 HV_{0.025} of hardness was obtained by niobium-boron based treatments. However, the best wear resistance was conferred in the boronizing coating.

Keywords: Niobium Boronizing; Diffusion layer; Pack cementation; Powder metallurgy; Thermodynamic calculations; Wear resistance

1. INTRODUCTION

Since wear is a phenomenon that occurs on the surface of the material, coatings can be an efficient solution by improving the wear resistance and at the same time reducing costs and maintaining the substrate tenacity. Besides, the coatings may be used to obtain other characteristics, such as oxidation resistance [1].

Multi-component boronizing is a thermochemical treatment to harden the surface in which boron and metal atoms diffuse into the metal substrate forming layers of metallic boride [2]. This treatment has been developed to improve even more characteristics and properties conferred by boronizing treatment, such as resistance in wear, corrosion and oxidation, which are achieved through the union of characteristics of different materials [2]. Niobium carbide coatings present high levels of hardness, strength, Young's modulus, melting temperature [4], and quite high corrosion resistance [5], making it suitable to use in high temperature environments [4]. However, the niobium carbide layer acts as a diffusion barrier [6], preventing the formation of a hard support layer. This type of coating leads to the "egg-shell effect", which occurs when a hard layer breaks when it is subjected to a localized force because the substrate is unable to provide proper support [1].

Niobium borides are recognized as potential candidates for structural applications in high temperature, mainly due to their high levels of melting temperature, mechanical strength, thermal and electrical conductivity, as well as good chemical stability [7]. It can also be an effective solution for wear applications, since niobium borides are harder than iron borides. Iron borides coatings exhibit hardness near to 2000 HV, while niobium boride coatings or niobium carbide coatings present hardness values in the range of 2500 - 2700 HV [3,7,8], that are between hard metals hardness (1200 - 1800 HV) and TiC coatings produced by CVD (3400-3800 HV) [2]. Regarding to the wear resistance, the boronizing treatment in H13 produced a decrease of 1.5 X in the samples wear when compared to the substrate.

Whereas the niobium boronizing treatment had a decrease of 9.7 X. This is mostly on account of high hardness levels achieved with these treatments [1].

In addition to that, in niobium and boron based coatings, the hard surface layer of NbB is supported by a dense layer of boride. The boride support layer is harder than layers obtained by a similar treatment made with carbon and nitrogen, while the NbB top layer is similar in hardness to the NbC layer [7].

Niobium boronizing treatment is usually carried out in subsequent stages of boronizing and niobizing [1,7,8]. Nevertheless, it can also be performed simultaneously. In a simultaneous niobium boronizing process, the elements Nb and B are added to the material during the same thermochemical treatment [3,9]. In some researches, the metallization step is performed before boronizing, such as treatments of multi-component boronizing with V, Cr and Ti on substrates of AISI 316L austenitic stainless steel [10] and also with Ni [11]. However, boronizing stage performed prior to metallization is commoner, since the metal carbide tends to act as a barrier to boron diffusion [1] [7] [8].

It is worth observing that these coatings with V, Cr and Ti are successfully produced on a steel with a high content of alloys and carbon, on AISI 316L [10].

Multi-component boronizing might be performed by Thermal-Reactive Diffusion (TRD) treatment. This process consists in a diffusion of one or more chemical elements to the substrate through a solid or liquid environment, followed by a solution and a precipitation to form carbides, nitrides or borides. The coating layers produced by this method are metallurgically bonded to the substrate and are very dense [4].

The composition of the mixture for TRD treatment by pack cementation, should include donors of the elements which are going to be deposited, an activator and a diluent. During the treatment, the activator and donor elements, react with each other forming gaseous reactant species (precursors). These precursor gases are absorbed and react with the

surface of the substrate. The gaseous by-products are recombined and reabsorbed into the gas phase [12]. A scheme of reactions during niobizing treatment by TRD is shown in Fig. 1.

An important condition to be observed for simultaneous multi-component boronizing is that the partial pressure of the precursor gases must be similar between them, otherwise there is no deposition [4]. The partial pressure of these gases depend on the compositions of powder mixtures and the treatment temperature [18].

Regarding the diffusion of elements in multicomponent boronizing, due to the small size of the B atom compared to the transition metal atoms of group VB (Nb, Ta) and VIB (Cr, Mo, W), B diffuses further of the surface occupying interstitial positions and forming a layer in the form of Fe_2B and FeB needles. While Nb forms a substitutional solution with iron (from the substrate) at the positions closest to the surface, affecting the diffusion of boron atoms and consequently the thickness of the coating [3].

Powder metallurgy (PM) is a very common technology for toolmaking. It allows to obtain materials with higher tenacity compared to casting. Moreover, one of its main advantages is the versatility for preparing alloys with precision [19].

The application of this technique can be divided into two major groups. One group comprises materials that cannot be processed by other routes, at least with certain properties; a typical example is the WC-Co hard metal. The other group includes precision parts. PM offers economical manufacturing of complex-shaped parts in large numbers, one example is the production of automotive gears [20].

