CoMoCrSi coatings prepared by high-velocity oxygen fuel spraying: microstructure and mechanical properties at elevated temperatures up to 800 °C

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Abstract
The microstructures, mechanical properties, and tribological behaviors from room temperature (RT) to 800 °C of HOVF-sprayed CoMoCrSi coatings were investigated in detail. The as-sprayed CoMoCrSi coatings were found to be predominantly composed of intermetallic Laves phases, i.e., Co7Mo6, Co3Mo2Si, Cr3Si, and some amorphous phases. The as-sprayed coatings possessed a compact and typical lamellar microstructure and balanced mechanical property; their Vickers hardness decreased from 855.9 ± 16 HV5.0 at RT to 583.9 ± 10 HV5.0 at 800 °C due to a normal soft phenomenon of material in hot environment. Further, between room temperature and 400 °C, the as-sprayed coatings suffered serious mechanical wear without any lubricant tribolayer forming on the worn surface, indicating that they would not function as good anti-wear materials at low temperatures. In particular, the coatings exhibited a brittle fracture coupled with abrasive wear at RT, obvious abrasive wear at 200 °C, and severe adhesive wear at 400 °C that with the highest friction coefficient of 0.65 and wear rate of 35.79 × 10⁻⁶ mm³/(N·m). As the test temperature increased to 600 and 800 °C, the friction coefficient of the coating decreased to 0.45 and 0.26, respectively, and the corresponding wear rates reached 0.135 × 10⁻⁶ mm³/(N·m) and 0.288 × 10⁻⁶ mm³/(N·m), with a difference of approximately two orders of magnitude between the low- and high-temperature wear rate. This result further confirmed that the as-sprayed coatings are a better choice of abrasion-resistant materials for high-temperature applications. After sliding tests at 800 °C, numerous metallic oxides i.e., Co3O4, MoO3, and bimetallic oxides such as CoMoO4 and Co2CrO4 of nanometer size (50–100 nm) were identified in the continuous protective layer formed on the worn surface. These oxides played an important role of lubrication and reduced direct contact between the coating and its counterpart during the sliding process, leading to a decrease in the friction coefficient and material loss. The main wear mechanisms of the coatings at this temperature range are slight adhesive wear coupled with abrasive wear.

1. Introduction
As one of the members of the Tribaloy family of alloys, CoMoCrSi has excellent strength, hardness, as well as superior anti-wear and anti-corrosion resistance between room temperature (RT) and 800 °C. It is therefore suitable for industrial applications, such as in aerospace, turbine, oil, pump, energy, and mining sectors [1–3].
And that is mainly because the alloy contains a large volume fraction of a hard, intermetallic Laves phase in a much softer Co-based alloy matrix [4]. In particular, the main alloying elements of the Co-based Tribaloy alloys are molybdenum, chromium, and silicon, among which silicon is a minor (~3 wt%) constituent [5]. Moreover, the Laves intermetallic phase is composed of Co, Mo, and Si with an approximate composition of Co3Mo2Si or CoMoSi, in which Mo and Si could improve the strength and wear properties of the Co-based matrix up to temperatures as high as 1230 °C. Cr could contribute to high corrosion resistance without the degeneration of the anti-wear resistance [3, 6].

Over the last few decades, various thermal spraying technologies, such as atmospheric plasma spraying (APS) [7], cold spraying [8–10], arc spraying [11], high-velocity oxygen fuel (HVOF) spraying [12, 13], and high-velocity air spraying (HVAF) [14, 15], have been developed and widely applied in the preparation of coatings. Furthermore, several studies with respect to the as-sprayed CoMoCrSi coating have attracted extensive attention of the researchers worldwide. Wang et al. [1] studied the cavitation erosion of APS-sprayed CoMoCrSi coatings before and after heat treatment at 800 and 1000 °C; the results indicated that heat treatment can significantly reduce the mean erosion depth of the coatings and the cavitation damage mainly involves the removal of splashes and delamination. Cai et al. [2] prepared HVOF-sprayed CoMoCrSi coatings using different spraying parameters, and reported that the properties of the coatings possessed good adaptability to the spraying parameters, and the main wear mechanisms changed from abrasive wear and delamination at RT to adhesive wear at elevated temperatures, up to 400 °C. Lusvarghi et al. [16, 17] examined the dry sliding performance of heat-treated CoMoCrSi coatings only at room temperature; they reported that heat treatment at 600 °C caused the appearance of submicrometric crystalline regions and improved the hardness as well as the elastic modulus of the coating, and that the friction coefficient and wear rate were definitely reduced. D’Oliveira aimed to understand the oxidation of CoCrMoSi coatings at 450 and 750 °C, and clarified the role of the oxide layer on the wear behavior of the coating at room temperature [18]. Further, Renz et al. assessed the high-temperature sliding wear behavior of Tribaloy® T400 block (chemical composition in wt%: 28.5 Mo, 8.5 Cr, 2.6 Si, and Co balanced), but carried out abrasive wear tests only at 40, 400, and 600 °C [19]. However, actual industrial processes and applications involve many wear modes such as ball on disc, pin on disc, ring on block, normal temperature, high temperature, reciprocating type, and rotation type. According to the available reports, a systematic investigation of the mechanical property, tribological performance and wear mechanism of as-sprayed CoMoCrSi coatings at various temperatures has rarely been performed to date. Therefore, it is essential to assess the mechanical properties and wear behaviors of as-sprayed CoMoCrSi coatings from room temperature to 800 °C.

