



## Full Length Article

## High-temperature sliding wear behaviour of HVOF-sprayed TiC-based hardmetals with HEA matrices

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## ABSTRACT

The present research aims to develop coating materials for sliding wear protection over a wide temperature range. Indeed, while hardmetal coatings deposited by thermal spraying are widely used to mitigate sliding wear, the conventional formulations face limitations. WC-based materials are not applicable above 400 °C, while Cr<sub>3</sub>C<sub>2</sub>-NiCr, despite its oxidation resistance, has good but not optimal wear resistance. Thus, in this work we explored TiC-based hardmetals with Cu- and/or Mo-containing high-entropy alloy (HEA) matrices as an alternative. We coated AISI 304 stainless steel plates with High Velocity Oxy-Fuel (HVOF)-sprayed hardmetals containing 60 vol% TiC in four different AlCuCrFeNi or Al(Cu)CrFeMoNi HEA matrices. All the coatings were 250–300 μm thick and very dense (porosity <1 vol%), with ~800–860 HV hardness and a largely FCC matrix. In dry sliding ball-on-disc tests against Al<sub>2</sub>O<sub>3</sub>, TiC-HEA coatings showed lower wear than a Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark at all temperatures (room temperature, 400 °C, 600 °C, and 800 °C). In particular, the specific wear rates of Mo-containing HEAs exhibited rather stable values  $\leq 3 \times 10^{-6}$  mm<sup>3</sup>/(N·m), whilst those of Cr<sub>3</sub>C<sub>2</sub>-NiCr increased gradually from  $\sim 2 \times 10^{-5}$  at room temperature to  $\sim 4 \times 10^{-5}$  mm<sup>3</sup>/(N·m) at 800 °C. The wear resistance of the Mo-based HEAs relied on the formation of continuous titanate- and molybdate-rich films by tribo-oxidation at 400 and 600 °C. At 800 °C, the TiC-HEA coatings formed a thick oxide scale and wear proceeded by abrasion and spallation of the scale itself, without affecting the underlying hardmetal. Overall, TiC-HEA hardmetal coatings emerge as interesting options for high-temperature sliding wear resistance.

## 1. Introduction

Hardmetal coatings by thermal spraying are often employed to provide sliding wear protection to mechanical components [1]. Among the many possible uses, the protection of components operating at high temperatures (400 °C and above) is particularly critical: WC-based hardmetals, widely employed at room temperature, are no more viable, because of insufficient oxidation resistance [2] and thermal expansion mismatch with ordinary substrate materials (e.g., steels [3]). Cr<sub>3</sub>C<sub>2</sub>-NiCr compositions are more frequently used in these conditions, because of their excellent oxidation resistance up to 900 °C [4], but they also exhibit some significant drawbacks. New chromium carbide phases precipitate within the NiCr matrix for prolonged high-temperature exposures, developing a continuous network of secondary carbides [5–8].

This may embrittle the material and cause failure under severe service conditions, as documented e.g. in [9]. Moreover, Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings are significantly less wear resistant than WC-based ones [10].

Thus, as an alternative, compositions based on a combination of WC and Cr<sub>3</sub>C<sub>2</sub> have been proposed and tested in the literature [1,2,11,12]. WC improves the hardness and wear resistance of the material, while enough Cr<sub>3</sub>C<sub>2</sub>, usually coupled with a Ni-based matrix, promotes the formation of protective complex oxides [2] instead of non-protective WO<sub>3</sub> as a high-temperature oxidation product.

However, the drawback of any WC-containing formulation is the use of W itself, a critical raw material subject to significant supply insecurity and price fluctuations [13]. Hence, developing novel material formulations free of WC could be desirable.

In our previous research, we showed that TiC-based hardmetals are

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promising materials, whose sliding wear resistance at room temperature is intermediate between that of WC-based and  $\text{Cr}_3\text{C}_2$ -based hardmetals [14–16]. The same result was also found by other authors [17–19]. TiC is intrinsically stable up to high temperatures via the formation of  $\text{TiO}_2$ ; hence, a TiC-based hardmetal formulation would in principle be viable for high-temperature applications. To develop a hardmetal suitable for high-temperature application, however, it is of paramount importance to select a proper matrix composition as well. The matrix must be oxidation resistant, maintain sufficient mechanical properties to function as an effective binder, and the possible interaction between the oxidation products of the matrix and the TiC hard phase must also result in stable and protective oxides.

In a recent paper, we explored matrix alloys chosen within the emerging category of high-entropy alloys (HEAs). We found that some compositions, particularly an  $\text{Al}_{0.5}\text{CuCrFeNi}_2 + 60 \text{ vol\% TiC}$  one, provided better room-temperature sliding and abrasive wear resistance than TiC-based hardmetals with “conventional” Ni- or Fe-based matrices [20]. Thus, it seems reasonable to consider HEA matrices also for high temperature applications. In fact, one potentially interesting advantage of HEAs compared with more conventional alloys is the better stability of their mechanical properties with increasing temperature [21,22].

Notably, the literature on HEAs as matrices of TiC-based bulk hardmetals is already quite rich, as reviewed in [23], but papers on TiC-HEA hardmetal coatings (i.e., coatings with at least 60 vol% hard phase) are scarce. Nonetheless, there are studies on thermally sprayed HEA coatings reinforced with lower amounts of TiC. Those studies do confirm the potential of the TiC-HEA systems for high-temperature sliding wear applications, since they show a tendency toward lower friction and wear with increasing temperature. For example, Yantao et al. [24] noted that, due to improved tribofilm formation, the specific wear rate of a laser-cladded  $\text{AlCoCrFeNiMo}_{0.8} + 20 \text{ wt\% TiC}$  coating (tested under unidirectional ball-on-disc conditions against  $\text{Si}_3\text{N}_4$ ) decreased from  $\sim 5 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  at room temperature to  $\sim 1.6 \times 10^{-7} \text{ mm}^3/(\text{N}\cdot\text{m})$  at  $700^\circ\text{C}$ , before increasing again to  $\sim 2.5 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  at  $900^\circ\text{C}$  because the tribofilm was excessively softened.

To understand how to choose proper HEA matrix compositions, it is useful to refer to the review by Kasar et al. [21]. They compiled a summary of the literature data concerning the sliding wear rates and friction coefficients measured with HEAs at various temperatures. From that data, it is possible to infer that the specific wear rates measured at high temperatures often do not scale with the hardness of the alloy. Rather, the tribological performance of HEAs at high temperature is mostly dependent on the tribo-oxidation behaviour. Stable and continuous oxide layers are usually conducive to better tribological performance, i.e., lower friction and wear, as also confirmed in another review by Cheng et al. [22]. For example, Yang et al. reported that the addition of Cu to a laser-cladded  $\text{FeCoCrNi}$  coating did not increase its hardness, but improved the sliding wear resistance, especially at  $600^\circ\text{C}$ , because it promoted the formation of a more uniform and protective tribofilm [25]. Likewise, optimal sliding wear resistance of laser-cladded  $\text{FeCrMnVSi}_x$  coatings at  $600^\circ\text{C}$  and  $800^\circ\text{C}$  was achieved at a Si content  $x = 1.0$  because this composition, though not being the hardest, provided a particularly compact and protective oxide layer [26]. Liu et al. [27] reported that a laser-cladded  $\text{CoAlTiWTa}$  coating formed a continuous oxide tribofilm in a unidirectional ball-on-disc test at  $600^\circ\text{C}$  against  $\text{Si}_3\text{N}_4$ , which prevented the adhesive wear that affected the uncoated Inconel 718 substrate. These observations are particularly useful to guide the selection of appropriate HEAs matrices for hardmetals. To bind the hard phase effectively, a matrix should be tough and ductile, rather than hard. The results summarized above indicate that, with a proper compositional design, a HEA matrix can possess these characteristics and at the same time be capable of favourable tribo-oxidational phenomena that would enhance the high-temperature sliding wear resistance of the resulting hardmetal.

Thus, it is necessary to identify which elements can be added to a HEA to achieve such favourable tribo-oxidational responses at high

temperatures. One option is to use refractory HEAs (RHEAs), such as  $\text{HfTaTiVZr}$  and  $\text{TaTiVWZr}$ , because they form highly protective tribo-oxide films [28]. Fan et al., for example, produced multilayer  $\text{VTiCrMo}/\text{VTiCrW}$  films by DC magnetron sputtering and found that the formation of mixed oxides provided good sliding wear resistance ( $\sim 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$ ) and low friction ( $< 0.2$ ) at  $700^\circ\text{C}$ . However, these alloys are based on expensive and strategically critical elements and would be incompatible with the present goal of avoiding the use of tungsten and similar materials. Another potentially disadvantageous feature for the application of RHEAs as the matrix of a hardmetal is their brittle-to-ductile transition, which typically occurs well above room temperature [29]. Thus, RHEAs would be effective matrices at high temperature, but they would embrittle the hardmetal at room temperature.

Looking at the literature on conventional coating materials, there are many studies on thermally sprayed Ni-based alloy coatings (e.g.  $\text{NiCrAlY}$ ,  $\text{NiAl}$ ) added with Ag, Mo and, optionally, with a secondary hard phase such as  $\text{Cr}_3\text{C}_2$  or  $\text{Cr}_2\text{O}_3$  [30–38]. All these papers show very consistent results: during sliding wear at temperatures above  $400^\circ\text{C}$  (usually evaluated under ball-on-disc configurations), tribo-oxidation results in lubricious Ag molybdates, such as  $\text{Ag}_2\text{MoO}_4$ ,  $\text{Ag}_2\text{Mo}_2\text{O}_7$ , and  $\text{Ag}_2\text{Mo}_4\text{O}_{13}$ . Sliding wear rates are typically  $\sim (1\text{--}2) \times 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$ , with friction coefficients going from  $\sim 0.3\text{--}0.5$  at  $400\text{--}500^\circ\text{C}$  down to  $\sim 0.2$  (or even less) above  $800^\circ\text{C}$ . A similar alloying strategy may be employed with HEAs, but Ag is an expensive material, and using a cheaper alloying element would be more cost-effective. Takeichi et al. [39] showed that Cu-molybdates are promising high-temperature solid lubricants as well. Hence, Cu may be added together with Mo. Kasar et al. [21] reported that Cu and Mo are also among the elements which help retaining hot hardness in HEAs; hence, they may have a twofold beneficial action. The amount of these elements, however, should be properly calibrated. Ujah [40] opined that Cu may oxidize too rapidly, thus leaving defects near the alloy surface and accelerating wear. Interestingly, Wu et al. [41] produced HVOF-sprayed  $\text{CrFeCoNi}$  coatings with individual equiatomic additions of either Cu, Mn, Al, or Mo, and found that not only did the sliding wear rates (under unidirectional ball-on-disc sliding conditions against  $\text{Si}_3\text{N}_4$ ) decrease from room temperature to  $500^\circ\text{C}$  and  $700^\circ\text{C}$ , consistent with the literature reviewed previously, but the addition of Mo provided the lowest wear and friction, especially at  $700^\circ\text{C}$ . The authors ascribed it to the formation of  $\text{NiMoO}_4$ , which was assumed to have high-temperature lubricity because of the presence of weak bonds in the structure, as they ascertained through DFT calculations. The simultaneous addition of Cu and Mo, however, was not explored.

Thus, the goal of the present work is to explore for the first time the sliding wear response of thermally sprayed TiC-based coatings with HEA matrices containing Cu, Mo or both, over a wide range of temperatures. Four distinct matrix alloy compositions were chosen to explore various possibilities within the vast HEA compositional space, as explained in detail in Section 2.1, and the High Velocity Oxygen-Fuel (HVOF) thermal spraying technique was employed for their deposition since it is a state-of-the-art process for the production of hardmetal coatings in the industry [42]; hence, this choice facilitates a future potential upscaling of the results of this work toward real use cases.

## 2. Materials and methods

### 2.1. Materials compositions and feedstock powder production

Four different hardmetals with TiC as hard phase but different HEA matrices were produced, as explained in the Introduction:

- $\text{Al}_{0.5}\text{CuCrFeNi}_2 + 60 \text{ vol\% TiC}$  (hereafter labelled as “ $\text{AlCu}+\text{TiC}$ ”)
- $\text{Al}_3\text{Cr}_6\text{Fe}_{31}\text{Ni}_{34}\text{Mo}_{26} + 60 \text{ vol\% TiC}$  (hereafter labelled as “ $\text{AlMo}+\text{TiC}$ ”)

**Table 1**

Structural and thermodynamic parameters computed for the HEA matrices.

| Parameter                                                                                                         | AlCuCrFeNi | AlCrFeMoNi | Mo10  | Mo13  |
|-------------------------------------------------------------------------------------------------------------------|------------|------------|-------|-------|
| $\delta_m = 100 \sqrt{\sum_{i=1}^n \chi_i \left(1 - \frac{r_i}{\sum_{i=1}^n r_i \chi_i}\right)^2}$<br>(%)         | 4.2        | 4.5        | 4.0   | 4.6   |
| $\Delta(EN) = 100 \sqrt{\sum_{i=1}^n \chi_i \left(1 - \frac{(EN)_i}{\sum_{i=1}^n (EN)_i \chi_i}\right)^2}$<br>(%) | 6.2        | 8.1        | 7.7   | 8.4   |
| $VEC = \sum_{i=1}^n (VEC)_i \chi_i$                                                                               | 8.5        | 7.9        | 8.2   | 8.12  |
| $\Delta H_{mix} = \sum_{i<j} 4\Delta H_{ij} \chi_i \chi_j$<br>(kJ/mol)                                            | -8.5       | -10.3      | -3.6  | -7.9  |
| $\Delta S_{mix} = -R \sum_{i=1}^n \chi_i \ln \chi_i$<br>[kJ/(mol·K)]                                              | 0.013      | 0.011      | 0.014 | 0.014 |
| $\Omega = \frac{T_m \Delta S_{mix}}{ \Delta H_{mix} }$                                                            | 2.5        | 2.2        | 7.2   | 3.3   |

 $\chi_i$  = mole fraction of the i-th element. $r_i$  = atomic radius of the i-th element. $(EN)_i$  = Pauling electronegativity of the i-th element. $(VEC)_i$  = valence electron concentration of the i-th element. $\Delta H_{ij}$  = enthalpy of mixing of the i-th and j-th elements. $T_m$  = average melting temperature of the alloy. $R$  = universal gas constant.

