Improvement of the Tribological Characteristics of AISI 8620, 8640 and 52100 Steels through Thermo-Reactive Treatments

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Abstract: The production of vanadium and niobium carbides (VC and NbC) layers on AISI 8620, 8640, and 52100 steels may increase hardness and wear resistance of substrates. Thermochemical treatments were performed at 1000 °C for 2 and 4 h. The characterization of the treated samples was carried out by means of Knoop microhardness tests, “calotest” type microadhesive wear test, layer adhesion test according to VDI 3198 standard, and X-ray diffraction. Compact and uniform layers of VC and NbC were obtained in all treatments, with hardness up to 2500 HK and microadhesive wear resistance far superior to that of the substrates, indicating the great efficiency of these treatments for tribological applications.

Keywords: carbides layers; thermo-reactive deposition; adhesive wear; VC; NbC

1. Introduction

The developments in the metal mechanical industry have been focused on the improvement of wear and corrosion resistance, while maintaining ductility and tenacity [1]. Production of surface coatings is a good solution for these purposes, significantly increasing service life, reducing operational costs, and avoiding probable failures of engineering components. Transition metals carbides, like niobium carbide (NbC) and vanadium carbide (VC), have a unique combination of physical properties, such as high hardness, high melting point, and high thermal conductivity, that are desirable for many technological applications [2,3]. These materials were successfully applied as coatings in metallic substrates using physical vapor deposition (PVD), chemical vapor deposition (CVD), and thermal spray methods with satisfactory results [4–6]. A technique called thermo-reactive deposition (TRD) is attracting attention, because of its advantages over other processes: it does not need complex equipment, costs less than the processes already mentioned, and the coatings provided by this method present good adhesion to substrate [1,7,8].

There are three ways to carry out the TRD process: (1) fluidized bed method, which utilizes a fluidizing gas with activators and carbide forming elements (CFE) powders at high speed to coat metal parts in a controlled atmosphere; (2) powder pack method, in which the parts are placed in a crucible filled with powders of CFE, activator, and inert filler, and; (3) salt bath immersion method, in which the parts to be coated are immersed in a salt bath containing CFE [9,10]. The salt bath immersion method was chosen because it does not need complex equipment such as CVD and PVD methods, and due to its low cost. This method consists in immerse metal parts in a molten salt bath for 0.5 to 10 h, at temperatures from 800 to 1250 °C, depending on the desired layer thickness of the layer.
The salt used is composed of Borax (Na$_2$B$_4$O$_7$·10H$_2$O) and CFE, which could be in form of pure metal, ferroalloy, or oxide powders, and, when needed, a reducer, usually aluminum. The material of the bath reacts with the surface of the substrate, meanwhile, carbon from substrate diffuses from the interior to the surface. The combination of these elements will form the coating layer [9–12]. Therefore, the steel substrate will be the source of carbon for chemical combinations with CFE present in the molten salt bath and consequently the growth rate of the coating will be dependent on the carbon content of the base material and the alloy elements added to the bath [13,14]. For this reason, a substrate with carbon content of 0.3 wt.% or higher is required in order to produce carbides coatings.

In recent studies, researchers achieved promising results with this technique on different metallic substrates, increasing wear resistance comparing with corresponding substrate. Soares et al. [15] studied the formation of niobium carbide layer on ductile cast iron with salt bath TRD technique. A regular coating with 31 µm thickness was obtained. The layer had good adhesion to substrate and increased hardness from 379 ± 40 HV$_{0.5}$ (substrate) to 2098 ± 115 HV$_{0.5}$ (layer) and, consequently, an increase of approximately 15 times in adhesive wear resistance.

Biesuz and Sglavo [16] evaluated vanadium carbide coatings applied on AISI 4140 steel by salt bath TRD and its formation kinetics. Consistent and adhesive VC layers were produced in all temperatures and times. VC layers with thickness up to 16 µm were obtained depending on the treatment parameters. The coating had an outstanding microhardness value of 2451 ± 236 HV$_{0.2}$, a clean and flat interface with the steel, good adhesion, excellent surface finish, low porosity, and absence of cracks. These characteristics are extremely important for a good wear resistant coating.

Ramírez-Ramos et al. [17] studied the tribological properties of NbC and VC coatings produced by salt bath TRD on AISI D2 steel. The layers grew uniformly, with flat interfaces, high hardness, and inferior coefficient of friction (COF) compared to the substrate, improving the steel durability under high wear applications.