The method of thermochemical treatment selected for this investigation was the TRD process by pack cementation, based on its low-cost, flexibility and simplicity, allowing complex geometry components to be coated [18].

The objective of this work was to investigate multi-component boron and niobium treatments in stages and simultaneously, on substrates of M2 manufactured by P/M. Simultaneous treatments would be faster than the ones in stages. Furthermore, the intention was to obtain a hard coating supported by a layer with intermediate hardness, in order to reduce the fragility of the coating. This layer with intermediate hardness could be formed by diffusing B into the substrate, as that produced by the conventional boronizing treatment.

2. MATERIAL AND METHODS

Multi-component boronizing treatments on substrates of M2 high speed steel were performed by TRD in solid medium, in stages or simultaneously.

For all types of treatments, the substrates were placed in alumina crucibles containing the coating mixture and treated by using a controlled atmosphere tubular furnace, except for boronizing. Inside the crucible, a layer of alumina was placed above the mixture (to remove the air inside the crucible) and a crucible lid was used (to avoid the escape of gases).

In the simultaneous treatments with amorphous boron, oxygen-getters consisting of porous samples of pure titanium were also placed above the treatment mixture. They performed the function of a sacrifice sample, reacting to the air contained within the crucible.

2.1. Target Materials

The substrates were produced by conventional powder metallurgy (P/M) in AISI M2 high speed steel, and the range of chemical composition is shown in Table I.

Carbon (0.5% by weight) was added to M2 steel powder to compensate the mass loss of this element during sintering. To facilitate the pressing, Acrawax binder (2% by weight over the total mass, M2+C) was added. This procedure was adopted because the M2 powder adopted had small particle size and high hardness.

Characteristics of the raw materials used for substrate manufacture, as well as for preparation of the thermochemical treatment mixtures are shown in Table II.

Green compacts were obtained in a uniaxial die under a pressure of 700 MPa and subsequently sintered under vacuum. The thermal sintering cycle consisted of three temperature levels: the first one at 450 °C for 15 min to remove the lubricant, the second one at 810 °C for 10 min to stress relief, and the last one at 1270 °C for 30 min to consolidate and reduce porosity.

The characterization of the substrate was made by geometric density and Vickers microhardness. For subsequent coating treatments, all samples were sanded up to 600 mesh granulometry, ultrasonically cleaned in alcohol and dried.

2.2. Boronizing Treatment

In boronizing treatments, a commercial powder mixture of Ekabor® trademark was used. A 10 mm high layer of this powder was placed in the container, below and above the

samples, to prevent the outflow of boronizing gases during treatment. The system was capped and sealed with silica sand above the lid.

The heating cycle used was based on a previous study [21], with parameters shown in Table III, as well as of other treatments. To avoid grain growth, the cooling was carried out in the oven up to about 800 °C and then to air, at room temperature of about 25 °C.

2.3. Niobizing Treatment

Niobizing treatments (Nb_20a) were performed with a mixture of 40%Nb (pure), 20%NH₄Cl and 40%Al₂O₃ by weight, based on previous studies [8,10,18,22,23]. For these treatments, niobium powder was sieved to obtain a maximum particle size of 100 µm.

2.4. Niobium Boronizing in Stages

In niobizing step, the mixture Nb_20a was adopted because it resulted in a more homogeneous NbC layer on the M2 substrate, which was observed in treatments of this investigation.

2.5. Simultaneous Niobium Boronizing

Simultaneous treatments were performed with compositions estimated by calculations in ThermoCalc®. The mixtures were denominated S_Eka and S_B and their compositions were respectively (30%Nb + 70%Ekabor®) and (55%Nb + 10%B + 3%NH₄Cl + 32%Al₂O₃), both by weight.

2.6. Characterization Techniques

The cross section of the coated samples was characterized by Scanning Electron Microscopy (SEM Phillips and SEM JSM 6360 Jeol) and Energy Dispersive Spectroscopy (EDS).

X-Ray Diffraction (XRD) analysis was performed in order to identify the phases composition of the coated samples, using monochromatic Cu K α radiation (Philips X'PERT MPD).

Microhardness tests (HV_{0.025}) were carried out to analyze the hardness gradient below the hard layer. Five hardness profiles were made on the cross section of each sample.

Samples of M2 were sanded with 1000-grit paper for wear tests. The roughness of the substrate and coated samples were obtained mapping the surface areas of the samples by a Leica DCM 3D confocal microscope and processing the data through Mountains Map Premium 7.0[®] software.

Dry pin-on-disk type wear tests were employed to determine the wear resistance and friction coefficient of the samples. Tests were conducted using a pin on disk tribometer, according to ASTM G99-04, at room temperature (approximately 25 °C) and relative humidity $\leq$ 50%. Other test conditions were: velocity of 0.2 m/s, load of 10 N, track radius of 4 mm, slip distances of 1000 m and sphere of Al₂O₃ with 6.0 mm of diameter and 2000 HV of hardness as a counterweight. Three trials per sample type were performed. Alumina spheres were chosen for the tests because their application better simulates what occurs in real applications. Moreover, they are suggested in ASTM: G99-05 [24].