- Al<sub>5</sub>Cr<sub>18</sub>Cu<sub>18</sub>Fe<sub>24</sub>Ni<sub>25</sub>Mo<sub>10</sub> + 60 vol% TiC (hereafter labelled as “AlCuMo10 + TiC”)

- Al<sub>8</sub>Cr<sub>16</sub>Cu<sub>16</sub>Fe<sub>16</sub>Ni<sub>31</sub>Mo<sub>13</sub> + 60 vol% TiC (hereafter labelled as “AlCuMo13 + TiC”)

The criteria for choosing these matrix compositions, which, apart from the first one, have not been documented in the literature, were:

- 1) To explore a range of systems which contain either Cu, Mo, or both.
- 2) To span a wide range of compositions. The more typical approach in the literature is to proceed by small additions of an element to the same base alloy. To the contrary, in this exploratory work we preferred to choose quite distant points in the wide compositional space of HEAs. In this way, it is possible to verify the occurrence of “cocktail effects” [43] and find interesting formulations that can later be refined through more focused studies with targeted, small changes.
- 3) To aim for FCC compositions. FCC HEAs are usually known for their better ductility [43]: in a hardmetal, the role of the matrix is indeed that of providing toughness, while hardness is contributed by the hard ceramic phase.

In the latter respect, using the atomic radius, valence electron concentration, electronegativity and melting temperature data for pure elements from [43], together with the dataset of binary mixing enthalpies provided as a supplementary material in [44], the characteristic structural and thermodynamic parameters for the four matrix compositions can be computed as listed in Table 1. All compositions possess an average atomic radius mismatch  $\delta_m < 5\%$  [45,46]; a mixing enthalpy  $\Delta H_{mix}$  well within the  $[-15 \text{ kJ/mol}, +5 \text{ kJ/mol}]$  range [45] and, in fact, always greater than  $-10 \text{ kJ/mol}$  [47]; and  $\Omega = T_m \Delta S_{mix} / |\Delta H_{mix}| > 1.1$  [48,49]. Thus, all alloys should exhibit a preference to form solid solutions rather than intermetallics, at least close to the solidus point, although another condition, i.e. that of having an average electronegativity mismatch  $\Delta(EN) < 6\%$  [46,50,51], is not met. Further, the valence electron concentration (VEC) of the alloys is close to or above 8, which indicates a predominantly single-phase FCC solid solution [45,52].

The AlCu+TiC composition, in particular, is the same that we used in our previous work on TiC-HEA hardmetals and was selected due to its promising room-temperature tribological responses [20]. For ease of

**Table 2**

HVOF deposition parameters.

| Parameter                               | TiC-HEA coatings | Cr <sub>3</sub> C <sub>2</sub> -25wt.%NiCr |
|-----------------------------------------|------------------|--------------------------------------------|
| Fuel (H <sub>2</sub> ) flow rate [SLPM] | 656              | 635                                        |
| O <sub>2</sub> flow rate [SLPM]         | 228              | 214                                        |
| Air flow rate [SLPM]                    | 274              | 235                                        |
| Equivalence ratio                       | 0.87             | 0.83                                       |
| Standoff distance [mm]                  | 250              | 250                                        |
| Powder feed rate [g/min]                | 20               | 50                                         |
| No. of cycles                           | 13               | 9                                          |
| Transverse speed [mm/s]                 | 750              | 750                                        |
| Pitch distance [mm]                     | 5                | 6                                          |

comparison, the results obtained in [20] in terms of microstructure, hardness, porosity, phase composition, and room-temperature sliding wear resistance on this composition are repeated in this work.

All feedstock materials were produced by MBN Nanomaterialia S.r.l. (Treviso, Italy) via mechanical alloying using a proprietary industrial high-energy ball milling (HEBM) process under an argon atmosphere and with a cooled milling chamber. The starting materials were elemental powders of aluminium, iron, chromium, nickel, molybdenum, and copper. Titanium carbide was synthesized in situ by adding titanium powder and graphite to the mix. The resulting powders were classified using cyclones and sieves to a nominal particle size range of  $-45 + 15 \mu\text{m}$ , packed and vacuum sealed to prevent oxidation.

## 2.2. Deposition of the coatings

The feedstock powders were HVOF-sprayed onto AISI 304 stainless steel plates of 60 mm length  $\times$  25 mm width  $\times$  3 mm thickness. Before spraying, the plates were grit-blasted using brown alumina abrasive of 30 mesh size at a pressure of 5.5 bar, which gave an eventual surface roughness  $R_a \approx 6 \mu\text{m}$ , and ultrasonically cleaned in acetone. The deposition was performed using a Diamond Jet 2600 hybrid HVOF torch (Oerlikon Metco, Wohlen, Switzerland) operated with a mixture of hydrogen (H<sub>2</sub>), oxygen (O<sub>2</sub>), and air. The torch was traversed linearly in front of a rotating turntable carrying the substrates. Traverse speed and turntable rotation were adjusted to obtain the required scan speed and pitch (Table 2). Substrate cooling and overspray removal were provided by fixed compressed-air jets (100 psi/689 kPa).

The coatings were deposited using the parameters shown in Table 2, which were obtained from our previous work on TiC-HEA coatings [20]. The peak surface temperature during deposition, measured with an IR pyrometer (OPTRIS CTLaser, Luchsinger srl, Curno, Italy), was  $\sim 450^\circ\text{C}$  in all cases. In every experiment, the deposition efficiency was calculated as the ratio between the mass of powder effectively deposited onto the steel plates ( $M_{\text{dep}}$ ) and the overall powder mass sprayed toward the plates ( $M_{\text{tot}}$ ).  $M_{\text{dep}}$  was obtained by weighing the plates on an electronic scale with a precision of  $\pm 0.01$  g before and after spraying.  $M_{\text{tot}}$  was calculated using the powder feed rate ( $\dot{m}$ ), the length ( $l$ ) and width ( $w$ ) of the steel plates, the torch/substrate traverse speed ( $v$ ), the pitch distance ( $p$ ), and the total number of torch cycles ( $N$ ), according to the following formula:  $M_{\text{tot}} = (l/p) \cdot (w/v) \cdot N \cdot \dot{m}$ .

As a benchmark, a  $\text{Cr}_3\text{C}_2$ -25 mass % (Ni – 20 mass % Cr) coating (hereafter simply referred to as  $\text{Cr}_3\text{C}_2$ -NiCr), a well-known solution for high-temperature wear protection, was also deposited on the same substrates. A commercially available feedstock (Woka 7202, Oerlikon Metco WOKA GmbH, Barchfeld, Germany; nominal particle size distribution:  $-45 + 15\ \mu\text{m}$ ) was sprayed using established process parameters (Table 2).

The in-flight velocity and surface temperature of the particles were measured using a SprayWatch 2i system. For these measurements, the torch was kept stationary and operated with the same gas flow rate and powder feed rate settings listed in Table 2. The SprayWatch camera was placed at an axial distance from the nozzle exit equal to the stand-off distance listed in Table 2 and at a radial distance within the focal range of the instrument. In all cases, the acquisition was manually started once the powder feed was stabilized to within  $\pm 4$  g/min of the desired value and was continued for 60–90 s. The data were then averaged.

### 2.3. Sliding wear testing

Dry sliding wear tests were performed under unidirectional ball-on-disc configuration using an  $\text{Al}_2\text{O}_3$  ball as a counterpart, because this setup simulates, to a first approximation, a wide range of sliding contact conditions against counterfaces containing hard asperities, such as other hardmetals or ceramics. Moreover,  $\text{Al}_2\text{O}_3$  possesses high hot hardness and does not undergo phase changes or bulk chemical reactions upon heating, thus making it well-suited for testing at high temperatures. Finally, extensive literature data are available concerning the sliding wear testing of similar hardmetal coatings against  $\text{Al}_2\text{O}_3$  counterbodies, which can be used for comparative purposes.

The tests were run in a THT tribometer (Anton Paar Tritec, Corcelles, CH), using 3 mm-diameter  $\text{Al}_2\text{O}_3$  balls with a normal load of 10 N, a relative sliding speed of 0.40 m/s, a total sliding distance of 5000 m and a track radius of 7 mm. Assuming elastic modulus and Poisson's ratio values of 370 GPa and 0.22 for  $\text{Al}_2\text{O}_3$ , and 250 GPa and 0.30 for the hardmetal coatings, the maximum and average hertzian contact pressures at the beginning of the test were estimated to be 2.8 GPa and 1.9 GPa, respectively. Based on our previous wear mapping of similar TiC-based hardmetals, these high-pressure conditions can trigger significant fatigue wear by brittle fracture in coatings with limited cohesive strength [53]. Thus, the chosen test conditions are suitable to reveal cohesion issues in the tested samples. Further, while the chosen contact pressures are higher than the nominal values in most applications, they are suitable to simulate unexpected or accidental peak pressures that can follow from misalignments due to tolerances, assembly errors, etc. These peak pressures are, in many practical cases, the true cause of wear losses not expected from design considerations.

Tests were carried out at room temperature,  $400^\circ\text{C}$ ,  $600^\circ\text{C}$ , and  $800^\circ\text{C}$ . For high-temperature tests, the base plate was induction-heated and the temperature was measured with a thermocouple on the rear face of the sample. Heating occurred in approximately 1 h in all cases, and an additional 40 min holding helped homogenize the temperature before

the test was started.

All tests were run in duplicate, using ground and polished samples with a  $3\ \mu\text{m}$  polycrystalline diamond finish. The samples and the balls were cleaned ultrasonically in acetone before and after each test. Ultrasonic cleaning after the test did not remove attached tribofilms, but removed loose particles left around the wear trace, which would have interfered with the SEM observations described in Section 2.4.

The wear volume loss of each sample was assessed by structured illumination microscopy (Confosurf, Confovis GmbH, Jena, Germany) and that of the ball was obtained by measuring the wear scar diameter with an optical microscope (Olympus GS30). The data was converted to specific wear rate by normalizing the volume loss over the normal load and the sliding distance. The friction coefficient was measured in real-time during each test using a load cell attached to the pin-holding arm and the average value at the steady state was computed.

### 2.4. Powders and coated samples characterization

The particle size distribution of the feedstock powders was verified by laser diffraction (Mastersizer 2000, Malvern Instruments, Malvern, UK) using the water dispersion technique (Hydro 2000-S, Malvern Instruments) with ultrasounds for de-agglomeration. The oxidation behaviour of the particles was evaluated through simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) in air (STA409, Netzsch, Selb, Germany). A powder sample of approximately 100 mg was inserted in an alumina crucible, with another empty crucible as reference, and heated to  $1290^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ .

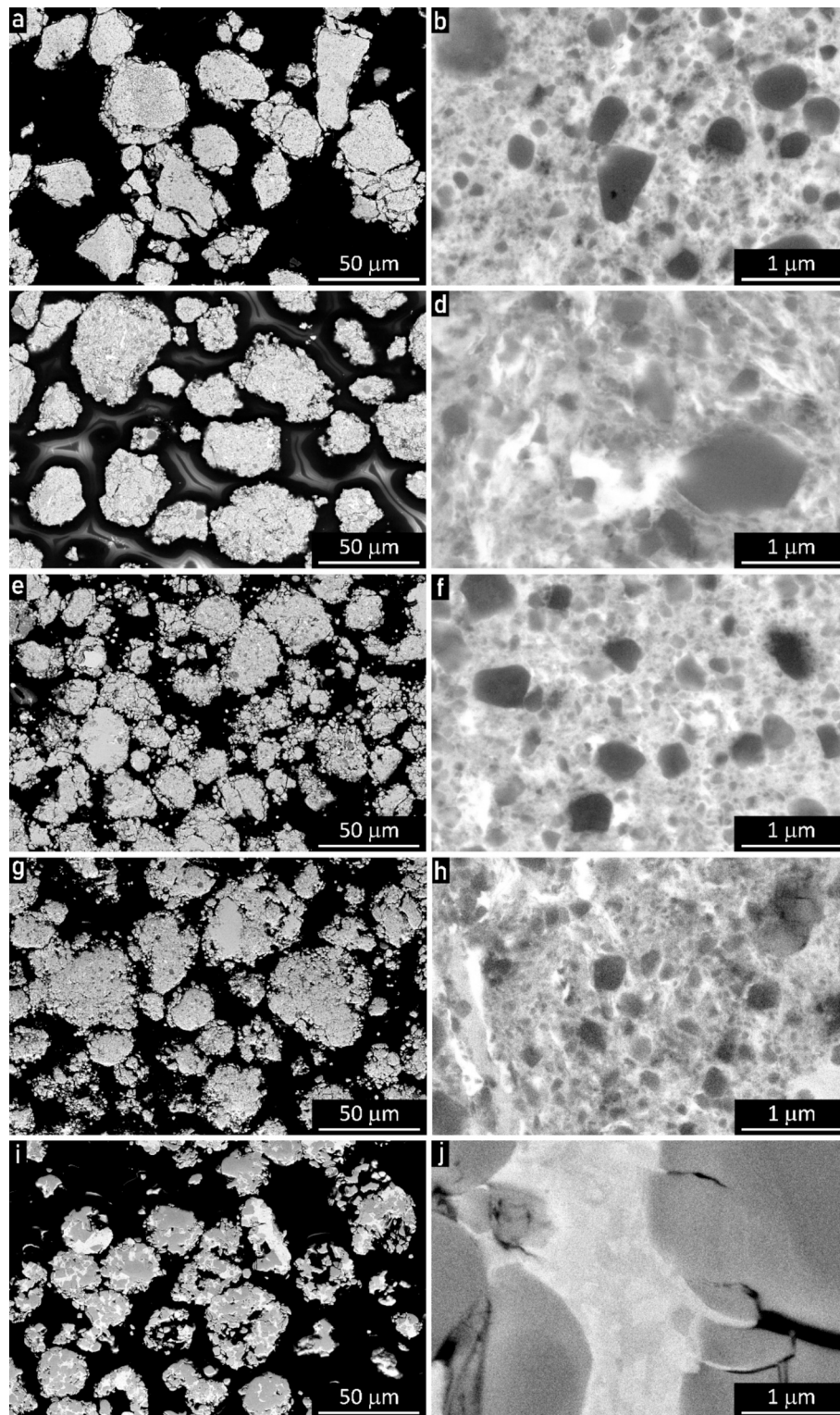
The crystalline phase composition of the powders and the coatings, both in as-deposited condition and after holding at high temperature during the sliding wear tests (outside the wear trace), was determined by X-ray diffraction (XRD: Empyrean, Malvern Panalytical, Almelo, The Netherlands). Diffraction patterns were acquired over a range of  $20^\circ \leq 2\theta \leq 85^\circ$  using Cu-K $\alpha$  radiation (wavelength:  $1.540598\ \text{\AA}$ ) from a conventional source operated at 40 kV and 40 mA. The step size was  $0.026^\circ$  and the counting time was 174 s/step.