The aim of the present investigation was to fabricate the CoMoCrSi coating on stainless steel 316 L alloys by the HVOF technique, and systematically investigate the microstructure, mechanical properties, as well as the tribological performance in the ball-on-disc mode at different temperatures (RT, 200, 400, 600, and 800 °C). Moreover, the wear mechanisms of the as-sprayed CoMoCrSi coatings at different temperatures were investigated and analyzed comprehensively to provide guiding principles for the application of CoMoCrSi coatings in sliding wear environment over a wide temperature range.

2. Material and methods

2.1. Preparation of the coatings

A feedstock powder (Metco Diamalloy 3001) with a nominal chemical composition of 28.5 wt% Mo, 17.5 wt% Cr, 3.4 wt% Si, and 50.6 wt% Co, hereafter referred to as a CoMoCrSi alloy, was obtained from Sulzer Metco. A scanning electron microscopy (SEM) image showing the surface morphology of the CoMoCrSi powder is presented in figure 1(a), where it is apparent that the powder particles are spherical with sizes ranging from 5 to 45 μm. The cross-sectional SEM image of the CoMoCrSi powder particle (figure 1(b)) confirms that the particles have a compact internal texture and the elements are uniformly distributed in the particle. Moreover, energy-dispersive x-ray spectroscopic (EDS) investigation (figure 1(c)) basically agrees with the nominal chemical composition of the CoMoCrSi powder. The CoMoCrSi coatings were fabricated by a Diamond Jet 2700 HVOF spraying equipment (Sulzer Metco, USA) manipulated with an IRB 2400/16 robot (ABB, Switzerland). Specifically, natural gas was used as the fuel, oxygen as the combustion improver, and nitrogen as the carrier gas for the powder feed, and the detailed spraying parameters are shown in table 1. Stainless steel 316 L alloy was used as the substrate. To improve adhesion between the coating and substrate, the substrates were first sandblasted, and then ultrasonically cleaned in a mixture of alcohol and acetone for 20 min.

2.2. Characterization of the coatings

A scanning electron microscope (TESCAN MIRA3, Czech Republic) equipped with an energy-dispersive x-ray spectrometer was employed to characterize the microstructures and worn surface morphologies of the as-sprayed coatings. The porosity of the as-sprayed coating was measured using an image analysis software.
in accordance with the ASTM E2109-01 (2014) standard for determining the area percentage porosity of thermally sprayed coatings. The porosity of the coating reported herein is the average value of five measurements carried out on randomly acquired images of the cross-section of the as-sprayed coating after 2000× magnification. X-ray diffraction (Rigaku D/max-RB, Japan, λ = 0.15 nm) was performed to determine the phase composition of the coatings before and after the wear tests; XRD was carried out in the angular range of 10−100° using Cu Kα radiation at a voltage of 40 kV and scan speed of 10° min⁻¹. The XRD patterns were analyzed using the Jade 6.5 software based on the standard ICSD pattern (51/54529) data files.

An MH-5-VM microhardness tester was employed to measure the cross-sectional harness and surface microhardness of as-sprayed coatings, with a load of 300 g and dwelling time of 10 s. Vickers hardness of as-sprayed coating was assessed using a high-temperature Vickers hardness tester (Archimedes, HTV-PHS30, UK) at room temperature (RT), 200, 400, 600, and 800 °C respectively. The tester was performed at a load of 5000 g and dwelling time of 5 s in low-vacuum oxygen-free environment. The specimens for the Vickers hardness were fixed at period of 5 min at each test temperature before indentation. Ten indents were implemented on every specimen, and the average of ten measured values is reported as the final result for both tests. In addition, the test parameters are different between the microhardness and Vickers hardness owing to the blurred and irregular indentation profiles under small applied load at high temperatures during the Vickers hardness test. Furthermore, the nano-mechanical properties of the oxide layer was assessed using a NHT02-05987 nano-indentation tester (CSM, Switzerland, specific test parameters: normal load = 10 mN, loading rate = 20 mN min⁻¹, dwelling time = 10 s).