The use of a more ductile counterweight in a pin-on-disk causes localized wear only on the counterweight due to the test geometry. However, this does not happen in fact, even when the material slides against more ductile parts, the wear occurs on both sides [25].

Friction coefficient values (μ) of wear tests were calculated through the friction force (F_f), measured by the equipment, and the applied load, according to the Coulomb equation (1):

$$F_f = \mu F_N \quad (1)$$

The volume of material removed was calculated using MountainsMap[®] software, from the mapping of the worn surface generated by the confocal microscope. In this software, first the surface levelling was done and second the volume of material removed was calculated, both by the method of least squares.

3. THERMODYNAMIC CALCULATIONS FOR SIMULTANEOUS NIOBIUM BORONIZING

ThermoCalc[®] was employed to provide useful guidelines for niobium boronizing coating. In this software, calculations are based on Gibbs energy minimization code (Scientific Group Thermodata Europe). For this investigation, SSUB4 database was used.

3.1. Simultaneous Niobium Boronizing Using Amorphous Boron

Initially, calculations were made considering a treatment mixture containing amorphous boron as a boron donor, metal niobium as a niobium donor and NH₄Cl as an activator; in an environment at atmospheric pressure and temperature of 1000 °C, which is usually used for boronizing steel [2].

In these calculations, the mass ratio was considered $m_{Nb}/m_B=4.5$, where m_{Nb} is the niobium mass and m_B is boron mass; in addition, 3 g of NH₄Cl was adopted [23–29].

Therefore, when the Nb mass was varied, the B mass was also varied, and the activator content remained constant. Alumina (Al_2O_3), which was used as a diluent, was not considered in the calculations, since this material is inert for these compositions.

Fig. 2 shows the gas composition as a function of Nb mass percent calculated by ThermoCalc®. The produced gases include boron chlorides, niobium chlorides, chloroboranes, and others; such as Cl and/or H gases and gases at pressures less than 10^{-6} atm, which are not plotted for simplicity.

In a codeposition treatment, for occurring simultaneously diffusion of the elements, the partial pressures of the gases containing these elements must be similar. According to Fig. 2, in simultaneous treatment with amorphous B, from 40 to 48% of niobium, the partial pressure of the B1Cl_3 gas is like that of Cl_4Nb gas, and it is greater than 10^{-4} atm, pressure generally used in boronizing. In this way, we can infer that this quantity of Nb would be enough to achieve codeposition of B and Nb.

In Fig. 3a mixture with 10%B – 45%Nb – 3% NH_4Cl (by weigh) was considered for estimation of the treatment temperature (a) and of the phases that are thermodynamically likely to be formed (b). As this graph, at 750 °C the partial pressures of the gases B1Cl_3 and Cl_4Nb are the same, and at 1000 °C they are similar (Fig. 3a). Therefore, temperatures from 700 to 1000 °C would be adequate for niobium boronizing.

The desired phase in this research is one consisting of boron and niobium. As predicted by ThermoCalc® (Fig. 3b), the fraction of phases formed changes little with temperature. Above 750 °C, the treatment would form approximately 0.9 B_2Nb , 0.06 NNb and 0.01 BNb (by weight fraction).

Calculations were also made to estimate the mass fraction of phases as a function of the depth of the sample cross-section, specifically, as a function of the Fe percentage, Fig. 4.

For these calculations, the same mixture composition, 10%B-45%Nb-3%NH₄Cl (by weight), iron of the substrate and a treatment temperature of 900 °C were considered. For a first approximation, the alloying elements of M2 steel were not considered in the estimate, although their presence may be significant. In addition, calculations were made considering that when the Fe amount increases, the available metal donor amount (B and Nb) decreases.

From Fig. 4, 0.9 by weight of the formed total phase is B₂Nb on the substrate surface, where would be a lower Fe content due to the coating formation, near 0 wt.% of Fe.

Phases with boron and iron or nitrogen, as well as a phase with niobium and nitrogen, are also present according to this prediction. The BFe₂ and NNb phase are present in greater amounts at positions closer to the surface, or for lower content of iron.

An estimate of simultaneous codeposition using a mixture with 10 wt.% of the NH₄Cl activator was also made. With this pack composition, the partial pressure of the precursor gases containing Nb and B did not increase in relation to the pack with 3 wt.% of the same activator. In addition, the solid phases formed through this pack would be constituted by less content of the B₂Nb phase than that mixture containing 3 wt.% of the same activator, therefore, the increase of the content of activator is not favorable.

By changing the activator to KBF₄, the precursor gases with Nb and B had very different partial pressures, they were lower than with the NH₄Cl activator, which would impair the codeposition.

These thermodynamic approximations are for an equilibrium state and do not take into consideration any kinetic factors or non-equilibrium processes, hence the experimental results might differ, and different phases might be deposited.

In summary, from the thermodynamic calculations performed, for a pack mixture containing 45% of niobium, 20% of amorphous boron and 3% of NH₄Cl (by weight); and a

treatment temperature of 900 °C, successful simultaneous niobium boronizing in M2 steel would occur.