Quantitative phase analysis of the powders and the as-deposited coatings was further performed by Rietveld refinement of the diffraction patterns, as implemented in GSAS with the EXPGUI interface [54,55]. Structural models were obtained from the Crystallography Open Database (COD) [56]. A pseudo-Voigt peak profile and a Chebyshev polynomial background were used. The refined parameters included scale factors, lattice parameters, zero shift, and peak profile coefficients. The quality of the refinements was assessed using agreement factors, yielding typical values of  $R_{\text{wp}} = 6\text{--}8\%$ ,  $\chi^2 = 2\text{--}4$  and  $R_F^2 = 5\text{--}13\%$ .

Spatially resolved assessment of the phases both within and outside the wear traces of ball-on-disc tested samples was carried out by micro-Raman spectroscopy (Labram Evolution HR, Horiba). The excitation source was a 532 nm-wavelength laser, focused through a  $100\times$  objective. The scattered light emerging from the sample was analysed using a 600 grooves/mm diffraction grating and a CCD detector.

The cross-sectional microstructure and the chemical composition of the feedstock powders, the as-deposited and the wear-tested coatings, as well as the surface morphology of the worn samples, were analysed using a scanning electron microscope (SEM: Nova NanoSEM 450, FEI – Thermo Fisher Scientific, Eindhoven, NL) equipped with an energy-dispersive X-ray spectroscopy (EDX) system (Quantax-200 microanalysis system with an XFlash 6|10 detector, Bruker Nano GmbH, Berlin, Germany). For cross-sectional observation, the powders and the worn samples were embedded in a two-component epoxy resin at room temperature. The worn samples were then cut using a resin-bound abrasive disc after mounting, thus preventing the detachment of surface layers. The cross-sections of the as-deposited samples, to the contrary, were first cut and then embedded in a phenol resin with a hot-mounting press. Grinding and polishing procedures were carried out using SiC papers (up to 2500 mesh), a  $3\ \mu\text{m}$  polycrystalline diamond slurry, and a colloidal





**Fig. 1.** Cross-sectional SEM micrographs (backscattered electrons imaging) of the AlCu+TiC (a, b), AlMo+TiC, (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h) and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) powders. Micrographs acquired at a magnification of 2000 $\times$  (a, c, e, g, i) and 100,000 $\times$  (b, d, f, h, j).

silica suspension.

The SEM micrographs of worn surfaces were acquired at an acceleration voltage of 8 kV, while the cross-sectional micrographs and all EDX spectra on surfaces and sections were acquired at 15 kV. The porosity of the as-deposited coatings was measured by image analysis on 8 micrographs acquired at 3000 $\times$  in backscattered electrons imaging mode along their section, using a MATLAB-based thresholding

procedure. Quantitative EDX analyses were performed on the polished cross-sections of the powders and the as-deposited coatings by acquiring spectra over three entire fields-of-view imaged at 400 $\times$ . When analysing the powders, carbon and oxygen were excluded from the quantitative results, because they are also contained in the mounting resin. The contents of carbon, oxygen and nitrogen in the powders were independently quantified by the oxygen combustion and inert gas fusion

**Table 3**

Characteristic percentile values of the particle size distributions (equivalent diameter) of all feedstock powders.

| Powder                               | d <sub>10</sub> (μm) | d <sub>50</sub> (μm) | d <sub>90</sub> (μm) |
|--------------------------------------|----------------------|----------------------|----------------------|
| AlCu+TiC [20]                        | 20.9                 | 33.3                 | 52.7                 |
| AlMo+TiC                             | 18.3                 | 35.2                 | 60.6                 |
| AlCuMo10 + TiC                       | 18.7                 | 33.2                 | 56.8                 |
| AlCuMo13 + TiC                       | 14.8                 | 29.6                 | 53.9                 |
| Cr <sub>3</sub> C <sub>2</sub> -NiCr | 23.5                 | 34.9                 | 51.6                 |

**Table 4**

Chemical composition of the TiC+HEA powders and coatings, measured by EDX analysis, inert gas fusion (oxygen and nitrogen contents in the powders) and combustion (carbon content in the powders) methods. The composition of the benchmark Cr<sub>3</sub>C<sub>2</sub>-NiCr coating is also provided. Results in mass %, normalized to 100%. N/A = measurement not available.

| Element         | AlCu + 60TiC [20] | AlMo + 60TiC | AlCuMo10 + TiC | AlCuMo13 + TiC | Cr <sub>3</sub> C <sub>2</sub> -NiCr |
|-----------------|-------------------|--------------|----------------|----------------|--------------------------------------|
| <b>Powders</b>  |                   |              |                |                |                                      |
| Carbon          | 10.44 ± 0.37      | N/A          | 9.32 ± 0.02    | 9.34 ± 0.04    |                                      |
| Oxygen          | 0.39 ± 0.01       | N/A          | 1.14 ± 0.02    | 1.18 ± 0.02    |                                      |
| Nitrogen        | 0.10 ± 0.01       | N/A          | 0.67 ± 0.03    | 0.72 ± 0.03    |                                      |
| Aluminium       | 2.32 ± 0.17       | 0.97 ± 0.13  | 1.36 ± 0.05    | 2.09 ± 0.05    |                                      |
| Silicon         | –                 | –            | –              | –              |                                      |
| Titanium        | 37.40 ± 0.24      | 40.33 ± 0.27 | 35.86 ± 0.09   | 35.54 ± 0.10   |                                      |
| Chromium        | 8.69 ± 0.09       | 2.92 ± 0.06  | 9.18 ± 0.11    | 8.19 ± 0.23    |                                      |
| Manganese       | 0.67 ± 0.01       | –            | –              | –              |                                      |
| Iron            | 11.75 ± 0.15      | 20.48 ± 0.58 | 13.12 ± 0.11   | 10.19 ± 0.09   |                                      |
| Nickel          | 17.99 ± 0.45      | 18.05 ± 0.39 | 12.62 ± 0.13   | 16.05 ± 0.20   |                                      |
| Copper          | 10.25 ± 0.40      | 0.88 ± 0.11  | 10.67 ± 0.27   | 9.07 ± 0.13    |                                      |
| Molybdenum      | –                 | 16.37 ± 0.23 | 6.06 ± 0.02    | 7.63 ± 0.07    |                                      |
| Tungsten        | –                 | –            | –              | –              |                                      |
| <b>Coatings</b> |                   |              |                |                |                                      |
| Carbon          | 10.38 ± 0.42      | 10.07 ± 0.13 | 9.22 ± 0.07    | 9.52 ± 0.15    | 8.72 ± 0.13                          |
| Oxygen          | 5.16 ± 0.13       | 7.06 ± 0.10  | 6.46 ± 0.01    | 7.26 ± 0.40    | 2.57 ± 0.07                          |
| Aluminium       | 1.97 ± 0.04       | 0.66 ± 0.04  | 1.21 ± 0.04    | 1.72 ± 0.02    | –                                    |
| Silicon         | 0.08 ± 0.03       | 0.07 ± 0.04  | –              | –              | –                                    |
| Titanium        | 33.30 ± 0.23      | 30.27 ± 0.23 | 31.94 ± 0.28   | 31.56 ± 0.34   | –                                    |
| Chromium        | 8.45 ± 0.03       | 2.52 ± 0.05  | 8.90 ± 0.13    | 7.40 ± 0.17    | 63.70 ± 0.01                         |
| Manganese       | 0.48 ± 0.04       | –            | –              | –              | –                                    |
| Iron            | 11.65 ± 0.19      | 18.15 ± 0.15 | 13.27 ± 0.21   | 9.97 ± 0.06    | –                                    |
| Nickel          | 18.35 ± 0.12      | 16.15 ± 0.35 | 12.99 ± 0.24   | 16.23 ± 0.06   | 24.44 ± 0.06                         |
| Copper          | 10.19 ± 0.12      | 0.76 ± 0.05  | 9.94 ± 0.53    | 8.78 ± 0.15    | –                                    |
| Molybdenum      | –                 | 14.30 ± 0.23 | 6.07 ± 0.15    | 7.56 ± 0.02    | –                                    |
| Tungsten        | –                 | –            | –              | –              | 0.57 ± 0.04                          |

methods, respectively, using the same equipment and procedures previously described in [20]. The aggregate results from EDX, inert gas fusion, and oxygen combustion were then renormalized to 100% and the

**Table 5**

Quantitative phase composition of the powders and coatings, by Rietveld analysis on XRD patterns (results in mass %, normalized to 100%).

| Phase                          | AlCu + 60TiC [20] | AlMo + 60TiC | AlCuMo10 + TiC | AlCuMo13 + TiC | Cr <sub>3</sub> C <sub>2</sub> -NiCr |
|--------------------------------|-------------------|--------------|----------------|----------------|--------------------------------------|
| <b>Powders</b>                 |                   |              |                |                |                                      |
| FCC                            | 49.7 ± 0.4        | 20.3 ± 0.8   | 9.9 ± 0.2      | 7.3 ± 0.2      | 24.5 ± 0.2                           |
| FCC - 2                        | –                 | 9.3 ± 0.2    | 3.4 ± 0.3      | 5.3 ± 0.3      | –                                    |
| BCC                            | 1.8 ± 0.2         | 10.6 ± 0.2   | 19.9 ± 0.3     | 19.6 ± 0.4     | –                                    |
| TiC                            | 48.5 ± 0.2        | 42.5 ± 0.2   | 58.2 ± 0.2     | 57.6 ± 0.2     | –                                    |
| Mo                             | –                 | 17.3 ± 0.1   | 8.6 ± 0.1      | 10.2 ± 0.1     | –                                    |
| Cr <sub>3</sub> C <sub>2</sub> | –                 | –            | –              | –              | 65.4 ± 0.2                           |
| Cr <sub>7</sub> C <sub>3</sub> | –                 | –            | –              | –              | 10.1 ± 0.4                           |
| <b>Coatings</b>                |                   |              |                |                |                                      |
| FCC                            | 44.3 ± 0.2        | 31.1 ± 0.2   | 39.6 ± 0.2     | 37.5 ± 0.2     | 30.9 ± 0.6                           |
| BCC                            | 0.7 ± 0.6         | –            | 1.0 ± 0.1      | 0.4 ± 0.1      | –                                    |
| TiC                            | 45.0 ± 0.2        | 67.5 ± 0.2   | 58.5 ± 0.2     | 61.5 ± 0.2     | –                                    |
| TiC <sub>1-x</sub>             | 0.6 ± 0.1         | –            | –              | –              | –                                    |
| MO                             | 9.1 ± 0.3         | –            | –              | –              | –                                    |
| MTiO <sub>3</sub>              | 0.4 ± 0.1         | 1.4 ± 0.4    | 0.9 ± 0.2      | 0.6 ± 0.1      | –                                    |
| Cr <sub>3</sub> C <sub>2</sub> | –                 | –            | –              | –              | 31.6 ± 0.3                           |
| Cr <sub>7</sub> C <sub>3</sub> | –                 | –            | –              | –              | 35.6 ± 0.5                           |
| Cr <sub>2</sub> O <sub>3</sub> | –                 | –            | –              | –              | 1.8 ± 0.2                            |

results are presented as mean ± standard deviation of three measurements.

The Vickers microhardness of the as-deposited coatings was measured at 3 N load on the polished cross-sections (Micro-Combi Tester, Anton Paar Tritec), with 20 indents for each sample.

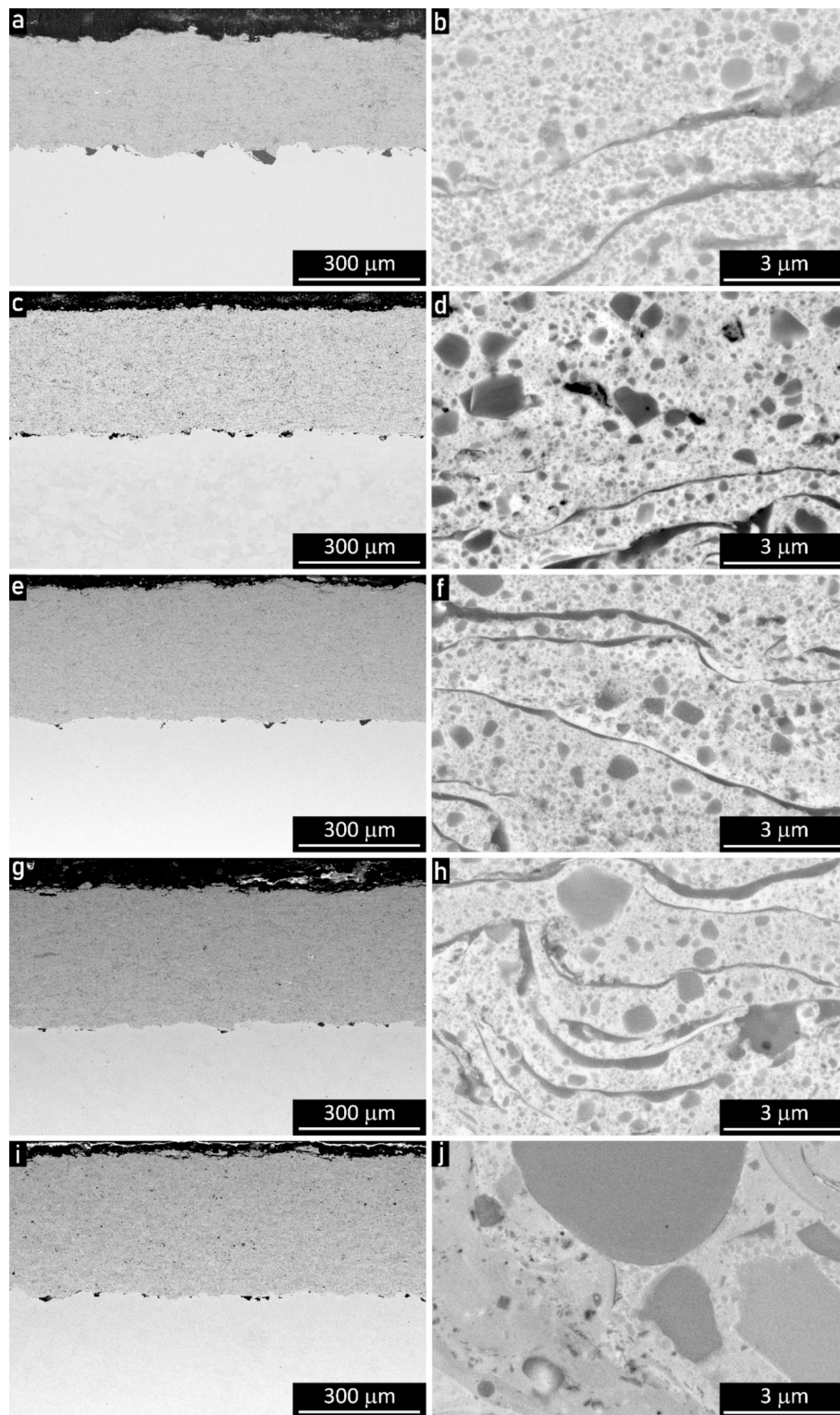
### 3. Results and discussion

#### 3.1. Microstructure and phase composition of powders and coatings

The TiC-HEA feedstock powders exhibited the typical morphology of materials processed by HEBM (Fig. 1a, c, e, g), consisting of slightly irregular particles with cracks arising from repeated welding and fragmentation. The particle size distributions measured by laser scattering were all similar to each other and to the Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark. The distributions were rather narrow and only slightly coarser than the nominal –45 + 15 μm size range (Table 3).