Günen et al. [18] evaluated codeposition of vanadium and chromium on AISI D2 steel using TRD by pack cementation. Higher treatment temperatures favored formation of vanadium carbides, of higher hardness when compared to chromium carbides, besides allowing production of smoother and uniform coatings. The coatings thickness obtained were from 11.3 µm to 23.2 µm. The COF values of all coated samples were lower than the one for the bare substrate. The average COF values decreased with increasing treatment temperature and time.

Stahin et al. [19] studied vanadium carbide coating formed utilizing TRD on AISI 52100. The coating thickness obtained was approximately 4 µm, with a hardness of 35.5 ± 7.5 Gpa. The COF value in dry conditions was reduced from 0.74 to 0.53 in the coated samples.

Table 1 summarizes the information presented.

| Coating | Substrate   | Thickness (µm) | Hardness Variation | CoF Variation | Reference |
|---------|-------------|----------------|--------------------|--------------|----------|
| NbC     | Ductile cast iron | 31          | 4.5 times higher   | -            | [15]     |
| VC      | AISI 4140    | 16           | 2.7 times higher   | -            | [16]     |
| NbC VC  | AISI D2      | 16.3–15.8    | 2–4 times higher   | 0.17 substrate COF | [17]     |
| (V-Cr-C)| AISI D2      | 11.3–23.2    | 2.7–3.4 times higher | 0.95–0.47 substrate COF | [18]     |
| VC      | AISI 52100   | 4            | -                  | 0.72 substrate COF | [19]     |

Fewer authors evaluated TRD coatings on AISI 8620 and 8640 steels that are widely used in the manufacture of gears, crankshafts, pistons, and bearings, activities that the components are subject to constant relative contacts during service, resulting in surface wear. Thus, in order to evaluate the improvement of the tribological properties, vanadium and niobium carbide layers were produced on AISI 8620, 8640, and 52100 steels and characterized in terms of their morphology, phase composition and tribological behavior.
2. Materials and Methods

Samples of the AISI 8620, 8640, and 52100 steels with dimensions of 25 × 20 × 5 mm were used in this work. The chemical compositions were determined with an Oxford Foundry-Master Pro optical emission spectrometer. The samples were ground with a SiC abrasive paper up to 600# grade. The AISI 8620 samples were pack carburized for 3 h at 900 °C and air cooled to increase the surface carbon content, allowing greater efficiency of TRD treatment. All steels were treated by thermo-reactive deposition at 1000 °C for 2 and 4 h in a molten salt bath composed of borax (81 wt.%), aluminum (3 wt.%) and ferrovanadium or ferroniobium (16 wt.%), followed by air cooling.

The layers were initially characterized in an optical microscope (Carl Zeiss Axiotech 100HD, Thornwood, NY, USA) to verify the formation and thickness of surface layers. X-ray diffraction analyses were performed in a X-ray unit (Rigaku Rotaflex model RU 200 B, Akishima, Japan) with normal scanning from 3 to 100 degrees, step width of Δθ = 0.2 degrees per second, Cu anode rotational with wavelength of 1.5418 Å, speed of 2 degrees per minute, and 40 kV of voltage and 60 mA of current. The datasheets provided by the XRD equipment were analyzed using the Inorganic Crystal Structure Database (ICSD) datasheets. Energy dispersion X-ray spectroscopy (EDS) analyses were carried out on a Bruker EDS system coupled on a scanning electron microscope (Phillips XL-30 FEG, Peabody, MA, USA) with operation voltage of 25 keV.

Knoop microhardness measurements (HK0.2) were carried out in perpendicular direction (10 indentations) to the layers surface to evaluate the average hardness and in the cross section (6 indentations) of the layers to evaluate the profile hardness (HK0.05). These measurements were made according to the scheme of Figure 1a, in order to evaluate the variation of hardness from the surface towards the substrate, the indentations were performed with a spacing of 5 µm between them in the region of the layer. All microhardness measurements were determined using a microhardness testing machine (Micromet 2100 Series Microhardness Testers, Buehler, Lake Bluff, IL, USA). Furthermore, in order to determine the wear resistance of produced layers, a fixed sphere microadhesive wear test “Calotest” type was used, as shown in Figure 1b.