The friction and wear behaviors of the as-sprayed coatings were evaluated using a ball-on-disc tribometer (CSM, Switzerland) at room temperature (RT), 200, 400, 600, and 800 °C in ambient atmosphere with a relative
humidity of 30 ± 5%. The tests were performed thrice to reduce the error and after maintaining for a fixed period of 20 min at different temperatures before the sliding friction. Moreover, before the tests, all specimens (with a size of ø 25 mm × 7 mm) were polished to reduce the surface roughness, then cleaned ultrasonically with acetone for 10 min, and dried with nitrogen. All tests were conducted with a normal load of 5 N, line velocity of 10 cm s⁻¹, rotating radius of 5 mm, and sliding distance of 200 m. Al₂O₃ ceramic balls (2400 HV, Ra ≤0.1 μm) with a diameter of 6 mm and density of 3.92 g cm⁻³ were used as the counterparts. The volume loss of the coating after the wear test was determined using a Micro-XAM-3D non-contact surface profiler (ADE Corporation, Massachusetts, USA). The wear rate (Kₐ, mm³/N·m) was calculated using the equation, 

\[ K_a = \frac{V_w}{P \times L} \]

as reported previously [20], where \( V_w \) is the wear volume loss in mm³, \( P \) is the normal load applied in newton (N), and \( L \) is the sliding distance in meter (m). The reported wear rates are the average values of five measurements. The phase composition of the worn surface after the tests was determined by the analysis of Raman spectra (Horiba Raman microscope, 532 nm He–Ne laser) recorded in the range of 100 to 1800 cm⁻¹.

3. Results and discussion

3.1. Microstructures of the coatings

The XRD patterns of the CoMoCrSi alloy powder and as-sprayed coatings are shown in figure 2. As indicated, the as-received CoMoCrSi powder registers a crystalline structure and consists mainly of a high fraction of hard intermetallic Laves phases, such as Co₃Mo₂Si (PDF#30-0449), Co (PDF#05-0727), CrSi₂ (PDF#35-0781), and Co–Mo intermetallic Co₂Mo₆ (PDF#29-0489) [1, 21]. However, the XRD pattern of the as-sprayed coating displays only two diffraction peaks at 43.6° and 78.8°, which was identified as a solid solution of Co and Cr and could be assigned to the Co₂Mo₆ (PDF#29-0489) and some intermetallic Laves phases such as Co₃Mo₂Si (PDF#15-0491), and CrSi₂ (PDF#35-0781) [22, 23]. As already revealed by other groups [20, 24], peaks of numerous phases disappear in the XRD pattern of the coating presumably because they were entirely dissolved in the melt matrix and their reprecipitation was hindered by impact quenching. The widened diffraction peaks at 43.6° and 78.8° indicate the presence of amorphous phases in the as-sprayed coatings. As a kind of precipitation-strengthening alloy, a thermally sprayed coating usually has amorphous (metallic glass) structures, which is also consistent with the nature of other CoMoCrSi coatings deposited by HVOF-technique [2, 16, 17]. As reported elsewhere [11], the melting and rapid solidification of the material during the spraying process result in the formation of the coating, and the transformation of phases and crystallization were undoubtedly hindered to some degree. The presence of amorphous phases in the coatings can be ascribed to the extremely high cooling rates experienced by the melted particles when they impact the relatively cold substrate at a specific velocity, which is conducive for the formation of amorphous phases. Furthermore, some intermetallic Laves phases in the form of the amorphous microstructure (metallic glass state) existing in the as-sprayed coatings could enhance the corrosion resistance, wear resistance, and high-temperature strength [21].

Figure 3 shows the top-surface and cross-sectional SEM images of the as-sprayed CoMoCrSi coating. It can be apparently seen that the as-sprayed coating exhibits a relatively rough surface. Pores, molten area, and half-molten particles are found on the top surface, as pointed by the arrows in figure 3(b). It can be concluded that the rapid impact of the molten and half-molten particles with a high velocity on the substrate surface at the end of
the spraying process could account for the relatively rough surface. Moreover, pores might have formed owing to the lack of follow-up particles striking the as-surface. However, the cross-sectional images display a compact structure for the as-sprayed coating with a thickness of 350 μm, as shown in figure 3(c). It is obvious that the as-sprayed coating has a typical lamellar structure with very few tiny pores (as pointed by arrows in figure 3(d)) randomly distributed throughout the coating; moreover, no significant cracks are observed within the coating or in the area at the interface with the substrate. The absence of unmelted particles within the as-sprayed coating can also be confirmed, indicating that the as-received CoMoCrSi powders have been fully melted and well deposited on the substrate. The as-sprayed coating registers a low porosity value of 0.53 ± 0.1%, as determined by the porosity analysis of the cross-sectional SEM images with a magnification of 2000×, which is similar to that of HVOF-sprayed Stellite-6 coatings with a porosity of 0.6%–4.9% [24] and the plasma-sprayed CoMoCrSi coatings with a porosity of 0.42 ± 0.1% [1], as well as the HVOF-sprayed CoMoCrSi coatings prepared under different spraying parameters [2].