At higher magnification, the powders showed a homogeneous dispersion of sub-micrometre and nanometre-scale TiC within a metallic matrix (Fig. 1b, d, f, h). The overall chemical composition of each powder was consistent with the nominally expected one (Table 4). However, within each particle, the matrix was not fully chemically homogeneous, indicating incomplete solid-state diffusion during HEBM. In particular, heavier elements—especially Mo in the Mo-containing compositions—appeared segregated as bright streaks, consistent with the corresponding EDX maps (Supplementary Material, Fig. S1). The distribution of the other matrix constituents was not fully homogeneous, either.

Correspondingly, XRD patterns (Fig. 3a-d and quantification in Table 5) revealed a multi-phase matrix. In all powders, the main phase was TiC, as expected, but in the matrix, BCC and FCC phases coexisted. The Mo-containing powders also included some crystalline Mo, consistent with the SEM and EDX results, and exhibited two shifted sets of peaks attributable to two distinct FCC phases. The broad diffraction peaks were characteristic of HEBM powders and reflected the residual



**Fig. 2.** Cross-sectional SEM micrographs (backscattered electrons imaging) of the AlCu+TiC (a, b), AlMo+TiC, (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h) and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) coatings. Micrographs acquired at a magnification of 400× (a, c, e, g, i) and 40,000× (b, d, f, h, j).

strains and high defect density introduced during milling. No residual Ti, graphite, or secondary carbides were detected, indicating that TiC formation during HEBM was complete.

The agglomerated and sintered Cr<sub>3</sub>C<sub>2</sub>-NiCr powder used as a benchmark (Fig. 1i, j) consisted of more rounded but also more porous particles containing comparatively coarse chromium carbides. In Fig. 1j, individual crystalline grains within the Ni—Cr matrix were visible via

the electron channelling contrast, since this powder did not experience the work hardening process of the HEBM powders. Two greyscale levels were also apparent within the carbide particles (Fig. 1j). Additional EDX spectra provided in the Supplementary Material (Fig. S2) showed that the brighter carbide regions (Fig. S2: spectrum 1) contained some nickel and (with all the limitations associated with the EDX quantification of this element) possibly a smaller amount of carbon.



**Table 6**

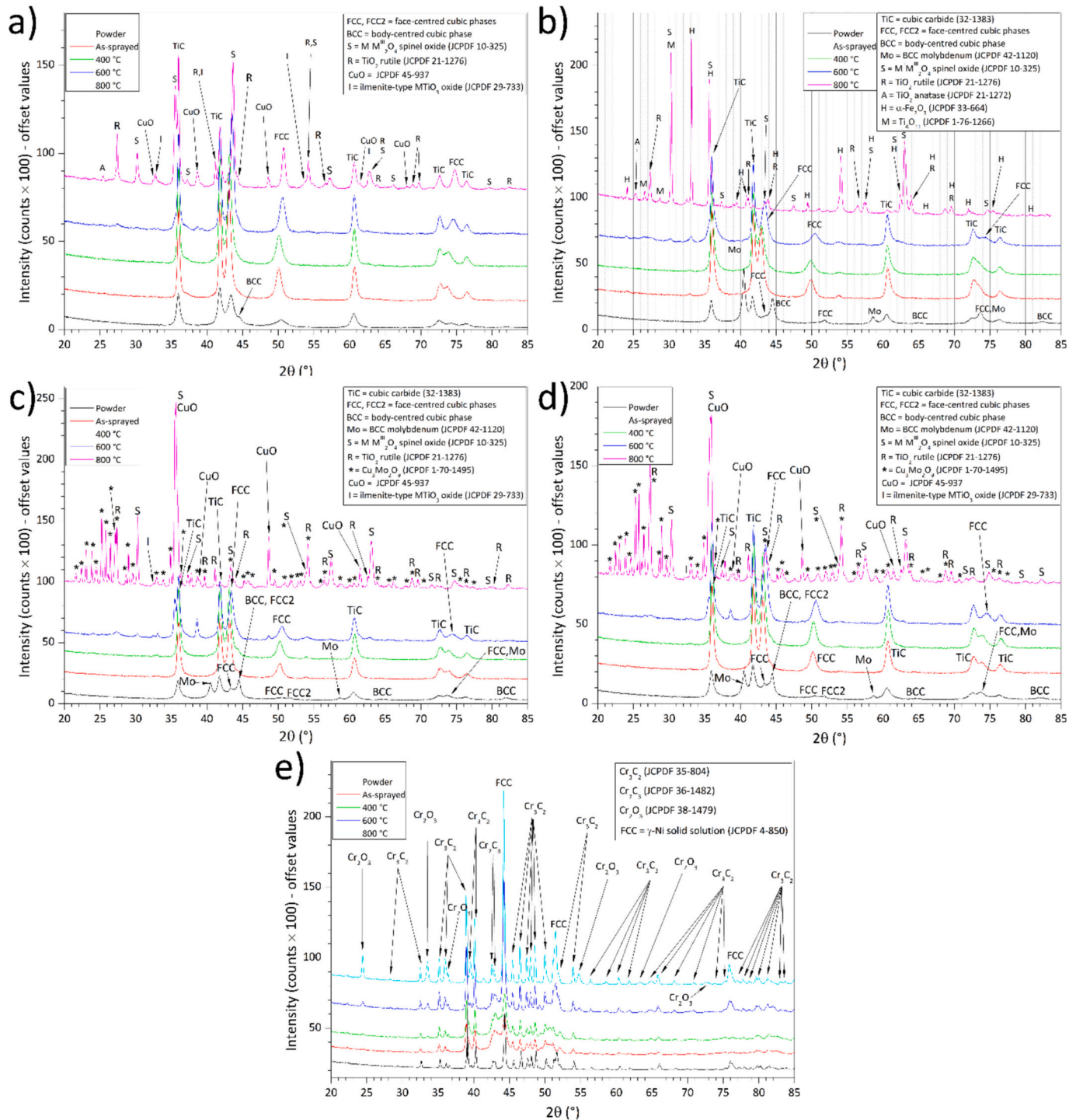
Deposition efficiency, microhardness, and porosity of the coatings.

| Coating                              | Deposition efficiency | Hardness (HV3N) | Porosity (vol%) |
|--------------------------------------|-----------------------|-----------------|-----------------|
| AlCu+TiC [20]                        | 55%                   | 819 ± 77        | 0.16 ± 0.04     |
| AlMo+TiC                             | 59%                   | 862 ± 90        | 0.15 ± 0.08     |
| AlCuMo10 + TiC                       | 59%                   | 807 ± 75        | 0.04 ± 0.02     |
| AlCuMo13 + TiC                       | 61%                   | 842 ± 52        | 0.04 ± 0.01     |
| Cr <sub>3</sub> C <sub>2</sub> -NiCr | 51%                   | 961 ± 127       | 0.64 ± 0.13     |

Accordingly, XRD showed the presence of Cr<sub>3</sub>C<sub>2</sub> and Cr<sub>7</sub>C<sub>3</sub> carbides

together with an FCC Ni—Cr matrix (Fig. 3e and Rietveld quantification in Table 5). The darker carbide regions were likely the Cr<sub>3</sub>C<sub>2</sub> phase whereas the brighter regions, containing some dissolved Ni and slightly less carbon, were consistent with Cr<sub>7</sub>C<sub>3</sub>. The diffraction peaks were markedly narrower than those of the HEBM powders, as expected.

After HVOF spraying, all TiC-HEA and Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings were very dense and 250–300 μm thick (Fig. 2a, c, e, g, i). The TiC-HEA coatings exhibited Vickers microhardness values of ~800–850 HV (Table 6), slightly lower than the Cr<sub>3</sub>C<sub>2</sub>-NiCr reference, while also showing lower porosity (<1 vol% and often near the detection limit, Table 6). Their



**Fig. 3.** XRD patterns acquired on the AlCu+TiC (a), AlMo+TiC (b), AlCuMo10 + TiC (c), AlCuMo13 + TiC (d) and Cr<sub>3</sub>C<sub>2</sub>-NiCr powders and coatings, in as-deposited condition and after heating to 400 °C, 600 °C, and 800 °C during the ball-on-disc sliding wear tests (outside the wear trace).



**Table 7**

in-flight velocity and surface temperature of the particles during HVOF spraying, measured by the SprayWatch 2i sensor (average  $\pm$  standard deviation).

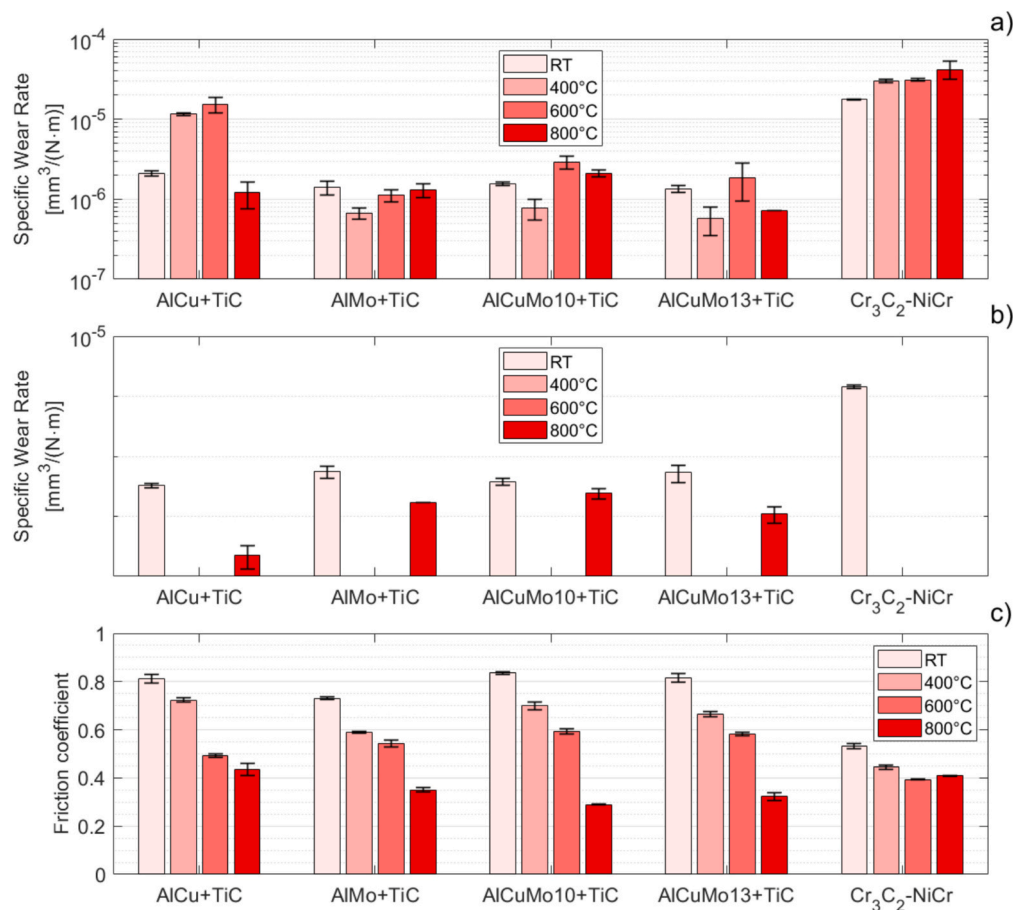
| Coating                              | Particle velocity (m/s) | Particle surface temperature ( $^{\circ}$ C) |
|--------------------------------------|-------------------------|----------------------------------------------|
| AlCu+TiC                             | 664 $\pm$ 141           | 1894 $\pm$ 12                                |
| AlMo+TiC                             | 687 $\pm$ 8             | 1992 $\pm$ 2                                 |
| AlCuMo10 + TiC                       | 683 $\pm$ 10            | 1950 $\pm$ 1                                 |
| AlCuMo13 + TiC                       | 698 $\pm$ 71            | 1958 $\pm$ 2                                 |
| Cr <sub>3</sub> C <sub>2</sub> -NiCr | 643 $\pm$ 43            | 1899 $\pm$ 2                                 |

deposition efficiency ( $\sim$ 55–60%) was even higher than that of Cr<sub>3</sub>C<sub>2</sub>-NiCr ( $\sim$ 51%), Table 6. Quantitative EDX results indicated that the metallic element ratios in the TiC-HEA coatings were essentially unchanged from the feedstock powders (Table 4).