In these tests were used tempered AISI 52100 steel spheres with 25.4 mm diameter and 60 HRC, submitted to a loading of 4 N, rotating at 400 rpm for 5, 10, 20, and 40 min, corresponding respectively to sliding distances of 160, 320, 640, and 1280 m. The volume of removed material (V) was calculated according to Equation (1), where d is the diameter of the caps measured by optical microscope and R corresponds to the radius of the sphere [13,14,20].

$$V = \frac{\pi d^4}{64R} \text{ for } d \ll R$$

The adhesion of the layers was determined by Rockwell C hardness test according to VDI standard 3198. According to this norm, there are four indentations maps, namely HF1 to HF4, which indicates great adhesion between layer and substrate. The indentations maps HF5 and HF6, which are characterized by occurrence of delamination or flakes in the failure area, are not acceptable results, indicating poor adherence [21–23].
Figure 1. Schematic representation of the (a) profile hardness in the cross section of the sample and (b) microadhesive wear of the calotest type.

3. Results

3.1. Metallography Analysis

The chemical compositions of the steels used were determined before the treatments by optical emission spectrometer and are presented in Table 2.

| Element (wt.%) | AISI 8620 | AISI 8640 | AISI 52100 |
|---------------|-----------|-----------|------------|
| C             | 0.24      | 0.45      | 0.85       |
| Mn            | 0.85      | 0.78      | 0.32       |
| Ni            | 0.43      | 0.42      | 0.03       |
| Cr            | 0.43      | 0.46      | 0.42       |
| Si            | 0.32      | 0.21      | 0.05       |
| Mo            | 0.16      | 0.15      | -          |
| P             | 0.03      | 0.02      | 0.01       |
| S             | 0.038     | 0.013     | 0.001      |
| Fe            | Balance   | Balance   | Balance    |
In Figure 2 is presented the optical micrographs of VC layers produced at 1000 °C for 2 and 4 h.

![Figure 2. Optical micrographs of vanadium carbide (VC) layers produced on AISI 8620 (a,d), 8640 (b,e) and 52100 (c,f) steels at 1000 °C for 2 h (a–c) and 4 h (d–f).](image)

In all substrates, compact carbides layers with a well-defined substrate interface were observed as indicated by the literature for this type of thermochemical treatment [1–3]. The thickness of the layers produced on AISI 8640 steel was inferior, due to its lower carbon content with relation to AISI 8620 and 52100, since AISI 8620 steel was carburized and its surface carbon content increased to approximately 0.8 wt.%. Matijević [24] explained that the absence of substantial interdiffusion is probably the reason for formation of the distinct and flat interface without transition zone, which is, in the layer/substrate interface, occurred a sharp decrease of V and carbon with increase of Fe atoms, indicating that there was not interdiffusion of V and Fe atoms.

The Figure 3 shows the optical micrographs of NbC layers formed on all steels for 2 and 4 h of treatment.

![Figure 3. Optical micrographs of niobium carbide (NbC) layers produced on AISI 8620 (a,d), 8640 (b,e) and 52100 (c,f) steels at 1000 °C for 2 h (a–c) and 4 h (d–f).](image)

As observed in VC layers, thickness of NbC layer increased with treatment time and the thinner layer was produced on the AISI 8640, due to their relative low carbon content as in the case of vanadium layers produced on the same substrate.
In all cases, a thin and flat carbide layer was formed on the substrates, which agrees with results reported by Fan et al. [25], who produced vanadium carbide layers by TRD in molten salt bath containing borax, $V_2O_5$, and Al powder. The authors explained that the formation of flat interface should be attributed to the low solubility products of vanadium carbide in austenite at treating temperature. Furthermore, at first, a thin carbide layer is formed and diffusion of CFE into substrate is suppressed, then the carbide coatings grow outwards due to reaction between CFE and carbon atoms supplied by the substrate [25]. In other words, there will be no transition zone and thus a distinct and flat interface would form due the outward growth of carbide layer [25]. Therefore, is clear that temperature is the most important parameter to control aiming the increase of the layer thickness layer, but treatment time is also a great option for this purpose. Soltani et al. [7] evaluated niobium carbide coatings produced on AISI L2 steel by TRD and observed that the thickness of coating increases according to time as a function of a parabolic law on the basis of classical kinetic theory as in the Equation (2) [7,25]:

$$X_{layer}^2 = K \cdot t$$

where, $X_{layer}$ is the thickness of layer (cm), $K$ is the parabolic growth rate constant related with the diffusion coefficient of the carbon carbide coating (cm$^2$/s). Then, the parabolic nature of the growth is due to the linear dependency of thickness on time. Assuming that, the diffusion of carbon in the carbide coating is the dominant factor affecting the coating layer thickness [7,25].