3.2. Mechanical property of the coatings

Figure 4 displays the variation in the microhardness starting from the substrate to the as-sprayed coating. It should be noted that the indentations were carried out on the selected homogenous areas to exclude the influence of the microstructural defects. The microhardness of the as-sprayed coating is obviously much higher than that of the substrate. Particularly, the substrate exhibits microhardness of 241 HV0.3, while the coating registers an average cross-sectional microhardness of 890.6 ± 19 HV0.3 and surface microhardness of 902.8 ± 32 HV0.3 (as shown in the inset in figure 4); the values are the averages of the microhardness values of ten different spots. Thus, there is approximately a four-fold difference between the microhardness of the as-sprayed coating and substrate. Moreover, the hardness of the surface and cross-section of the coating is not significantly different, which indicates that the as-sprayed coatings exhibit a balanced mechanical property. In addition, the microhardness of the as-sprayed coating is also higher than those of the HVOF-sprayed CoCrW coatings (635 ± 75 HV0.3) [25] and the HVOF-sprayed CoMoCrSi coatings obtained with different spraying parameters (550–650 HV0.3) [2].

The uniform compact structure (figure 3) combined with certain amount of amorphous phases present in the as-sprayed coating can account for its higher hardness; in particular, no slip planes are available for easy dislocation movement under the cut-in load because of the lack of an ordered crystalline structure, which definitely hinders the plastic deformation, leading to higher hardness [17]. As shown in figure 5, the Vickers hardness values of the as-sprayed coatings obviously decrease with an increase in the temperature. In particular, the Vickers hardness values drop from 855.9 ± 16 HV5.0 at RT to 656.2 ± 22 HV5.0 at 400 °C (drops by 23.3%) and to 583.9 ± 10 HV5.0 at 800 °C. Further, the drop in hardness is quite small at the temperatures above
400 °C. The results coincide well with those of previous available studies [19], where the hot hardness of Triboloy™ T400 materials (with a similar chemical composition as that of Diamalloy 3001) drops from 724 ± 22 HV at 40 °C to 449 ± 6 HV at 400 °C and 294 ± 4 HV at 600 °C, in which the hot hardness corresponding to macro hardness are given in estimated equivalent Vickers hardness. It can also be inferred that the hot hardness of the as-sprayed coatings is not influenced by the thermal hardening or oxide formation, which is a normal softening phenomenon of materials in hot environment, because the indentations are made in a short time and in low vacuum condition with argon. In addition, the minimal difference between the microhardness (902.8 ± 32 HV0.3) and the Vickers hardness (855.9 ± 16 HV5.0) at RT can be ascribed to the error associated with the measurement instrument and normal applied load, which can therefore be ignored.

3.3. Tribological behaviors of the coatings

3.3.1. Tribological properties of the coatings

Figure 6 demonstrates the steady-state friction coefficient and wear rate of the CoMoCrSi coating at different test temperatures. The values were recorded over the entire duration of the test and those were averaged from three individual tests. As indicated, the coating exhibits the highest friction coefficient of 0.65 at 400 °C and the lowest friction coefficient of 0.26 at 800 °C. In particular, the friction coefficient of the as-sprayed coating decreases slightly from 0.57 at RT to 0.52 at 200 °C, then increases to 0.65 at 400 °C, showing the same variation trend as the T-400C alloy in the temperature range of RT to 450 °C [4]; the T-400C alloy (14 wt% Cr, 26 wt% Mo, 2.6 wt% Si, Co balanced) was developed with increased Cr content based on the conventional T-400 alloy and still belongs to the Co-Mo-Cr-Si Tribaloy family. Then, the friction coefficient decreases to 0.45 at 600 °C and...
0.26 at 800 °C, which is superior to that of the HVOF-sprayed Stellite-6 coating with a friction coefficient of 0.43 at 800 °C [24]. Compared with the steady-state friction coefficients, the real-time friction coefficient curves as a function of the friction distance show a random variation, which is more intuitive for describing the friction process at different test temperatures. Therefore, the real-time friction coefficient curves recorded at different test temperatures are used to analyze the sliding process (figure 7). There are indeed obvious variations in the friction characteristic at different test temperatures. As indicated, the friction coefficient curves in the temperature range of RT–400 °C fluctuate more markedly compared to those of 600 °C and 800 °C. At high temperatures (600 and 800 °C), the coatings show the same flat curves after a short running-in period and maintain a relatively stable state over a distance of more than 180 m. It can be concluded that lower the friction coefficient is, the smoother and steadier the friction state is. This directly indicates that the as-sprayed coatings register satisfactory friction properties at high temperatures. Consequently, it could also be inferred that some additional effective high-temperature lubricants were generated in the wear track during the high-temperature sliding process. The related features are discussed in detail in the following section.