3.2. Simultaneous Niobium Boronizing Using Ekabor®

For a pack containing Ekabor® as source of boron instead of amorphous B, the composition of the generated gas as a function of the Nb mass percent was also calculated. Ekabor® powder is composed by 5B₄C, 90SiC and 5KBF₄ (percentage by weight) [2]. The presence of C in the pack could be significant since C might react with any O present and create a reducing atmosphere which might affect the mechanism of coating deposition [12].

The computation was made in a way that by increasing the content of niobium, the content of Ekabor® was decreased in the same proportion. SiC present in Ekabor® was taken into consideration in the calculations, since according to ThermoCalc®, it reacts with Nb to form Si₃Nb₅.

According to calculations for a pack containing Ekabor®, Fig. 5, at pressures above 10⁻¹⁶ atm there are no gaseous species containing Nb, the content of Nb would have to be greatly increased to achieve the simultaneous niobium boronizing.

It is also worth noting that the partial pressure of 10⁻¹⁶ atm is much lower than the pressure of 10⁻⁴ atm achieved by gases containing B or Nb generated from a pack with amorphous B pack instead of Ekabor®, Fig. 2.

Considering a mixture with Ekabor® and 30 wt.% of Nb, calculations by ThermoCalc®, not shown here, predicted the formation of 0.05 wt. of liquid potassium fluoride (FK), which would not be good in a surface treatment, as the powder particles of mixture would stick to the substrate resulting in a rough surface.

4. RESULTS AND DISCUSSION

4.1 Substrate

The experimental properties of M2 powder supplied by the manufacturer are shown in Table IV. The relative geometric density of the substrate produced by P/M was $(97.8 \pm 0.8)\%$ of the calculated theoretical density, which was 7.98 g/cm^3 considering an addition of 0.5 wt.% of C.

4.2 Microstructure and Phases of the Coatings Deposited on M2

Fig. 6 presents the microstructure of all types of coating investigated in this work and Table V the compositions of regions or points highlighted in this figure.

The cross-section of the boronized substrate (treatment B, Fig. 6a) shows three different regions. Near the surface, a dark grey region was identified as FeB; below this there was the formation of Fe₂B (according other research [33]) and in sequence, there is the substrate. These mentioned phases, FeB and Fe₂B, did not present different hardness values according Student's T-test, $(2133 \pm 266) \text{ HV}_{0.025}$ and $(2015 \pm 254) \text{ HV}_{0.025}$ respectively.

The Fe - Fe₂B interface, as well as Fe₂B - substrate interface exhibited a slight saw-tooth morphology, which can be less pronounced than in boronized plain steels. The alloying elements present in AISI M2 steel become the mentioned interfaces smoother than those in plain steel [33–36].

The dark grey region is constituted for FeB, since in regions closer to the surface there is greater diffusion of boron to form the FeB phase instead of Fe₂B. Moreover, the presence of FeB can be verified by XRD, Fig. 7, with 00-032-0463 pdf number.

Other phases constituted by B and M2 elements were also identified by XRD (Fig. 7), as the phase of Mo₂B, with 00-025-0561 pdf standard number. The total boron layer reached a thickness of 35 to 45 µm. The Fe₂B phase was not identified by XRD, this may have occurred because this phase was formed below the surface of the sample [33–36].

Fig. 6b shows the cross-section of the sample treated by the mixture Nb_20a, where a clearer region on the top was identified as NbC by EDS (Table V) and XRD (Fig. 7). This coating reached a thickness of about 11 µm. There was no intermediate layer between it and the matrix, as can be seen in Figure 6a and Table V (region 3), where the last one shows the absence of Nb. This can also be verified by the hardness of the region below the hard layer, which had a similar value to the matrix, 1000 HV_{0.025}, (Figure 8).

On the surface of the boronizing - niobizing coating (Fig. 6c), BNb treatment, there was small or no amount of niobium according to EDS, region 4 and 6 and point 5 of Table V. The present microstructure looks like that obtained by boronizing treatment (Fig. 6a), showing boron phases as FeB (standard 00-032-0463) and Fe₂B (00-036-1332) according to XRD, Fig. 7. These results were different from the other research, in which niobium borides were identified in a coating on the M2 steel produced by a treatment like BNb treatment of this work [8].

The niobizing - boronizing treatment, NbB treatment, resulted in the formation of a highly porous layer, of about 10 µm thickness (Fig. 6d). This coating was composed of NbC (00-010-0181), FeB (00-032-0463), among other compounds identified by EDS and XRD (Table V and Fig. 7). The formation of NbB₂ (00-035-0742) cannot be confirmed by XRD.

The formation of NbB may occur preferentially in high chromium steels such as AISI H13 [10] steel or D2 [9] , unlike the M2 steel, due the chemical equilibria involved among the elements present in these steels.

In H13 there is already CrC during niobization, and since Nb and Cr have similar electronegativity, CrC remains stable even in the presence of Nb. As Nb does not bind to carbon at first, it becomes available to bind to B present in the steel and which was bound to the iron (phases FeB and Fe₂B). The electronegativity difference between Nb and B is higher than between Fe and B, this explains the formation of NbB.