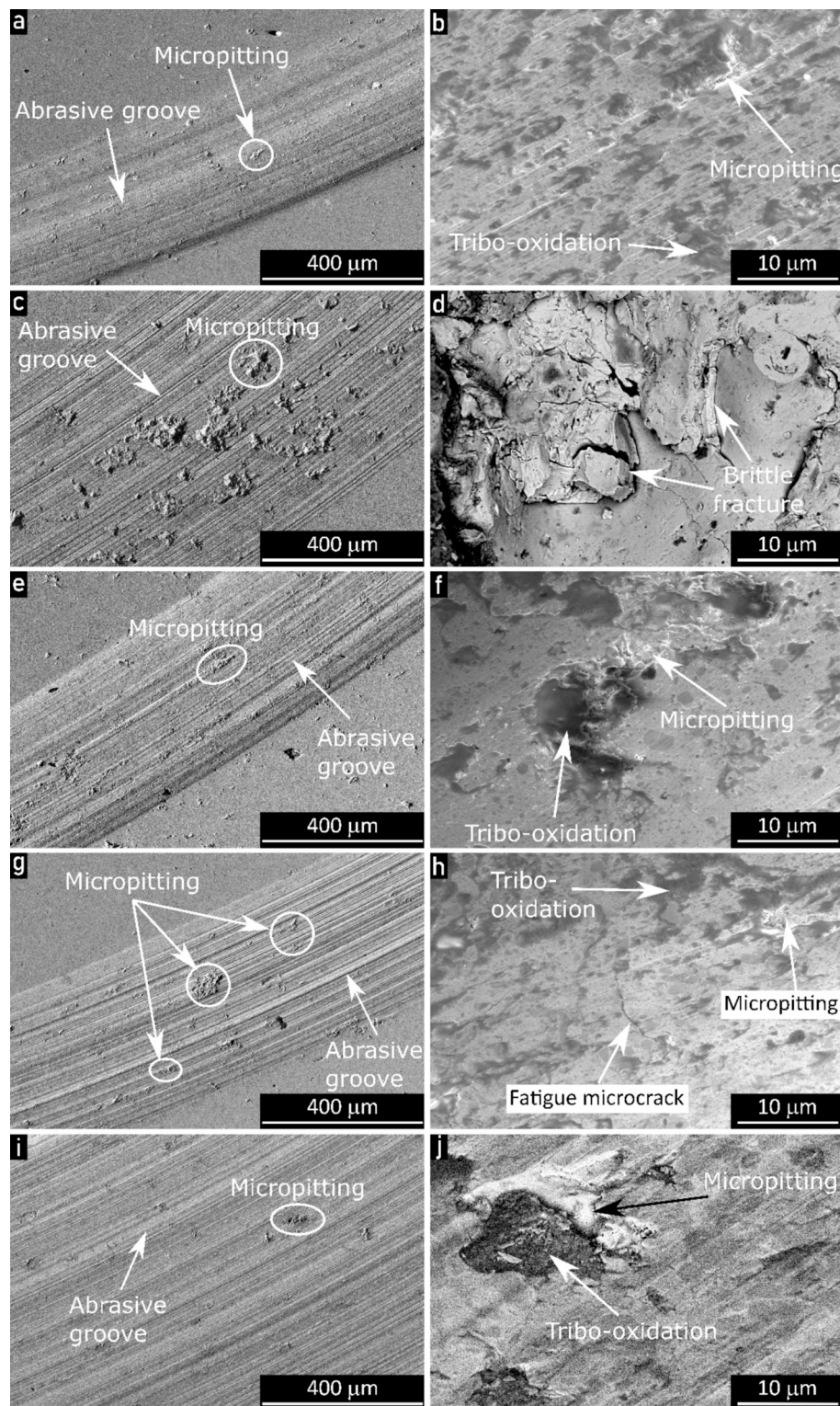
However, higher-magnification cross-sectional views (Fig. 2b, d, f, h) revealed two main differences between TiC-HEA powders and coatings. First, the intra-lamellar chemical heterogeneity disappeared. Correspondingly, the matrix phase constitution was simplified: the coatings' matrices were almost entirely FCC, with only trace BCC, often at the XRD detection limit (Fig. 3a-d and Table 5). This likely corresponded to the high-temperature phase composition of the HEA matrices. The high-temperature condition was quenched-in by the rapid cooling of the splats after deposition, preventing further evolution and elemental segregation. The second FCC phase seen in the Mo-containing powders did not appear in the coatings, nor did any free Mo phase, at least within the detection limits of the XRD technique. Matrix homogenization followed from its melting during the HVOF process: indeed, the surface temperature of the particles was in the range 1900–2000  $^{\circ}$ C (Table 7), i.

e. above the melting range of all matrices. Consequently, compositionally heterogeneous areas could dissolve and mix in the liquid state, aided by the extensive flow as the particles impinged at  $\sim$ 650 m/s (Table 7), quickly spreading out into the thin lamellae seen in Fig. 2b, d, f, h.

The second change was that oxide inclusions formed as elongated features around lamellae (Fig. 2b, d, f, h). Their fraction could not be quantified reliably by image analysis because in the SEM micrographs their backscattering contrast was similar to that of TiC. A weak signal from the oxide phases also appeared in the XRD patterns of the as-deposited coatings (Fig. 3a-d, Table 5), revealing the formation of a cubic MO phase (especially in the AlCu+TiC coating) and of an MTiO<sub>3</sub> ilmenite-type oxide (in the other samples). The oxide amounts computed by Rietveld refinement (Table 5) were anyway quite low, compared to the visual appearance of the cross-sectional SEM micrographs (Fig. 2b, d, f, h). Probably, XRD underestimated the oxide content owing to the weaker scattering of oxides relative to the transition metal-rich matrix. Therefore, the diffraction intensities of the oxide inclusions were not proportional to their volume fraction. A quantification of the oxygen content by EDX analysis (again with all the limitations associated with the quantification of light elements) showed a significant oxygen content of 5–7 mass % in the TiC-HEA coatings (Table 4). Oxidation could be regarded as another consequence of the high particle temperatures during HVOF, which accelerated the reactions with all oxidizing agents. The latter include not only environmental oxygen, but also the water vapour produced by the hydrogen-oxygen combustion in the HVOF process. Oxidation could take place both during the flight period and immediately after deposition, until the spread-out lamella was still hot enough to oxidize rapidly. This type of oxidation was identically seen in



**Fig. 4.** Specific wear rates of the coated samples (a), the ball counterpart (b), and average steady-state friction coefficients (c) measured in the ball-on-disc tests. Missing bars in panel (b) indicate that ball wear is not measurable due to the absence of a proper wear scar. Data for the AlCu+TiC composition at room temperature is from [20].



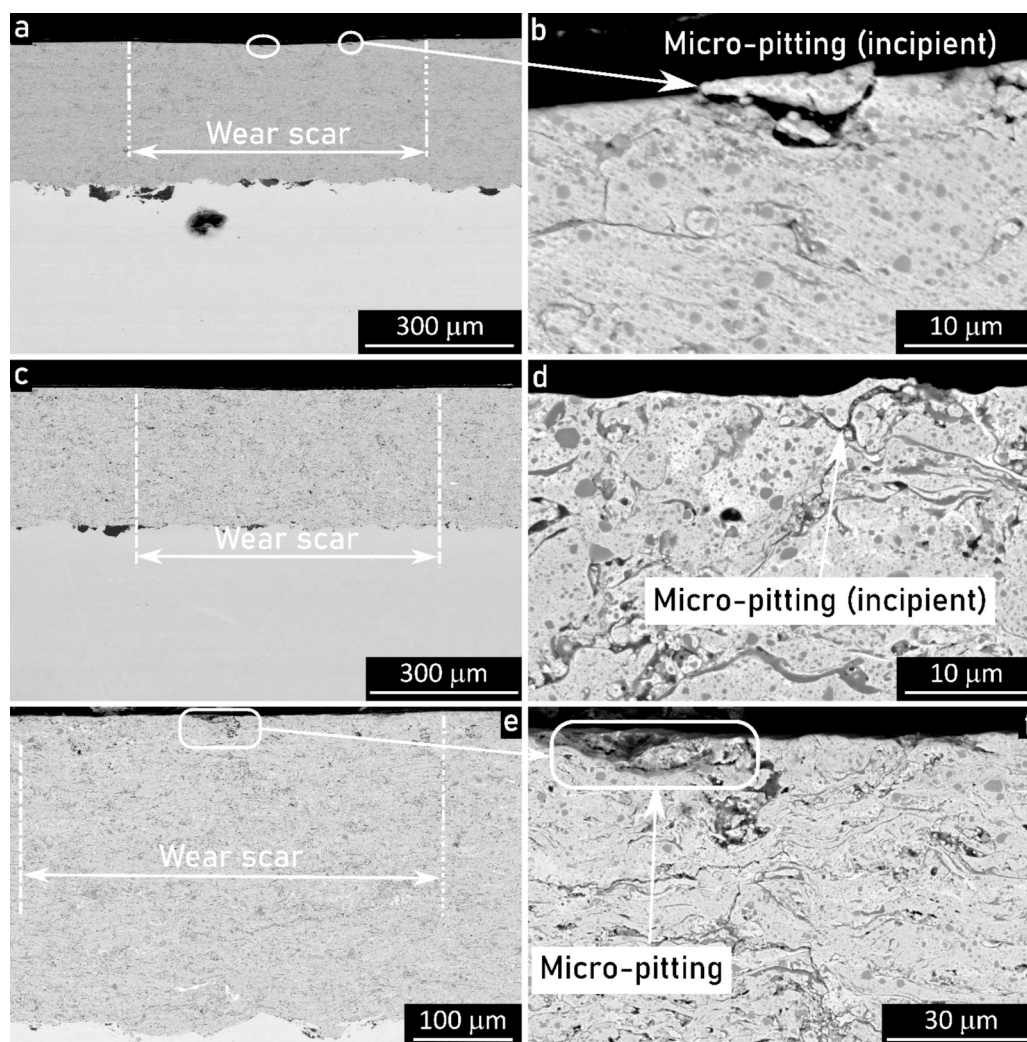
**Fig. 5.** SEM micrographs showing the morphologies of the wear traces produced after ball-on-disc tests at room temperature on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h), and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) coatings – overviews at 400× magnification (a, c, e, g, i) and details at 10000× magnification (b, d, f, h, j). Examples of the main features are marked and labelled on the micrographs.

all the TiC-based hardmetal formulations we studied in the past, with both “standard” and HEA matrices [14–16,20].

Interestingly, there were much fewer oxide inclusions in the Cr<sub>3</sub>C<sub>2</sub>-NiCr coating (Fig. 2i, j). XRD patterns (Fig. 3e and Table 5) identified a small amount of Cr<sub>2</sub>O<sub>3</sub>, but the EDX analyses showed only approximately 2.6 mass % oxygen in the Cr<sub>3</sub>C<sub>2</sub>-NiCr coating. The surface

temperatures of the sprayed particles were basically the same in all cases (Table 7). The Cr<sub>3</sub>C<sub>2</sub>-NiCr particles were also quite porous, i.e., they had a high specific surface area to interact with oxidizing agents. There can be two reasons why, notwithstanding these considerations, the TiC-HEA particles oxidized more than Cr<sub>3</sub>C<sub>2</sub>-NiCr. One is that the HEBM particles, with their high strain levels and, therefore, numerous lattice defects,





**Fig. 6.** SEM micrographs showing the cross-section of the wear traces produced after ball-on-disc tests at room temperature on the AlCu+TiC (a, b), AlMo+TiC (c, d), and AlCuMo13 + TiC (e, f) coatings – overviews at 400 $\times$  magnification (a, c, e) and details at 20000 $\times$  magnification (b, d, f). Examples of the main features are marked and labelled on the micrographs.

were particularly reactive toward oxygen. The same consideration was made for example to justify the substantially higher oxidation degree of HVOF-sprayed HEA coatings compared with Stellite coatings [57]. The other possible explanation is that the main oxidation products of  $\text{Cr}_3\text{C}_2\text{-NiCr}$  were Cr oxides, which, at very high temperatures, are known to transform into volatile  $\text{CrO}_3$ . Therefore,  $\text{Cr}_3\text{C}_2\text{-NiCr}$  may have in fact oxidized during spraying, but only a fraction of the resulting products was retained in solid form as  $\text{Cr}_2\text{O}_3$  within the coating, while most of it was volatilized.

Despite the high particle temperatures (Table 7) and complete matrix melting, fine TiC grains, including nanometric ones, were retained in the coatings (Fig. 2b, d, f, h), and TiC remained the main crystalline phase (Fig. 3a-d, Table 5). The decarburized  $\text{TiC}_{1-x}$  phase with hexagonal lattice was almost entirely absent, except for a small fraction in the AlCu+TiC coating. However, in some of the Mo-containing compositions, Rietveld quantification suggested an implausible increase in TiC fraction from powder to coating (Table 5). While a good retention of the TiC phase was expected based on the SEM micrographs, the overall amount of TiC should have decreased slightly due to dissolution in the molten matrix, as it did in the AlCu+TiC composition. Most likely, the seemingly increased fraction of TiC in some of the coatings was an artefact caused by the formation of some amorphous phase after spraying. Because Rietveld refinement accounts only for crystalline phases, any amorphous material causes the crystalline phase fractions to