In addition to the friction coefficient, wear rate is another important indicator of the tribological performance of a material. As shown in figure 6, the wear rate of the as-sprayed coating increases from $12.51 \times 10^{-6}$ mm$^3$ N·m at RT to $24.77 \times 10^{-6}$ mm$^3$/(N·m) at 200 °C and $35.79 \times 10^{-6}$ mm$^3$/(N·m) at 400 °C. However, the wear of the coating is greatly alleviated as the temperature is increased to 600 and 800 °C, and then wear rate is reduced to $0.135–0.288 \times 10^{-6}$ mm$^3$/(N·m) at these temperatures. A difference of about two orders of magnitude is observed between the values at 400 and 600 °C. Overall, the largest wear rate and the highest friction coefficient at 400 °C suggests that the as-sprayed coatings display poor tribological performance.
at this temperature, in agreement with a previous report [19]. The wear track depth profiles of the coatings are shown in figure 8, which demonstrate a similar tendency of variation as the wear rate. The maximum width and depth of the wear tracks increase with an increase in the temperature from RT to 400 °C; however, the depth profiles change from sunken to convex ones at higher temperatures (as pointed by arrows in figure 8), suggesting different wear mechanisms at different test temperatures. Figure 9 exhibits the three-dimensional profile of the wear tracks corresponding to the test temperatures, which can intuitively reflect the wear conditions of the as-sprayed coating at different test temperatures. As the test temperature is increased from RT to 400 °C, the wear tracks are found to be deeper and wider, and the average wear volume of the coating changes from $29.7 \times 10^6 \, \mu m^3$ at RT to $82.7 \times 10^6 \, \mu m^3$ at 400 °C. When the test temperature is increased further to 600 and 800 °C, the wear tracks are found to be shallow and distinctly narrow. The average wear volume decreased to $1.4–6.0 \times 10^6 \, \mu m^3$ in this temperature range, and the wear of the as-sprayed coating was greatly alleviated, implying that the as-sprayed coating exhibits better sliding wear resistance at higher temperatures compared to that in the lower temperature range. Moreover, the wear tracks at higher temperatures display obvious accumulation of the wear debris, as evidenced by numerous protrusions that emerge on the edge of the wear track, as pointed by arrows in figures 9(e), (f).

3.3.2. Wear mechanism of the coatings
In order to explain the wear mechanism of the as-sprayed coatings in a wide temperature range, the coatings after friction tests at different temperatures were characterized by means of SEM, EDS, XRD, and Raman analysis. As indicated in figure 10, the coatings tested at different temperatures exhibit various worn surface morphologies, implying the operation of various wear mechanisms. Moreover, the widths of the wear tracks at low temperatures are higher than those at high temperatures, which can well verify the results in figure 8. For the coating tested at RT, the wear track registers a very rough surface, and numerous spallations (as pointed by arrows in figure 10(a)) can be observed on the worn surface, indicating that many parts of the coating material were pulled off from the contact area during the sliding process. In the regional magnified image (figure 10(b)), the worn surface displays a brittle fracture, and many nanometer-sized fine particles are distributed in this area (as shown in the inset in figure 10(b)). As reported in previous studies [16], many hard Laves phases with brittle feature exist in the CoMoCrSi alloy, which suffer brittle fracture under alternating applied load during the sliding process, thereby causing fatigue failure. This is more so for the as-sprayed coating with higher hardness owing to the existence of amorphous phases. In fact, the process of fatigue crack propagation involves the augmentation of many crack propagations under constant dynamic loading. In particular, numerous tiny cracks and pores existing within the coating will grow and join with each other under alternating applied load, and then grow toward the contact surface, resulting in final spallation failure [26]. Moreover, the fragments will be subjected to the repeating crush during the sliding process, which results in many fine nanometer-sized particles (as shown in the inset in figure 10(b)). According to the EDS results, these fine particles are enriched in chromium, molybdenum, cobalt and oxygen (as shown in spectrum 1 in figure 11); on the contrary, the smooth area lacks oxygen (as shown in spectrum 2 in figure 11). In general, small particles are oxidized more easily, which may be responsible for this phenomenon. These results suggest that the coating tested at RT exhibits a brittle fracture coupled with abrasive wear mechanism, that is, mechanical wear.
At 200 °C, the wear track presents a smooth and flat surface (figure 10(c)), as well as numerous obvious grooves (as pointed by arrows in figure 10(d)), suggesting an abrasive wear mechanism. Numerous tiny spallations can also be seen in the wear track (as pointed by arrows in figure 10(d)); the ploughing of the detached hard phases in the wear track during the sliding process could account for the formation of grooves. These spallation areas mainly consist of cobalt, chromium, molybdenum, and oxides on the basis of EDS results (as shown in spectrum 4 in figure 11). Similar to the wear track at RT, the smooth and flat area is enriched in cobalt, chromium, and molybdenum, and lack of oxygen (as shown in spectrum 3 in figure 11).