In M2 steel, the carbon atoms present in the molybdenum carbides, inherent of this steel, prefer the Nb atoms to these metallic elements due to the electronegativity difference between them. Then, these carbides are broken down to the formation of niobium carbides during niobization. Also because of the difference in the electronegativity (E), the Nb element binds more easily to C ($E_{Nb} - E_C = 1.6 - 2.5 = 0.9$ eV) than to B ($E_{Nb} - E_B = 1.6 - 2.0 = 0.4$ eV) [37].

In the coating produced by the boron-based mixture for simultaneous treatment, S_B (Fig. 6e), there was the formation of a layer with NbC and Fe₂B, according to XRD (Fig. 7), standards 00-038-1364 and 00-036-1332 respectively, among other phases. The presence of Nb on the surface was also confirmed by EDS, point 11 in Table V. However, phases consisting of B and Nb at the same time were not identified, although they were predicted by ThermoCalc®. This may be connected to the presence of MoC and WC in M2 as previously explained, since the calculations were made based on a Fe-based substrate. Below the NbC layer, Ti and C were identified in a porous region by EDS, point 12 in Table V. The element Ti diffused from the getter oxygen, compact of Ti, which was placed on the mixture during this thermochemical treatment. It is possible that this region has

boron, not only carbon. However, this technique does not allow to differentiate elements of low atomic weight.

The simultaneous treatment with the S_Eka mixture resulted in greater carbide refinement and distribution near the substrate than in boronizing, compare Fig. 6f with Fig 6a. These carbides are of elements from M2, such as V, W, Mo, as observed by EDS, Table V. The presence of Nb and B was not detected through EDS, however, Fe₂B (00-036- 1332) and NbC (00-038-1364) phases were identified by XRD (Fig. 7).

4.3. Hardness

The coatings conferred hardness values higher than the substrate, with exception of S_Eka treatment (Fig. 8).

The S_B and Nb_20a treatments presented hardness values of approximately 3200 HV_{0.025} and the B treatment approximately 2000 HV_{0.025}.

The S_Eka treatment resulted in lower hardness at some points of the hardness profile than the M2 substrate. The other treatments conferred similar or higher hardness values along the hardness profile than the M2 substrate. These comparisons were made based on Student's T for paired data, with a 95% confidence level.

Comparing the S_B treated sample to the M2 substrate (Fig. 8), at various points along the hardness profile the S_B sample showed lower hardness. However, comparing the hardness values of S_B samples along to the hardness profile, no point presented lower hardness than at 85 µm from the surface (Fig. 8) (where diffusion is very unlikely).

It is important to note that, only the boronizing coating resulted in gradual variation of hardness along the distance from the surface. This transition zone of intermediate hardness is important to support the hard layer and to become the coating less brittle.

4.4. Roughness

Fig. 9 presents Sa height parameters of the substrate and coated samples. According to the Test-T of hypotheses, all types of coatings presented higher Sa roughness than the substrate, with a 95% confidence level. This roughness increase is related to the occurrence of phase changes and the formation of new phases on the samples surface. The difference between the specific volumes of the substrate and the newly formed phases leads to a dimensional change, which increases the surface roughness of the samples [10].

Among the treatments, B and S_Eka conferred the lowest roughness. The S_B coating had a large dispersion of the Sa values, indicating heterogeneity in the surface roughness. The wear resistance of a coating is affected by hardness, coefficient of friction [9], roughness, ductility among other factors [2,38].

Considering the hardness, if only this property modifies the wear resistance, all coatings (except for S_Eka) should have a higher wear resistance than the substrate, since they had a higher hardness than the substrate, especially S_B and Nb_20a, Fig. 8.

The boronizing and S_Eka treatment conferred the lowest roughness between the treatments. In both treatments, the phases formed on the substrate surface are composed of B and elements of M2, such as FeB, Fe₂B and CrB (Fig. 7), therefore these phases must be related to low roughness.

4.5. Volume of Material Removed and Coefficient of Friction

According to wear tests results (Fig. 10), the boronizing treatment resulted in less material removed than the untreated substrate. The high hardness, low roughness and low

coefficient of friction (Fig. 10) of the boronized coating contributed to its higher wear resistance.

The other treatments presented an average of material removed equal to the substrate, with a 95% confidence level. The high dispersion of the volume removed values from other coatings, Fig. 10, can be explained by both, the high roughness values of these coatings (Fig. 9) and low hardness in the region underlying the hard layer, which should withstand the coating. There is a greater facility of crack initiation in surface roughness or roughness, which leads to a disintegration of the coating [1].

The S_B samples presented a very high volume of material removed and for simplicity, its result was omitted in Fig. 10. Although the S_B coating has exhibited such low wear resistance, further studies on simultaneous treatment with boron and niobium are recommended, given the high hardness attained.

Concerning the coefficient of friction, Fig. 10, the formation of a hard layer obtained from the treatments promoted lower coefficients of friction than the substrate, with at least a 92% confidence level. Except for the S_B treatment, it resulted in high dispersion of coefficient of friction.