The thickness ($\mu$m) of the produced layers on all treated steels are shown in Table 3.

### Table 3. Thickness of layers produced by thermo-reactive deposition (TRD) for all treatments time.

| Treatment Time | AISI 8620 (VC) | AISI 8620 (NbC) | AISI 8640 (VC) | AISI 8640 (NbC) | AISI 52100 (VC) | AISI 52100 (NbC) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 2 h            | 8.57 $\mu$m    | 8.28 $\mu$m    | 4.29 $\mu$m    | 4.14 $\mu$m    | 8.6 $\mu$m     | 8.31 $\mu$m     |
| 4 h            | 15.30 $\mu$m   | 15.17 $\mu$m   | 8.89 $\mu$m    | 8.25 $\mu$m    | 14.86 $\mu$m   | 14.79 $\mu$m    |

It can be observed that the increase of treatment time produced thicker layers for the same temperature. It suggests that the time is also important parameter to control the layer growth. Fan et al. [25] studied formation of vanadium carbide layers on an AISI H13 steel for 1 and 6 h at 920 °C and 1000 °C. They observed that the dominant factor affecting the coating mechanism is the diffusion of carbon in the vanadium carbide, which is in agreement with the classical kinetic theory. Besides that, the growth kinetics of vanadium carbide layers on several steel substrates are significantly different from each other on at the same treating temperature, which suggests that the characteristics of substrates is other important factor to thickness layer, as well as temperature and treatment time.

Furthermore, the type of TRD process is another important factor. Considering that fact, the salt bath processes showed excellent efficiency, practically doubling the layer thickness when compared to others processes, as pack method. From this result, authors observed that the CFE content did not affect strongly the carbide layers produced. [25]

The substrates treated for 4 h showed thicker layers, therefore, those were the samples selected to proceed with the XRD, EDS, microhardness and microadhesive wear tests.

### 3.2. X-ray Diffraction and EDS Analysis

The diffractograms of the layers produced on all the substrates in the bath with ferrovanadium and ferroniobium addition are presented in Figure 4.
Figure 4. X-ray diffraction of vanadium carbide (VC) and niobium carbide (NbC) layers formed on AISI 8620, 8640, and 52100 steels treated for 4 h. Dashed lines represent the position of VC and NbC references, respectively.

From these diffractograms, it was possible to verify the formation of VC phase (Pessal and Yashima, 1968; ICSD code 619057), typical in the TRD treatments, and also the formation of V₈C₇ (De Novion et al., 1966; ICSD code 43259) and probably V₄C₃ (Ghaneya and Carlson, 1985; ICSD code 619052) compounds, as observed by Strahin et al. [16]. Such complex crystalline structures are formed due to the fact that the vanadium carbide is a non-stoichiometric transition metal carbide [24,26]. The occurrence of more than one phase is possibly due to some closely small peaks to each peak line in high diffraction angle region which is induced by the heterogeneity of C/V ratio in the layer [25]. In addition, diffraction peaks occurred at incidence angles of approximately 37°, 43°, 63°, 75°, 80°, and 95° (2θ) for the crystallography planes (111), (200), (220), (311), (222), and (400), respectively.

In the case of niobium carbides, diffractograms confirm the formation of a single phase of NbC (Rudy et al., 1963; ICSD code 108170) on all substrates and the diffraction peaks occurred at incidence angles of approximately 34°, 40°, 58°, 69°, 73°, 87°, and 97° (2θ) for the crystallography planes (111), (200), (220), (311), (222), (400), and (331), respectively. For both VC and NbC, these results are also similar to those found in the literature for this type of treatment and CFE used [27–30].

The EDS analysis was used to verify the vanadium and niobium distribution from the specimen surface as showed in Figure 5. It can be observed that the vanadium and niobium contents are high at the surface and decrease in abrupt form when the substrate is reached. Furthermore, the results indicate no chemical contamination from the molten bath, for this purpose was applied a high beam energy (25 keV) to determine any contamination of other heavy metals that could form other carbides.
3.3. Microhardness and Wear Tests

Average hardness measurements of vanadium and niobium carbide layers produced on all substrates for 4 h of treatment were performed. It is important to note that the average hardness and wear resistance of the substrates were evaluated in the samples after the layers were removed. The reason for this is that the same treatment conditions must be preserved for the coated and uncoated substrate, respectively, for comparison purposes. Hardness values achieved approximately 2448 ± 60 HK0.2 for materials coated with vanadium carbide, which is 7 times higher than the average hardness of the substrates (350 ± 5 HK0.2). In the case of niobium carbides layers, the hardness values reached 2394 ± 34 and 360 ± 8 HK0.2, respectively to material coated and uncoated, that is 6.6 times high than the average of the substrates. These results are in accordance with the ones presented by others authors, in which the layers achieved average hardness in the range of 2175–22,270 HK and 2180–2512 HK, respectively to vanadium and niobium carbide layers [27–29].