When the temperature is increased to 400 °C, the worn surface exhibits a relatively flat morphology with some dark spots (figure 10(e)). When a dark area (figure 10(f)) is magnified, in particular, numerous fish-scale patterns (as pointed by arrows in figure 10(f)) appear on the worn surface, which is a sign of adhesion wear. As shown in figure 5, the Vickers hardness values dropped by 23.3% from 855.9 ± 16 HV5.0 at RT to 656.2 ± 22 HV5.0 at 400 °C, which implying the soften of the coating. It is inferred therefore that the coating has been severely abraded during the sliding process, which can be responsible for the increased friction coefficient and wear rate (figure 6). Similar to the aforementioned EDS results of the coating tested at RT and 200 °C, the metallic elements are abundance in the smooth gray areas (as shown in spectrum 5 in figure 11) and the rough dark areas mainly consist of oxides (as shown in spectrum 6 in figure 11). Further, the high oxidation stability of the Laves phase can account for the much smaller oxidation area on the worn surface (as pointed by arrows in figure 10(e)). It is also worth noting that the fish-scale-patterned area is enriched in chromium and oxygen, and the other smooth portion in the analyzed area is enriched in cobalt, molybdenum, and silicon, according to the elemental maps acquired in the part of figure 10(f) (figure 12), although no obvious differences are noticed between the results of spectrum 5 and spectrum 6. That is, the portions rich in cobalt, molybdenum and silicon exhibit superior anti-wear resistance during the sliding process, which is well consistent with the reports that the
Figure 10. SEM images of the wear tracks on the CoMoCrSi coating after tribological tests: RT (a) (b), 200 °C (c) (d), 400 °C (e) (f), 600 °C (h) (i), 800 °C (j) (k).
hard Laves phase rich in molybdenum and silicon could improve the strength and wear properties of the Co-based matrix [21, 25].

In addition, the coatings after friction tests were characterized by XRD to identify the newly formed phases. Comparison of the XRD patterns of the coatings tested at room temperature, 200, and 400 °C (figure 13(a)) with that of as-sprayed coating (figure 2) indicates that no new phase is generated after the friction tests at these temperatures, and the coatings still consist mainly of a solid solution based on Co and Cr, and some amorphous phases. However, the Raman analyses conducted on the different areas in the wear track indicate the generation of some oxides. Particularly, no characteristic peaks can be observed in the spectra corresponding to the light areas in the optical micrographs (spot 1, spot 2, and spot 3 on the worn surface of the coatings tested at RT, 200, and 400 °C respectively, as shown in figure 14, implying that no oxidation occurred in these areas and they mainly consist of intermetallic compounds. On the contrary, some new phases can be identified as Co$_3$O$_4$ (Raman peaks located at 194, 488, 522, 618, and 691 cm$^{-1}$) [27, 28] and MoO$_3$ (typical peaks signal at 115, 144, 189, 238, 337, 658, 818, and 995 cm$^{-1}$) [29–31] by the Raman analyses in the black areas (as shown in figure 14 (RT, 200 °C, and 400 °C)), and the results coincides well with the EDS results (figure 11). It should be noted that the area of the wear track characterized by the micro-Raman analysis is much smaller than that characterized by the XRD analysis, and the quantity of the new oxides is very low; thus, these oxides can only be detected by Raman analysis. As reported by Alexander Renz [19], adherent and stable oxides formed on the Tribaloy®T400 (with a similar chemical composition to that of Diamalloy 3001) above 540 °C. We speculate that these thermodynamically stable Co and Mo oxides, i.e., Co$_3$O$_4$ and MoO$_3$ may be generated at the flash temperature.
during the sliding process. Despite having a layer-type structure and good lubrication characteristic \(^{[32]}\), these non-uniform and low adherent Co\(_3\)O\(_4\) and MoO\(_3\) oxides can easily be ground off when the coating makes contact with the counterpart, and they can form fragments that act as third bodies and aggravate the abrasion. As a whole, the amount of the new phases generated after the friction tests at RT, 200 and 400 °C is too little, and moreover, no complete and continuous tribolayer formed on the worn surface, which can account for the high friction coefficient and wear rate at these temperatures. Moreover, the Vickers hardness of as-sprayed CoMoCrSi coating decreased significantly from RT to 400 °C. It can also be inferred that the as-sprayed coatings would be more and more easily ground off during the sliding process with the temperatures increasing to 400 °C, resulting in increased wear rate. Consequently, the wear mechanisms of the as-sprayed CoMoCrSi coatings change from a brittle fracture coupled with abrasive wear at room temperature to severe abrasion along with adhesive wear due to the softening of the coating at 400 °C, indicating a more severe mechanical wear of the coating. It can be concluded that the as-sprayed coatings do not have suitable anti-wear properties at low temperatures.