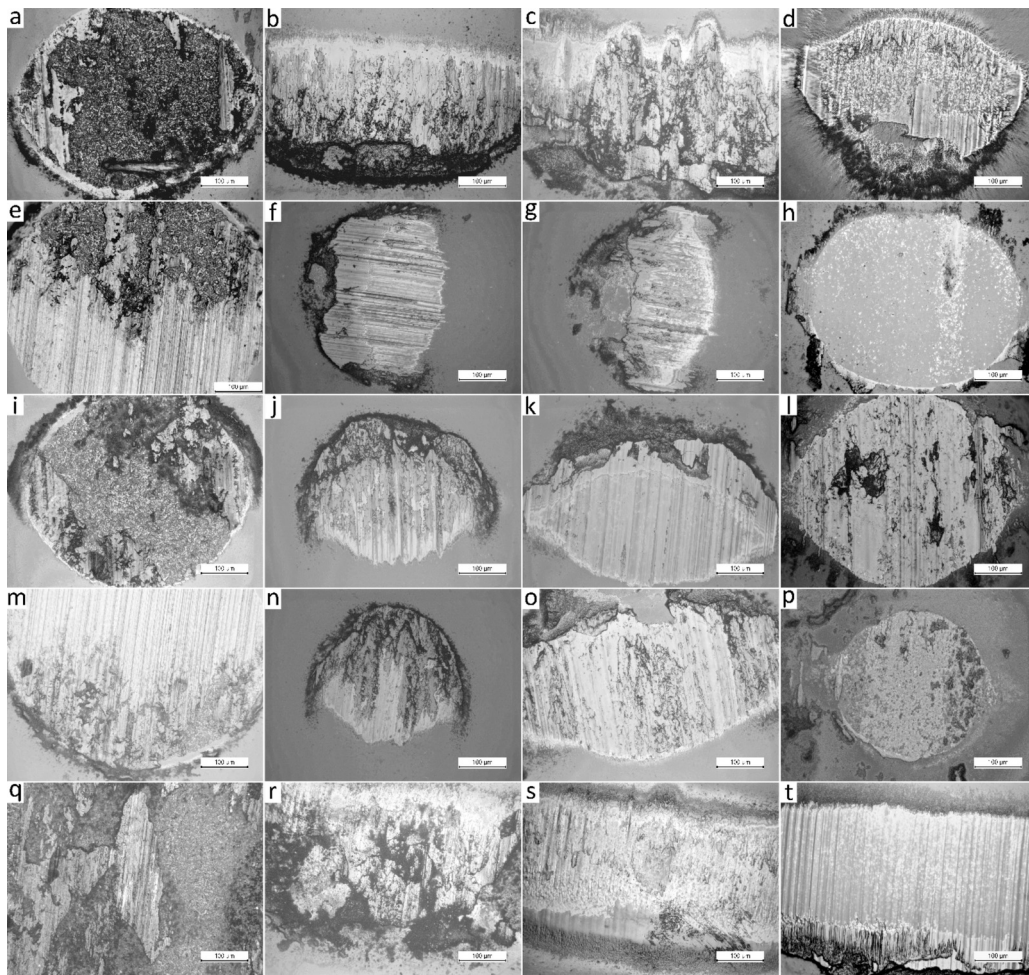
be overestimated when normalized to 100%. This was probably the case for the samples in this work. Rapid cooling and an alloy composition featuring elements with different atomic radii are two of the factors known to promote amorphization of a metal alloy [58]. As shown in Table 1, the average atomic radius mismatch in the present HEA compositions was, in fact, relatively limited. Nonetheless, the combination of Mo and Al, with their larger atomic radii, together with a slight amount of C released by the dissolution of TiC, with its low atomic radius, could fulfil at least in part the second condition. Impact-quenching provided for the first condition, i.e., the high cooling rate.

As a final note, the phase composition of  $\text{Cr}_3\text{C}_2\text{-NiCr}$  was also affected by the spraying process (Fig. 3e, Table 5). Apart from a significant broadening of the diffraction peaks of the Ni-based matrix due to impact-quench grain refinement, the overall carbide fraction decreased, probably due to dissolution, decarburization, and rebounding of the coarse carbide particles [59]. The fraction of  $\text{Cr}_7\text{C}_3$  also increased at the expense of  $\text{Cr}_3\text{C}_2$ , consistent with decarburization. Overall, chromium carbides appear more strongly affected by HVOF spraying than TiC.

### 3.2. Sliding wear results

Across the investigated temperature range, all TiC-HEA coatings exhibited lower specific wear rates than the  $\text{Cr}_3\text{C}_2\text{-NiCr}$  benchmark (Fig. 4a). At room temperature, TiC-HEA wear rates clustered around





**Fig. 7.** Optical micrographs (200 $\times$  magnification) of the wear scars on the  $\text{Al}_2\text{O}_3$  ball after testing against AlCu+TiC (a–d), AlMo+TiC (e–h), AlCuMo10 + TiC (i–l), AlCuMo13 + TiC (m–p), and  $\text{Cr}_3\text{C}_2\text{-NiCr}$  (q–t) at room temperature (a, e, i, m, q), 400  $^\circ\text{C}$  (b, f, j, n, r), 600  $^\circ\text{C}$  (c, g, k, o, s), and 800  $^\circ\text{C}$  (d, h, l, p, t). All scalebars correspond to 100  $\mu\text{m}$ .

$(1.5\text{--}2.0) \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ . With increasing temperature, AlCu+TiC showed a pronounced increase to  $\sim 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$  at 400–600  $^\circ\text{C}$ , followed by a decrease to  $\sim 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  at 800  $^\circ\text{C}$ . In contrast, the Mo-containing compositions retained specific wear rates  $\leq 3 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  throughout, and specifically fell below  $1 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  at 400  $^\circ\text{C}$ . The  $\text{Cr}_3\text{C}_2\text{-NiCr}$  benchmark showed a monotonic increase in specific wear rate with temperature, reaching  $\sim 4 \times 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$  at 800  $^\circ\text{C}$ , i.e. over one order of magnitude higher than the TiC-HEA coatings at the highest test temperature. It is noteworthy that the specific wear rates of the TiC-HEA coatings were of the same order of magnitude as for previous TiC-based systems [14–16] tested against an  $\text{Al}_2\text{O}_3$  counterpart at 10 N load, but using a 6 mm-diameter ball instead of a 3 mm-diameter one as in the present work. This means that the TiC-HEA coatings could withstand reasonably well the higher contact pressures we employed here through the use of a smaller ball. By contrast, the specific wear rates of the  $\text{Cr}_3\text{C}_2\text{-NiCr}$  benchmark were almost one order of magnitude higher than the values we had measured with a 6 mm-diameter  $\text{Al}_2\text{O}_3$  ball (always at 10 N load) [10,60], indicating a significant deterioration of the tribological response under a higher contact pressure.

The trends in terms of specific wear rates experienced by the  $\text{Al}_2\text{O}_3$  ball (Fig. 4b) were similar for all four TiC-HEA coatings. At room temperature, the specific wear rate of the ball was always around  $(3\text{--}6) \times 10^{-8} \text{ mm}^3/(\text{N}\cdot\text{m})$ , while no measurable wear occurred at 400  $^\circ\text{C}$  and 600  $^\circ\text{C}$ . At 800  $^\circ\text{C}$ , the wear loss of the ball became measurable again, though the specific wear rate values were very low,  $< 1 \times 10^{-8} \text{ mm}^3/$

(N·m). The  $\text{Cr}_3\text{C}_2\text{-NiCr}$  reference caused more severe wear to the ball at room temperature ( $\sim 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ ), but no measurable wear at 400  $^\circ\text{C}$ , 600  $^\circ\text{C}$ , and 800  $^\circ\text{C}$ .

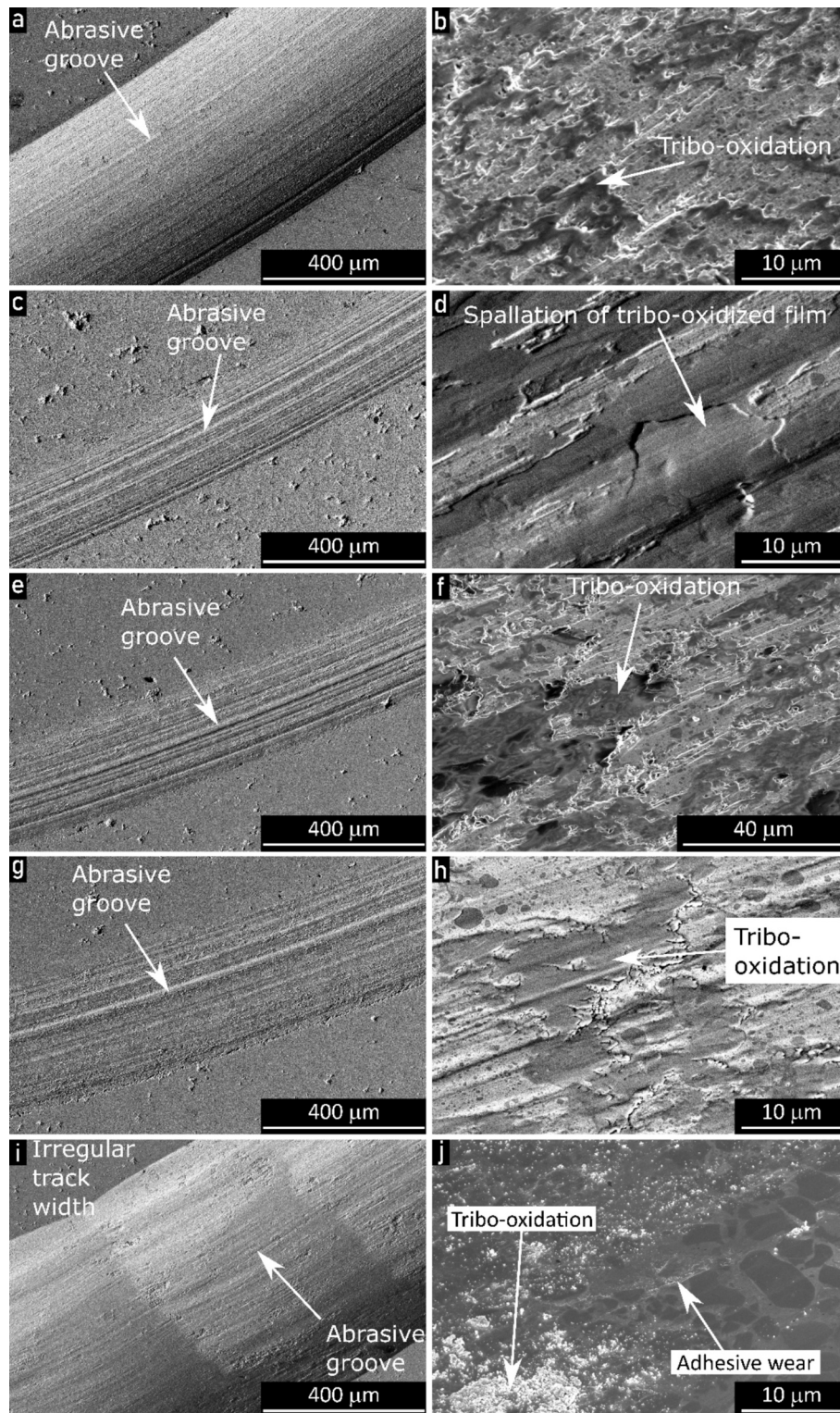
Friction decreased with increasing temperature for all coatings (Fig. 4c). At room temperature, the TiC-HEA coatings produced higher friction ( $\sim 0.7\text{--}0.8$ ) against the  $\text{Al}_2\text{O}_3$  counterbody than did the  $\text{Cr}_3\text{C}_2\text{-NiCr}$  benchmark ( $\sim 0.5$ ). The difference narrowed at higher temperatures, because the friction coefficient produced by the TiC-HEA coatings decreased more markedly. At 800  $^\circ\text{C}$  the Mo-containing coatings produced even less friction ( $\sim 0.3$ ) than the benchmark ( $\sim 0.4$ ), while the AlCu+TiC composition produced a slightly higher friction coefficient of  $\sim 0.44$ .

### 3.3. Sliding wear mechanisms

#### 3.3.1. TiC-HEA coatings at room temperature

The above trends can be interpreted in light of the wear mechanisms. At room temperature (Fig. 5a–h), all TiC-HEA coatings exhibited a combination of surface fatigue and abrasive wear, as indicated by micro-pits and shallow grooves, respectively. Micro-pitting was probably favoured by the relative brittleness of the coatings at room temperature. Under cyclic loading, microcracks initiated (e.g., Fig. 5g) and propagated in a brittle manner especially along lamellar boundaries (as seen particularly in Fig. 5d), leading to the detachment of small fragments with limited evidence of ductile deformation. Cross-sectional views of the wear tracks, shown in Fig. 6 for some of the present coatings,





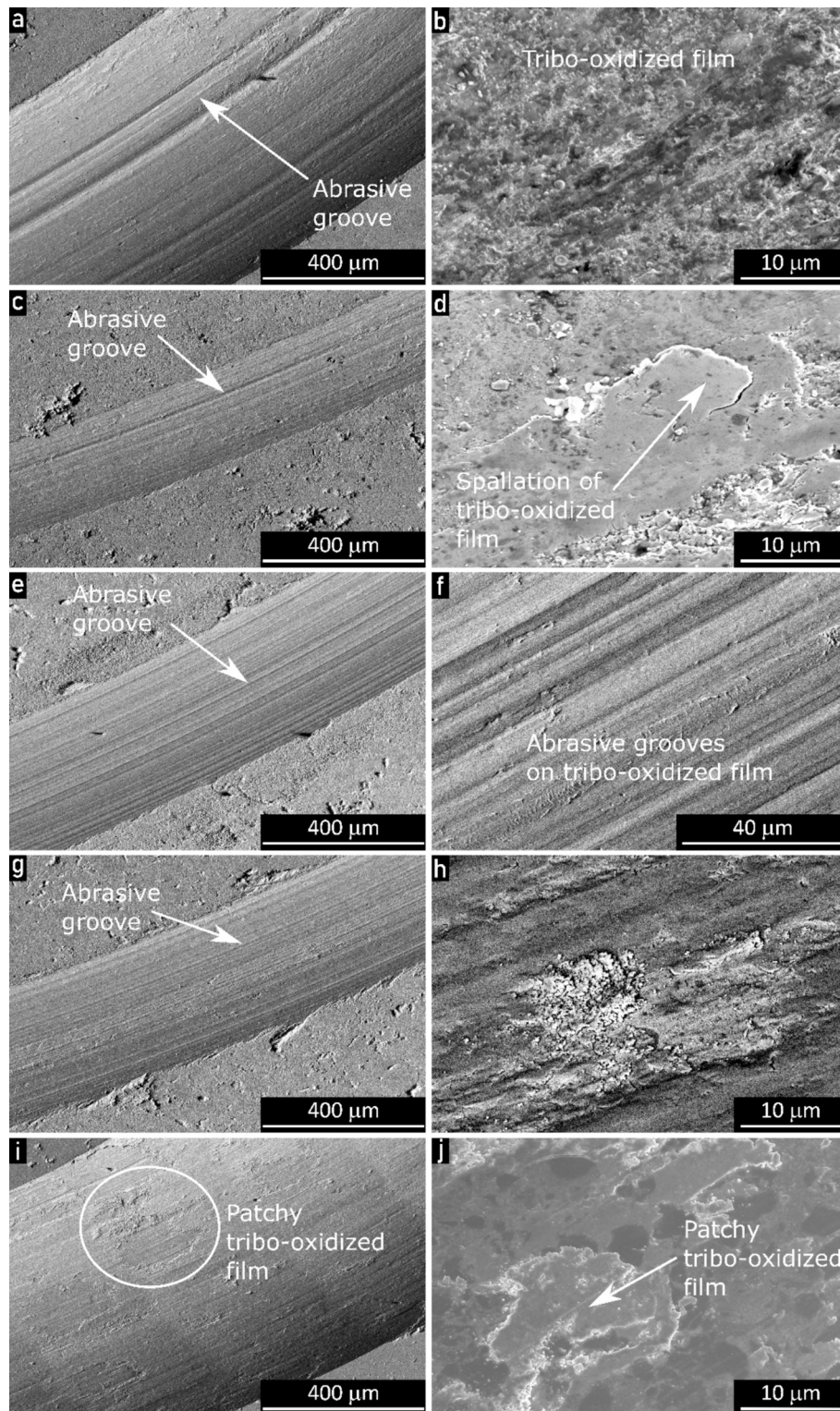
**Fig. 8.** SEM micrographs showing the morphologies of the wear traces produced after ball-on-disc tests at 400 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h), and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) coatings– overviews at 400× magnification (a, c, e, g, i) and details at 10000× magnification (b, d, f, h, j). Examples of the main features are marked and labelled on the micrographs.

confirmed that pits were generally confined to small areas and that cracks followed pre-existing interlamellar interfaces, consistent with the mild wear rates seen in Fig. 4a. Abrasion was probably a secondary mechanism and was promoted by the concurrent roughening of the Al<sub>2</sub>O<sub>3</sub> counterbody, which, as seen in the optical micrographs of Fig. 7a, a, e, i, m, q, was due to wear and the build-up of an irregular layer of

transferred material.