The hardness profiles of the VC and NbC layers are shown in Figure 6.

In all TRD treatments was possible to observe three similar behaviors: (I) measurements of microhardness are approximately equal in the layer; (II) the microhardness decreases into interface and (III) there is an abrupt drop in the region near the layer-substrate interface, due to the reduction in C content by diffusion of this element from the substrate towards the surface.
Figure 6. Microhardness profiles of (a) vanadium carbide (VC) and (b) niobium carbide (NbC) layers produced for 4 h. The vertical lines represent the approximate thickness of the coatings on AISI 8620 (dash line), 8640 (dot line), and 52100 (dash-dot line).

The microadhesive wear test results are shown in Figure 7 for VC and NbC layers produced.

Figure 7. Microadhesive wear for (a) vanadium carbide (VC) and (b) niobium carbide (NbC) layers produced for 4 h.

An increase up to 15 times in the microadhesive wear resistance of all VC layers in relation to the substrates was observed. The volume of removed material of VC layers in all substrates was approximately the same, indicating the coating high wear resistance independently of the substrate. The NbC layers presented wear performance up to 15 times higher than the substrates. The regions
inside the caps formed in wear test on the VC and NbC layers, and their respectively substrates for a sliding distance of 1280 m are presented in Figure 8.

![Image showing wear regions inside the caps produced on vanadium carbide (VC) layers and uncoated substrates for AISI 8620, 8640, and 52100 treated for 4 h.](image)

**Figure 8.** Optical micrographs of wear regions inside the caps produced on vanadium carbide (VC) (a–c) layers and uncoated substrates (d) AISI 8620, (e) 8640, and (f) 52100 treated for 4 h.

The wear mechanism in each sample could be determined. Thus, three-body abrasive wear in the caps of Figure 8a,b and an adhesive wear region, with larger regions of layer transfer in Figure 8b were detected. Besides, Figure 8c showed two-body abrasive wear and small spots of adhesive wear. Images of the caps formed on uncoated substrates are presented in Figure 8c–e for comparison purposes. In the case of samples coated with niobium carbide and their respectively uncoated substrates, caps are showed in Figure 9. The cap Figure 9a, the mechanisms observed were two-body abrasive wear and also adhesive wear with transfer and detachment of material during the relative sliding between the carbide layers and the sphere [32]. The two-body abrasive mechanism also occurred in sample Figure 9b,c showed regions of grooves.

![Image showing wear regions inside the caps produced on niobium carbide (NbC) layers and uncoated substrates for AISI 8620, 8640, and 52100 treated for 4 h.](image)

**Figure 9.** Optical micrographs of wear regions inside the caps produced on niobium carbide (NbC) (a–c) layers and uncoated substrates (d) AISI 8620, (e) 8640, and (f) 52100 treated for 4 h.

3.4. VDI 3198 Standard Adhesion Test

The layers adhesion in the substrates was evaluated according VDI 3198 standard and the results are presented in Figure 10.
All the layers presented excellent adhesion on the respective substrates, without occurrence of large areas of delamination, characterizing acceptable failure patterns according to the VDI standard. Furthermore, regions of indentations are in accordance to the four indentation maps (HF1–HF4), indicating great adhesion between layer and substrate. In this case, no delamination or flakes failures areas at the perimeter of indentations craters were observed [21].

4. Conclusions

Uniform vanadium and niobium carbides layers were obtained with high hardness and good adhesion to the respective substrates.

For all treatment conditions, increases in the carbide coating thickness occurred with the increase of treatment time. All layers presented superior microadhesive wear resistance than the respective substrates, indicating its great effectiveness.

The formation of carbides layers by TRD is an excellent alternative for protection of engineering components applied in aggressive wear situations. Besides that, it is a low-cost method, with good reproducibility and easy application. This, combined with lubricants, can drastically increase the performance of engineering components.

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