Normally lower values of coefficient of friction are associated with a lower abrasion wear [8]. In this work, the coatings presented lower coefficient of friction than the substrate, but similar volume removed. This may be associated with the high roughness of these coatings, which facilitates material removal.

The boronized samples presented a mean coefficient of friction like the other coated samples (Fig. 10), despite the lower roughness (Fig. 9).

The variation of the coefficient of friction with sliding distance for the substrate and coated samples of this research is shown in Fig. 11. The boronizing coating resulted in the lowest variation of the coefficient of friction. BNb coated samples had an increase in the coefficient

of friction and dispersion of coefficient values with the distance. The higher dispersion of the coefficient of friction may be related to the coating disintegration and subsequent acting as a lubricant.

5. CONCLUSIONS

In this study, boroniobizing heat treatments were carried out on P/M AISI M2, and then properties and wear behavior of obtained coatings were investigated. The following conclusions can be pointed from the results:

1. In the boron-niobium based coatings, niobium carbides, iron borides and niobium borides were formed. The B_2Nb phase was provided by the niobizing followed by boronizing treatment (NbB).
2. The phases produced during the treatments differed slightly from those predicted by ThermoCalc® since the B_2Nb phase should have been formed by the simultaneous niobium boronizing using amorphous boron (S_B), but only NbC was formed, among other phases without Nb.
3. Due to the higher electronegativity difference between Nb and C than between Mo and C (present in the carbides of M2 steel), in M2 steels the Nb element can tend to destabilize these carbides and form NbC instead of BNb or B_2Nb .
4. The coating produced by simultaneous S_B and niobizing (Nb_20a) treatments reached a hardness higher than 3000 HV_{0.025}. However, there was not a gradual change in hardness values below the hard layer as expected.
5. The coatings had a higher roughness compared to the substrate. In spite of this, most of the hard coatings had a lower coefficient of friction than the substrate.

6. Boronizing treatment conferred the higher wear resistance among the surface treatments investigated.
7. Boron-niobium based treatments resulted in an average of material removed similar to the substrate, which can be associated with both high surface roughness and low hardness in the region underlying the hard layer.
8. Further studies on niobium-boron based treatments on M2 steel are needed to obtain a harder diffusion layer below the BNb or NbC coating. Since these coatings had a higher hardness and lower roughness than boronizing coating.

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REFERENCES

- [1] G.S. Takeya, F.E. Mariani, A.N. Lombardi, G.E. Totten, L.C. Casteletti, Characterization of coatings obtained by boriding niobizing treatment of an AISI H13 steel, *Mater. Perform. Charact.* 5 (2016) 396–405.
- [2] A.K. Sinha, Boriding (Boronizing) of Steels, in: *Handb. Heat Treat.*, V.4, ASM International, 1991: pp. 978–1000.
- [3] N. Suwattananont, Multi-component boron coatings on low carbon steel AISI 1018,

New Jersey Institute of Technology, 2010.