Interestingly, the Mo-containing samples exhibited more micro-pits (Fig. 5c, e, g) than the AlCu+TiC sample (Fig. 5a). This may be due to the presence of an amorphous phase, as discussed in Section 3.1, since amorphous metallic phases are definitely more brittle than a crystalline FCC phase. Specifically, the AlMo+TiC coating (Fig. 5c) exhibited a



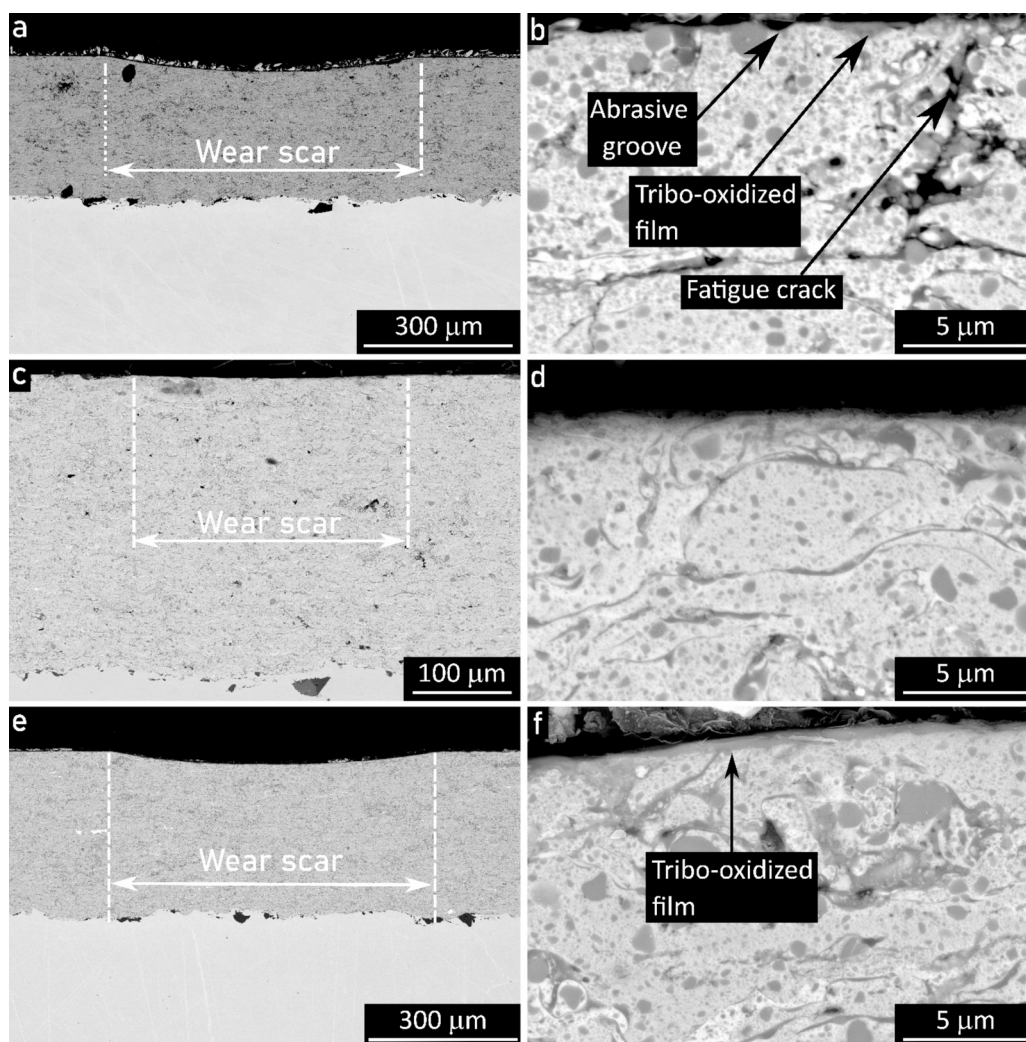


**Fig. 9.** SEM micrographs showing the morphologies of the wear traces produced after ball-on-disc tests at 600 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h), and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) coatings– overviews at 400× magnification (a, c, e, g, i) and details at 10000× magnification (b, d, f, h, j). Examples of the main features are marked and labelled on the micrographs.

somewhat broader wear track, with the most micro-pitting among all samples. However, its specific wear rate was comparable to the other samples (Fig. 4), i.e. the wear track was also a bit shallower than the others. This may be due to the fact that this coating, though suffering from more micropitting, experienced less severe abrasive grooving. It would be consistent with its slightly higher hardness (Table 6).

In addition to surface fatigue and abrasion, a third mechanism operated on all systems in i.e., tribo-oxidation. The formation of patchy oxide layers on the worn surfaces is suggested by the optical micrographs of the counterparts (Fig. 7a, a, e, i, m, q), showing transfer material with dark colour, indicative of the formation of oxides. SEM views of the wear traces on the coatings also show patches of material with a





**Fig. 10.** SEM micrographs showing the cross-section of the wear traces produced after ball-on-disc tests at 400 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), and AlCuMo13 + TiC (e, f) coatings – overviews at 400× magnification (a, c, e) and details at 20000× magnification (b, d, f). Examples of the main features are marked and labelled on the micrographs.

darker contrast (Fig. 5). Some EDX spectra of these patches are shown in the Supplementary Material (Fig. S3 and Fig. S4 for the AlCuMo10 + TiC and AlCuMo13 + TiC samples, respectively). They confirmed that the dark patches consisted predominantly of oxides of the coating material (Fig. S3a: spectra 1–5; Fig. S4a: spectra 1–3). The oxide patches did not contain significantly more Al than the surrounding material (Fig. S3a: spectra 7–8; Fig. S4a: spectrum 4). Indeed, the wear loss of the ball was almost two orders of magnitude lower than that of the coating (Fig. 4a, b); hence, the ball did not meaningfully contribute to the overall volume of debris in the tribosystem. Tribo-oxidation was most likely due to a low-speed mechanism [61], given the limited sliding velocity employed in this work. Namely, the debris caught between the mating bodies became highly reactive through repeated fragmentation, and it eventually oxidized in contact with the environmental air.

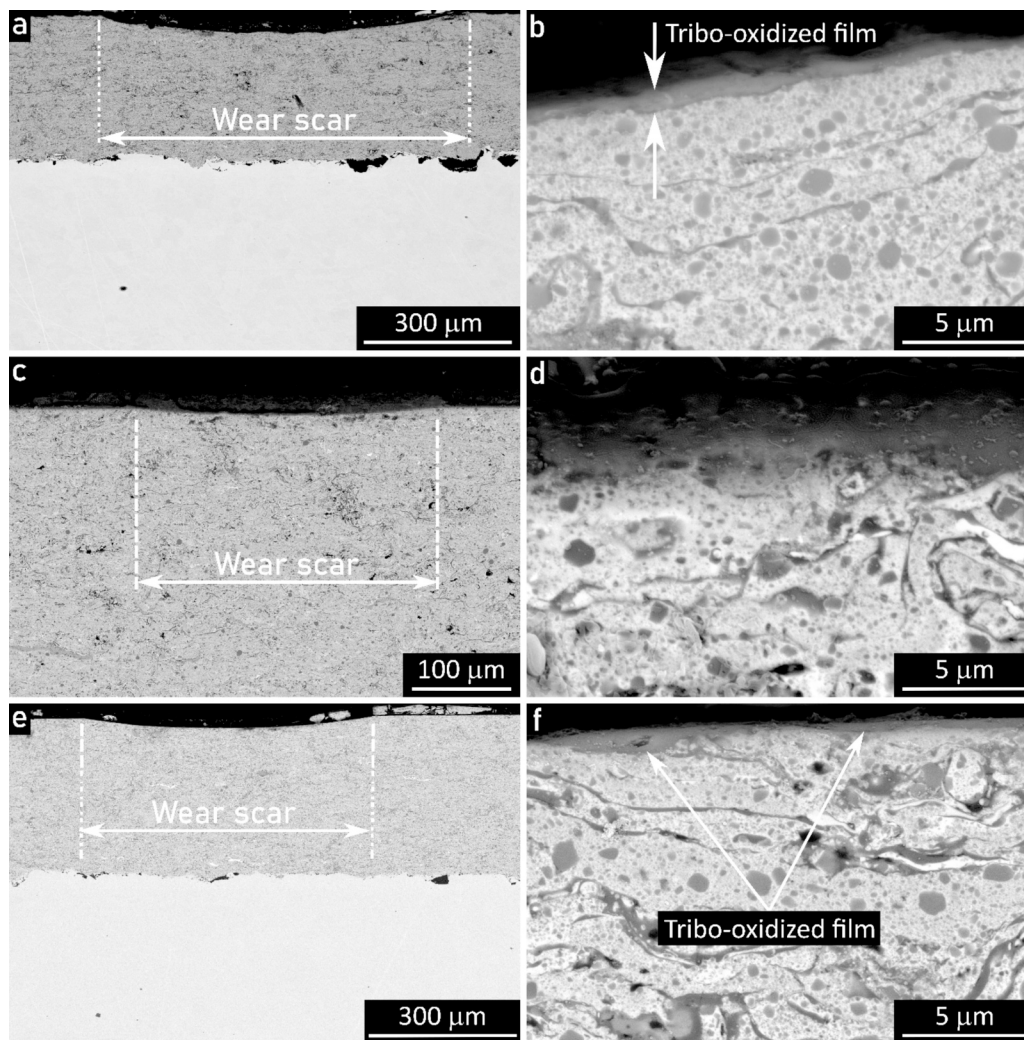
Raman spectra (Fig. 14) indicated that the oxides mainly comprised MTiO<sub>3</sub> titanates, where M stands for one or more transition metals, and, in the Mo-containing compositions, molybdates. Specifically, the main Raman peak around 700 cm<sup>-1</sup> and the weaker bands around 600 cm<sup>-1</sup>, 400 cm<sup>-1</sup>, 350 cm<sup>-1</sup> and 300 cm<sup>-1</sup> that appeared in all the spectra of Fig. 14 belonged to the vibration modes of the [TiO<sub>6</sub>] coordination octahedron in titanates [62]. Additional bands between 830 cm<sup>-1</sup> and 930 cm<sup>-1</sup> in the spectra of the Mo-containing coatings (Fig. 14b–d) could be attributed to the vibration modes of the [MoO<sub>4</sub>] coordination structure in molybdates [63]. The detection of compounds such as titanates and

molybdates, which, though being based on the most abundant constituents of each coating (Ti, Mo), also comprised various other cations, was consistent with their elemental composition (Fig. S3a, spectra 1–5; Fig. S4a, spectra 1–3). The proportions among the various metallic elements were indeed approximately the same as in the base material. This is consistent with a tribologically induced oxidation reaction that affected the entirety of the debris particles. All constituents thus participated to this process, as opposed to a more selective oxidation, characteristic of a spontaneous (not tribologically induced) process. The breadth of the Raman peaks, suggesting poor crystallinity, was also consistent with the intense mechanical action that the debris particles were subjected to during the low-speed tribo-oxidation process.

Despite the compositional dependent differences among the tribologically induced oxides, their influence on the behaviour of the coatings was probably limited, as testified by the very similar wear rate values. This was probably due to the irregular and patchy nature of the tribo-films formed on the wear traces of the coatings at room temperature, which offered limited protection against the contact with the counterface.

### 3.3.2. TiC-HEA coatings at high temperatures

Increasing the test temperature to 400 °C and 600 °C produced three main changes. First, surface fatigue (micro-pitting) was largely suppressed in all coatings (Fig. 8a–h, Fig. 9a–h). Cross-sections also no



**Fig. 11.** SEM micrographs showing the cross-section of the wear traces produced after ball-on-disc tests at 600 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), and AlCuMo13 + TiC (e, f) coatings – overviews at 400× magnification (a, c, e) and details at 20000× magnification (b, d, f). Examples of the main features are marked and labelled on the micrographs.

longer showed the detachments of small fragments observed at room temperature (Fig. 10, Fig. 11). Only in Fig. 10b could a microcrack be seen near the surface of the AlCu+TiC sample. Second, abrasive grooves deepened, particularly for AlCu+TiC, which also exhibited the highest wear loss among the TiC-HEA coatings, to the point that the grooves could sometimes be recognized also on its cross-sectional view (Fig. 10b). Third, tribofilm coverage increased, indicating greater role of tribo-oxidation; however, the extent of coverage depended on the composition.