At 600 °C, the worn surface of the coating is relatively smooth and flat, and a layer of a continuous film of various oxides can be apparently seen in the wear track (figures 10(h), (i)). In addition, only a few tiny cracks and slightly abraded patterns (as pointed by arrows in figure 10(i)) can be observed on the worn surface, implying that the wear of the coating is greatly alleviated and the coating exhibits a slightly adhesive wear mechanism. As the friction tests are performed at elevated temperatures under ambient atmosphere, the coatings are subjected to severe oxidation and a number of new peaks appear in the XRD pattern of the coating tested at 600 °C (figure 13(b)). However, the widened diffraction peaks at 43.6° and 78.8° indicate that the coating still contained mainly of CoCr solid solution and some amorphous phases. Furthermore, the intensity of the new peaks is low, suggesting the quantity of these phases is small. In particular, these new peaks could be identified as the Co\(_3\)O\(_4\) (PDF\#42-1467), CoMoO\(_4\) (PDF\#21-0868), Co\(_2\)SiO\(_4\) (PDF\#29-0508), and Co\(_2\)CrO\(_4\) (PDF\#24-0326). In addition, the Raman analysis of the coating tested at 600 °C effectively confirms the above conclusion. According to the Raman results of different spots on the worn surface (figure 14 (600 °C)), numerous new peaks can be attributed to CoMoO\(_4\) (367, 816, 876, and 937 cm\(^{-1}\)) \(^{[33, 34]}\), Co\(_2\)SiO\(_4\) (1352 and 1594 cm\(^{-1}\)), \(^{[35, 36]}\) and Co\(_2\)CrO\(_4\) (550 and 680 cm\(^{-1}\)), apart from the peaks of Co\(_3\)O\(_4\) and MoO\(_3\), mentioned above. As reported in previous study \(^{[18]}\), the metallurgical stability of CoMoCrSi coatings at high temperatures is related to the oxidation stability of the Laves phase, and their oxidation products could play an important role in determining their wear characteristics. Moreover, primary elements were uniformly distributed in the oxide layer, according to the result presented in figure 15 (acquired from the portion of figure 10(i)). In addition, the characteristic
peaks in the Raman spectra acquired from different spots on the worn surface further well verify the intact stability of the oxide layer. Furthermore, the nano-mechanical properties of the oxide layer are presented in figure 16. The ratio of hardness and elastic modulus ($H/E$) is consistent with the wear conditions, that a large $H/E$ ratio value corresponds to high anti-wear resistance [37]. The worn surface at 600 °C exhibits higher $H/E$ ratio compared to that of the as-sprayed coating and the worn surface at 800 °C. The oxides form a distinct oxide layer (figure 10(i)) with high anti-wear resistance and adhesion in the contact area, is not easily broken into fragments during the sliding process. They act as a protective barrier for CoMoCrSi coatings and reduce direct contact
between the coating and its counterpart during the sliding process, resulting in lower friction coefficient and material loss.

The SEM image of the wear track of the coating tested at 800 °C (figure 10(h)) shows a much narrower (with the width of ~120 μm) and smoother wear track, indicating a slight abrasive wear mechanism. Surprisingly, as shown in figure 10(k), numerous polygonal particles, 3–5 μm in size, emerge on the worn surface, demonstrating the crystallization of the materials. Moreover, these polygonal particles are enriched in molybdenum, cobalt, and oxygen (as shown in spectrum 7 in figure 11), which is consider as CoMoO₄ (PDF #21-0868). The gray areas are enriched in chromium, cobalt, and oxygen (as shown in spectrum 8 in figure 11), which is identified as Co₂CrO₄ (PDF #24-0326). The XRD analysis show numerous new diffraction peaks appear in the XRD pattern of the coating (especially in the range of 10°–45°) after the friction test at 800 °C (figure 13(c)). Moreover, some MoO₃ (PDF #21-0569) could be detected apart from the oxide phases identified in the coating tested at 600 °C, indicating that the coating began to crystallize at this temperature, which is consist with the result that a marked exothermal peak appeared at 812 °C due to oxidation of the alloy [17]. In addition, these phases can also be detected by Raman analysis, and the characteristic peaks acquired from different spots on the surface show satisfactory repeatability, as shown in figure 14-800 °C. In particular, the peaks can be as attributed to Co₃O₄ (194, 488, 522, and 618 cm⁻¹) [27, 28], MoO₃ (115, 144, 189, and 238 cm⁻¹) [29–31], CoMoO₄ (345, 367, 816, 876, and 937 cm⁻¹) [33, 34], and Co₂CrO₄ (550 and 680 cm⁻¹) [38].

Figure 14. Raman spectra of the worn surfaces of the CoMoCrSi coating after the tribological tests at different temperatures.
Figure 15. Elemental maps acquired from the top-left portion of figure 10(i).