- [4] T. Arai, S. Harper, Thermoreactive Deposition/Diffusion Process for Surface Hardening of Steels, in: *Handb. Heat Treat.*, V.4, ASM International, 1991: pp. 1000–1013.
- [5] F.A.P. Fernandes, J. Gallego, C.A. Picon, G. Tremiliosi Filho, L.C. Casteletti, Wear and corrosion of niobium carbide coated AISI 52100 bearing steel, *Surf. Coatings Technol.* 279 (2015) 112–117. doi:10.1016/j.surfcoat.2015.08.036.
- [6] A.H. Üçisik, C. Bindal, Fracture toughness of boride formed on low-alloy steels, *Surf. Coatings Technol.* 94–95 (1997) 561–565.
- [7] S.S. Pazarlıoğlu, Ö. Kon, Ş. Şen, U. Şen, Niobium boride coating on the surface of AISI 1010 by a duplex treatment, *Usak Univ. J. Mater. Sci.* 2 (2012) 199–204.
- [8] U. Sen, S.S. Pazarlıoğlu, S. Sen, Niobium boride coating on AISI M2 steel by boro-niobizing treatment, *Mater. Lett.* 62 (2008) 2444–2446.
- [9] C.K.N. Oliveira, C.L. Benassi, L.C. Casteletti, Evaluation of hard coatings obtained on AISI D2 steel by thermo-reactive deposition treatment, *Surf. Coatings Technol.* 201 (2006) 1880–1885. doi:10.1016/j.surfcoat.2006.03.036.
- [10] V. Samadi, A. Habibolahzade, Evaluation of microstructures and wear properties of duplex boride coatings, *Mater. Sci. Technol.* 26 (2010) 41–46.
- [11] T. Wierzchoh, P. Biefliski, K. Sikorski, Formation and properties of multicomponent and composite borided layers on steel, *Surf. Coatings Technol.* 73 (1995) 121–124. doi:10.1016/0257-8972(94)02365-4.
- [12] S.A. Tsipas, M.R. Vázquez-alcázar, E.M.R. Navas, E. Gordo, Boride coatings obtained by pack cementation deposited on powder metallurgy and wrought Ti and Ti – 6Al – 4V, *Surf. Coat. Technol.* 205 (2010) 2340–2347.
- [13] Z.D. Xiang, J.S. Burnell-Gray, P.K. Datta, Aluminide coating formation on nickel-base superalloys by pack cementation process, *J. Mater. Sci.* 36 (2001) 5673–5682.
- [14] D.N. Tsipas, K.G. Anthymidis, Y. Flitris, Deposition of hard and/or corrosion resistant, single and multielement coatings on ferrous and nonferrous alloys in a fluidized bed reactor, *J. Mater. Process. Technol.* 134 (2003) 145–152.
- [15] K.G. Anthymidis, N. Maragoudakis, G. Stergioudis, O. Haidar, D.N. Tsipas, A comparative study of boride coatings obtained by pack cementation method and by fluidized bed technology, *Mater. Lett.* 57 (2003) 2399–2403.
- [16] N. Voudouris, C. Christoglou, G.N. Angelopoulos, Formation of aluminide coatings on nickel by a fluidised bed CVD process, *Surf. Coatings Technol.* 141 (2001) 275–282.
- [17] A. Squillace, R. Bonetti, N.J. Archer, J.A. Yeatman, The control of the composition and structure of aluminide layers formed by vapour aluminising, *Surf. Coatings Technol.* 120–121 (1999) 118–123.
- [18] S.A. Tsipas, M.R. Vázquez-Alcázar, E.M. Ruiz Navas, E. Gordo, Boride coatings obtained by pack cementation deposited on powder metallurgy and wrought Ti and Ti–6Al–4V, *Surf. Coatings Technol.* 205 (2010) 2340–2347.
- [19] A. Cremonezi, A.N. Klein, A. Loberto, D. Rodrigues, D.T. de A.F. Filho, *A metalurgia do pó: alternativa econômica com menor impacto ambiental*, 1ª Ed., Metallum eventos técnicos e científicos, 2009.
- [20] H. Danninger, C. Gierl-Mayer, Advanced powder metallurgy steel alloys, in: Y.Z. Isaac Chang (Ed.), *Met. Surf. Eng.*, Woodhead, 2013: pp. 149–201.
- [21] A.P. Krelling, Estudo do comportamento tribológico do aço AISI H13 submetido a tratamento termoquímico de boretção, (Unpublished Master's thesis), Universidade do Estado de Santa Catarina, 2012.
- [22] U. Sen, Kinetics of niobium carbide coating produced on AISI 1040 steel by thermo-

- reactive deposition technique, *Mater. Chem. Phys.* 86 (2004) 189–194.
- [23] U. Sen, Kinetics of titanium nitride coatings deposited by thermo-reactive deposition technique, *Vacuum*. 75 (2004) 339–345.
 - [24] American Society For Testing and Materials, G99-05: standard test method for wear testing with a pin-on-disk apparatus, West Conshohocken, n.d.
 - [25] J.C.G. Milan, M.A. Carvalho, R.R. Xavier, S.D. Franco, J.D.B. De Mello, Effect of temperature, normal load and pre-oxidation on the sliding wear of multi-component ferrous alloys, *Wear*. 259 (2005) 412–423.
 - [26] M. Bejar, E. Moreno, Abrasive wear resistance of boronized carbon and low-alloy steels, *J. Mater. Process. Technol.* 173 (2006) 352–358.
 - [27] C. MERİÇ, S. SAHİN, S.S. YILMAZ, Investigation of the effect on boride layer of powder particle size used in boronizing with solid boron-yielding substances, *Mater. Res. Bull.* 35 (2000) 2165–2172.
 - [28] S. Sahin, C. Meric, S. Saritas, Production of ferroboron powders by solid boronizing method, *Adv. Powder Technol.* 21 (2010) 483–487.
 - [29] C. Martini, G. Palombarini, M. Carbuichio, Mechanism of thermochemical growth of iron borides on iron, *J. Mater. Sci.* 39 (2004) 933–937.
 - [30] C. Martini, G. Palombarini, G. Poli, D. Prandstraller, Sliding and abrasive wear, *Wear*. 256 (2004) 608–613.
 - [31] N.G. Kaidash, L.N. Chetverikova, R.N. Nikitenko, Diffusion alloying of metals and alloys, in: *Int. Conf. DIFTRANS*, Sofiyivka, Cherkasy region, 2007: pp. 68–76.
 - [32] N. Gidikova, Vanadium boride coatings on steel, *Mater. Sci. Eng. A*. 278 (2000) 181–186.
 - [33] E.A. dos S. de Almeida, A.P. Krelling, J.C.G. Milan, C.E. da Costa, Micro-abrasive wear mechanisms of P/M AISI M2 steel with different surface treatments, *Surf. Coatings Technol.* 333 (2018) 238–246. doi:10.1016/j.surfcoat.2017.10.020.
 - [34] I. CAMPOS, U. RAMIREZ, G. VILLAVELAZQUEZ, C. FIGUEROA, G. RODRIGUEZ, Study of microcracks morphology produced by Vickers indentation on AISI 1045 borided steels., *Mater. Sci. Eng. A*. 475 (2008) 285–292.
 - [35] L. Gutierrez-Noda, C.A. Cuao-Moreu, O. Perez-Acosta, E. Lorenzo-Bonet, P. Zambrano-Robledo, M.A.L. Hernandez-Rodriguez, The effect of a boride diffusion layer on the tribological properties of AISI M2 steel, *Wear*. 426–427 (2019) 1667–1671. doi:10.1016/j.wear.2019.01.089.
 - [36] I. Ozbek, C. Bindal, Kinetics of borided AISI M2 high speed steel, *Vacuum*. 86 (2011) 391–397.
 - [37] Pauling Electronegativity Values, *Chem. Libr.* (2019). [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Electronegativity/Allred-Rochow_Electronegativ](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Electronegativity/Allred-Rochow_Electronegativ) (accessed September 21, 2019).
 - [38] K. Holmberg, A. Matthews, H. Ronkainen, Coatings tribology — contact mechanisms and surface design, *Tribol. Int.* 31 (1998) 107–120.

6. TABLES

Table I. Range of chemical composition of Osprey AISI M2 steel reported by manufacturer.

Powder	Manufacturer data								
	Chemical composition (wt.%)								
M2	Fe	C	Cr	Ni	Mo	Si	Mn	W	V
	Bal.	0.78-	3.75-	0.3	4.5-	0.2-	0.15-	5.50-	1.75-
		1.05	4.5		5.5	0.45	0.4	6.75	2.2

Table II. Characteristics of raw materials reported by manufacturers.

Raw Materials	Manufacturer	Density (g/cm ³)	Particle Size (μm)
Amorphous Boron	Sigma-Aldrich Química S.A.		
Ekabor® 1- V2	ESK Ceramics GmbH & CO		
Metal niobium	CBMM		400
C (graphite)	Istam	2.24	D50=18
Acrawax® C Atomized	Lonza Inc.	0.97	D90=13

Table III. Parameters of Boronizing (B). Niobizing (Nb_20a) and Simultaneous niobium boronizing (S) treatments.

Treatment	Atmosphere	Temperature (°C)	Time (h)	Heating rate (°C/min)
B	Uncontrolled	1000	2	10
Nb	Argon	1000	4	10
S	Argon	1000	4	10

Table IV. Experimental Data of Osprey AISI M2 Steel

Powder	Experimental data	
	Density (g/cm ³)	Size particle (μm)
M2	8.1	D50=11.65
		D90=24.90

Table V. Semiquantitative chemical composition by EDS of regions and points of the sample microstructures (Fig. 6).

Region/ Point analysed	Chemical composition (wt.%)									
	B	C	Si	V	Cr	Fe	Nb	Mo	Ti	W
1		3.0		0.8	4.9	90.2		1.1		
2		4.9		2.7	3.0	26.5		21.0		41.9
3		4.0	1.1	0.8	4.1	87.7		2.3		
4		3.0		0.8	4.9	90.2		1.1		
5		14.9				2.3	81.0			1.8
6		3.0		0.8	4.1	89.2		1.6		1.3
7		6.5		1.7	4.1	78.1	1.9	2.6		5.0
8		3.7		0.7	3.9	91.6				
9		5.3		2.2	4.7	73.4		4.4		10.0
10		13.7		1.7		3.3	81.4			
11	6.9	6.9		0.9	1.4	24.9		17.1		42.1
12		4.1	0.2	0.7	4.6	90.4				
13		4.7	1.4	2.7	6.2	77.6	4.2	3.3		
14						8.9	91.1			
15		10.9		3.6	1.7	24.1	1.9	7.3	41.8	8.7
16		5.3		1.8	5.7	85.1		0.6		1.5
17		4.6		3.0	2.5	28.3		21.6		40.0
18		11.3		30.3	3.7	8.0		16.5		30.3
19		2.6	2.1	1.8	6.6	84.2		2.9		
20		3.4			2.4	91.5		1.0		1.4

7. FIGURES

Fig. 1. Niobizing by TRD treatment in solid medium.

Fig. 2. Gas composition for a pack mixture containing NH_4Cl activator, boron amorphous and niobium as a function of the Nb mass percent.

(a)

(b)

Fig. 3. (a) Gas composition and (b) mass phase fraction as a function of temperature for a pack mixture containing niobium, boron amorphous and NH_4Cl activator.

Fig. 4. Mass fraction of the formed phases (5 solid and 1 gaseous) as a function of the iron percent. for treatment at 900 ° C with a pack mixture containing niobium. boron amorphous and the NH_4Cl activator.

Fig. 5. Gas composition for a pack mixture containing Ekabor® and niobium as a function of Nb mass percent.

Fig. 6. (a – f) Different coatings deposited on M2. identified above the respective image.

Fig. 7. X-ray diffraction spectra of different coatings deposited on M2.

Fig. 8 Microhardness profiles along the cross section of the substrate and coating samples.

Fig. 9. Average height Sa of samples under different conditions.

Fig. 10. Volume of material removed and coefficient of friction of samples under different conditions.

Fig. 11. Coefficient of friction versus sliding distance of the substrate and different coatings.