Figure 16. Nano-mechanical properties of the as-sprayed coating and the worn surface tested at 600 and 800 °C.
Consequently, the polygonal particles and the gray areas on the worn surface are considered to be CoMoO$_4$ and Co$_2$CrO$_4$, respectively. It is worth noting that these bimetallic oxides, i.e., CoMoO$_4$, Co$_2$CrO$_4$, and Co$_2$SiO$_4$ belong to the members of the olivine mineral family; they have an orthorhombic structure and consist of a hexagonally closed-packed oxygen array in which half of the octahedral sites are occupied by cobalt atoms [39]. In addition, the intensity of the peaks corresponding to CoMoO$_4$, Co$_2$CrO$_4$, and Co$_2$SiO$_4$ is stronger than that of the sample tested at 600 °C, suggesting the big quantity of these bimetallic oxides. The Vickers hardness of coating decreases to 583.9 ± 10 HV$_5.0$ at 800 °C, suggesting the coating is more easily worn down during the friction process. It can therefore be concluded that those bimetallic oxides play a key role as lubricants at this temperature, leading to a lower friction coefficient than that of the sample tested at 600 °C.

To acquire more proof that accounts for the superior friction and wear behavior of the coating tested at 800 °C, the cross section of the wear track at 800 °C was characterized (figure 17). A continuous glaze layer with a thickness of 50–100 nm can be obviously seen on the worn surface; it is composed of primary elements apart from oxygen and aluminum according to the EDS result (figure 17), demonstrating that the counterpart Al$_2$O$_3$ material was transferred to the worn surface. It can be inferred that the glaze layer primarily consists of an amorphous phase with excellent mechanical properties, according to our previous report on the NiCoCrAlYTa coating [40], in case of which the protective layer on the worn surface was found to mainly consist of a significant amount of the amorphous phase and a small amount of the crystal phase. Another interesting fact is that the coating grains under this layer get refined and reach nanometer size (figure 17), which can be attributed to both the actions of the applied load and frictional heat. In addition, the worn surface of the coating tested at 800 °C registers a hardness of ~14.4 GPa and an elastic modulus of ~237.9 GPa (figure 16), which can be attributed to the glaze layer and fine-grained strengthening that can effectively resist the external indentation. The H/E ratio (0.06) of the worn surface at 800 °C is lower than that of the worn surface at 600 °C (0.064), which well explains the result that the former possesses a slightly higher wear rate than the latter (figure 6). The development of a
protective nano-sized glaze layer on top of the worn surfaces is also the reason for its much lower friction coefficient and wear rate, because the protective layer prevents direct contact between the coating and its counterpart during the sliding process.

4. Conclusions

Herein, CoMoCrSi coatings were fabricated by a HVOF spraying technique, and their microstructure, mechanical and tribological properties, as well as the wear mechanisms at various temperatures were systematically investigated. The main conclusions of the investigation are as follows:

1. The as-sprayed coatings with a compact and typical lamellar microstructure mainly consisted of the intermetallic Laves phases, i.e., $\text{Co}_7\text{Mo}_6$, $\text{Co}_3\text{Mo}_2\text{Si}$, $\text{CrSi}_2$, and some amorphous phases. The combination of the compact structure and a certain amount of amorphous phases in the coatings could account for the high microhardness of the coating. The Vickers hardness of the coating decreased from $855.9 \pm 16 \text{ HV}_5$ at RT to $583.9 \pm 10 \text{ HV}_5$ at $800 \degree C$ merely due to a normal softening phenomenon of materials in hot environment.

2. The coating exhibited a brittle fracture coupled with abrasive wear mechanism at RT, an obvious abrasive wear at $200 \degree C$, and a severe adhesive wear at $400 \degree C$. With an increase in the test temperature, the friction coefficient decreased from 0.65 at $400 \degree C$ to 0.26 at $800 \degree C$, with the wear rate a difference of approximately two orders of magnitude between the low- and high-temperature, further indicating that the as-sprayed coating can be a good abrasion-resistant material for high-temperature application. The main wear mechanisms of the coating in the high temperature range are slight adhesive wear coupled with abrasive wear.

3. Numerous metallic oxides i.e., $\text{Co}_3\text{O}_4$, $\text{MoO}_3$ and bimetallic oxides identified as $\text{CoMoO}_4$, $\text{Co}_2\text{CrO}_4$, and $\text{Co}_2\text{SiO}_4$ formed a continuous protective layer with nanometer size ($50–100 \text{ nm}$) on the worn surface and thus reduced direct contact between the coating and its counterpart during the sliding process, leading to a lower friction coefficient and a decrease in material loss.

Moreover, as detailed investigations on the impact of these bimetallic oxides on the tribological performance of materials are rarely reported, it is significant to figure out how they play the role of lubricants during the high-temperature sliding wear process by analyzing their atomic structure and bond length, which we plan to study in the future.

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