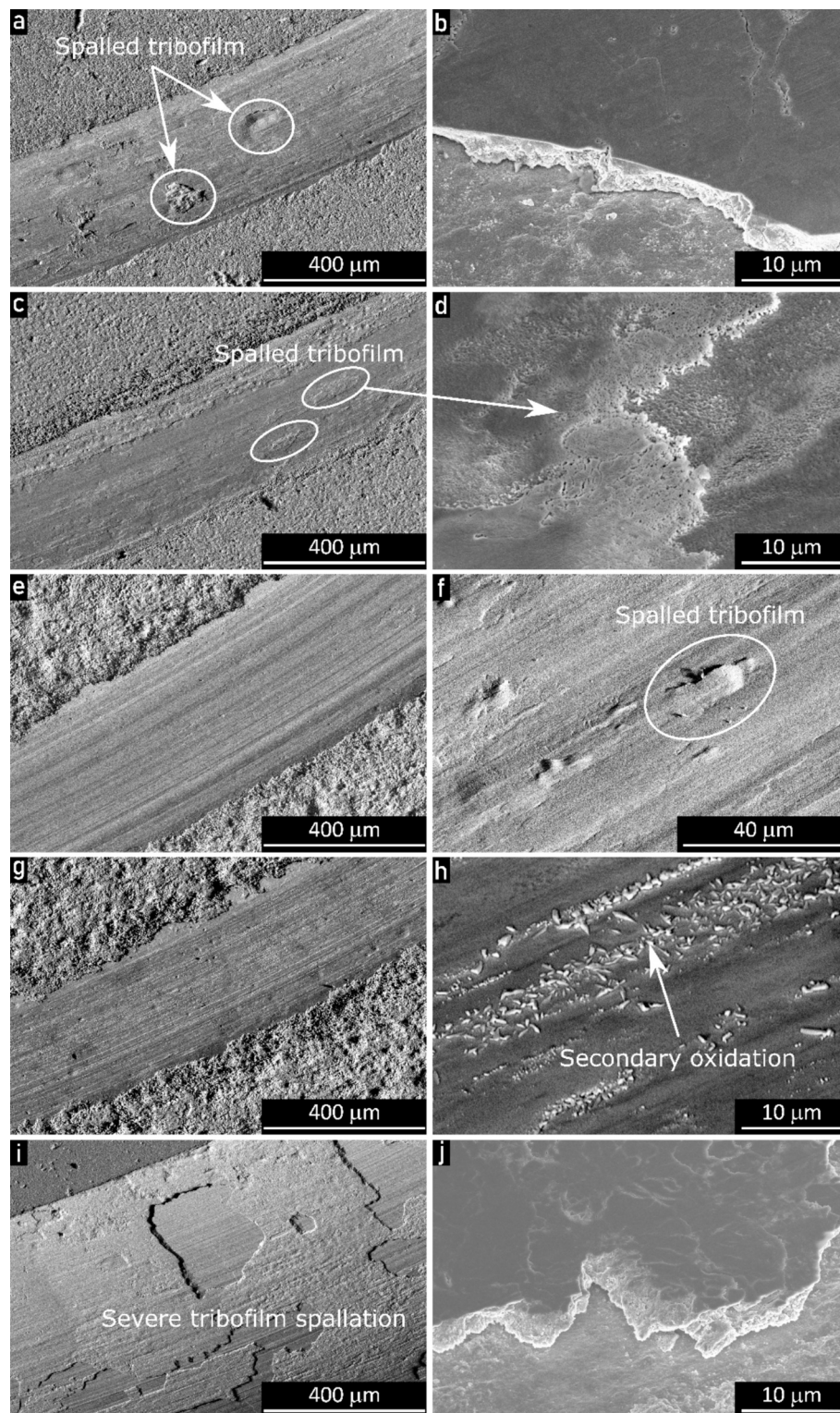
At 400 °C, AlCu+TiC still showed a discontinuous film (Fig. 8b and Fig. 10b), whereas AlMo+TiC developed very continuous tribofilm (Fig. 8d), although it was so thin that it was barely visible on the cross-section (Fig. 10d). The AlCuMo10 + TiC (Fig. 8e, f) and AlCuMo13 + TiC (Fig. 8g, h, Fig. 10e, f) compositions represented an intermediate situation, where the tribofilm was not fully continuous, but provided better coverage than on the AlCu+TiC coating. The comparison between the cross-sectional views of the film on the AlCu+TiC (Fig. 10b) and the AlCuMo13 + TiC (Fig. 10f) coatings also corroborated this observation. The more protective films on the Mo-containing coatings probably explained their lower wear loss (Fig. 4a).

EDX showed that tribofilms retained the overall elemental proportions of the base material (Supplementary Material, Fig. 3b: spectra 2 and 4; Fig. 4b: spectra 1–3, 5, 7). Raman spectra further distinguished these tribofilms (Fig. 15b, d, f, h) from the thermally grown oxides

outside the wear track (Fig. 15a, c, e, g), confirming that the oxides within the track were tribologically induced. In fact, the Raman spectra acquired outside the wear scar changed from point to point, reflecting the formation of different oxides on distinct phases. XRD patterns (Fig. 3a–d) did not assist much with the identification of the thermally grown oxides, because they were too thin and could not produce a significant diffraction signal. On the other hand, the Raman spectra revealed titanium oxides, including rutile and anatase, which were the result of the oxidation of the TiC particles, and Fe-based oxides, mainly  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and, secondarily, spinel oxides, which grew on the matrix. In contrast with the point-by-point variability of the outer scale, each tribofilm always returned consistent spectra, characterized by broad bands, again indicative of the poor crystallinity caused by the repeated action of contact stresses. The band around 700 cm<sup>-1</sup> could be assigned to titanates and/or spinel oxides (without secondary peaks, this band cannot be assigned unambiguously to either phase), the band around 830 cm<sup>-1</sup> in the Mo-containing samples belonged to molybdates. Thus, once again, these films were the result of the tribologically induced oxidation of debris fragments.

The findings from Raman spectroscopy also indicated a correlation between the more uniform tribofilms on the Mo-containing compositions and the formation of molybdates. Whether this was a causative correlation, namely whether the uniformity of the tribofilm was indeed due to the presence of molybdates, cannot be ascertained



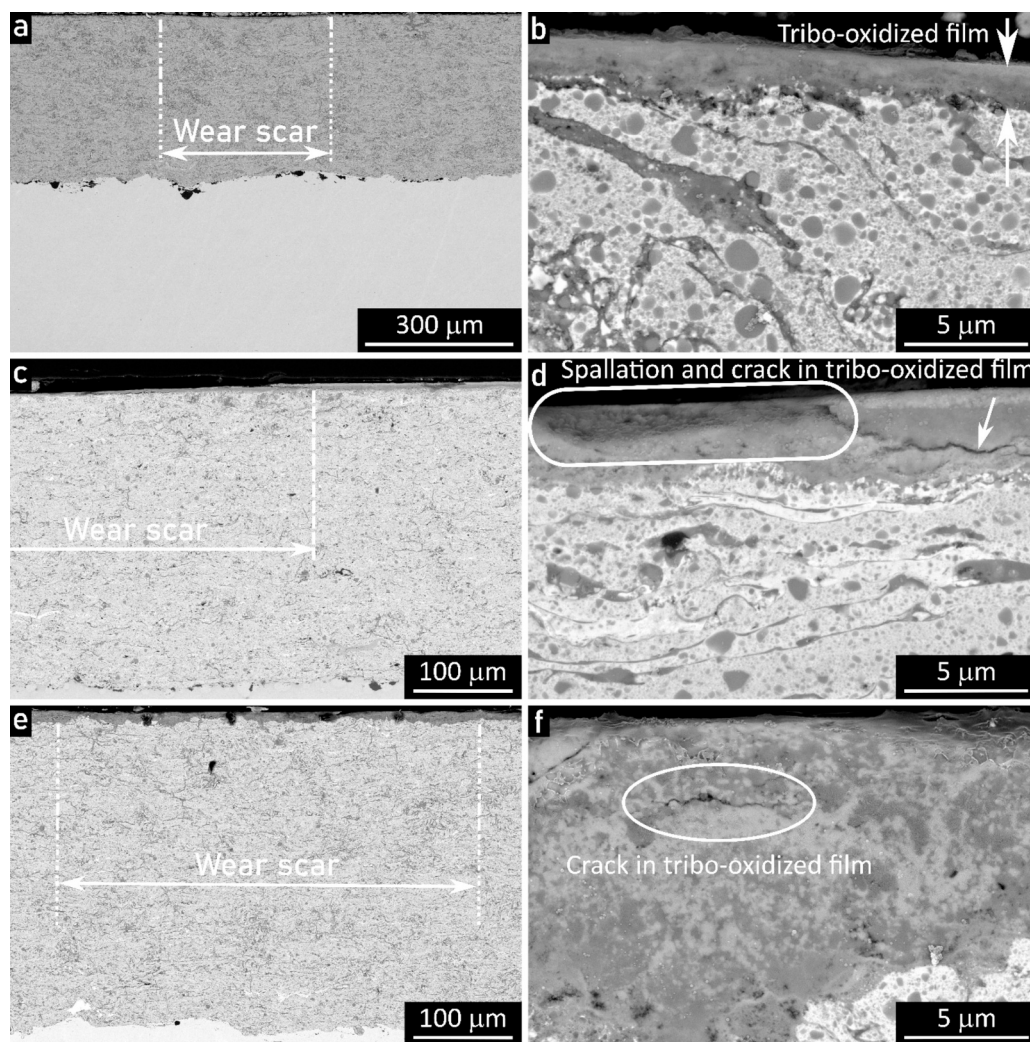


**Fig. 12.** SEM micrographs showing the morphologies of the wear traces produced after ball-on-disc tests at 800 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), AlCuMo13 + TiC (g, h), and Cr<sub>3</sub>C<sub>2</sub>-NiCr (i, j) coatings– overviews at 400× magnification (a, c, e, g, i) and details at 10000× magnification (b, d, f, h, j). Examples of the main features are marked and labelled on the micrographs.

unambiguously, but many types of molybdates are known to be high-temperature solid lubricants. They can be easily smeared along a wear track during sliding because of their layered structure, which allows shearing along planes with weaker bonding [39,64]. From a crystal-chemistry point of view, molybdates consist of the combination of a cation ( $\text{Mo}^{6+}$ ) with high ionic strength, i.e. high charge/radius ratio, and

a cation (a transition metal cation like  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.) with smaller ionic strength [65].  $\text{O}^{2-}$  anions form a tight coordination shell around the cations with high ionic strength and thus effectively shield them. Consequently, the coordination shells are bound only by bridges formed by the cations with lower charge/radius ratio: this bonding can be weakened at high temperature, allowing the material to flow plastically





**Fig. 13.** SEM micrographs showing the cross-section of the wear traces produced after ball-on-disc tests at 800 °C on the AlCu+TiC (a, b), AlMo+TiC (c, d), and AlCuMo13 + TiC (e, f) coatings – overviews at 400× magnification (a, c, e) and details at 20000× magnification (b, d, f). Examples of the main features are marked and labelled on the micrographs.

under a shear stress [66].

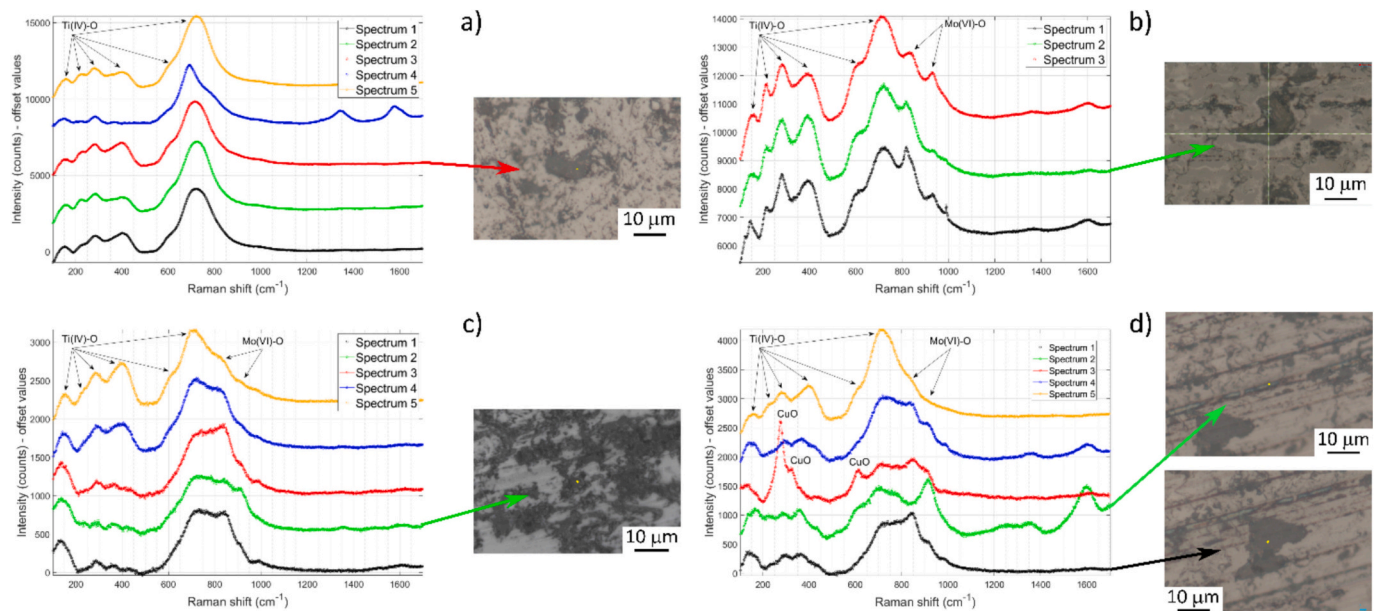
At 600 °C, tribofilms became largely continuous in all coatings (Fig. 9a–h), being often clearly visible in the cross-section as well (Fig. 11b, f). Wear proceeded mainly by abrasion of the tribofilms – abrasive grooves were visible in the low-magnification views of Fig. 9a, c, e, g – and spallation, as seen especially in the magnified views of Fig. 9d. Despite the continuity of all tribofilms, the Mo-containing coatings maintained lower wear rates, as previously noted in Section 3.2 and Fig. 4a. Their tribofilms indeed still contained molybdates, as revealed by the micro-Raman spectra in Fig. 16d, f, h. In fact, at 600 °C the molybdate peaks became even stronger, in proportion to the titanate peak, than at 400 °C. On the other hand, the AlCu+TiC coating still developed a tribofilm based only on titanates (Fig. 16b). Thus, the better protectiveness of the molybdate-rich tribofilms in comparison to the one based only on titanates seems to be confirmed by the results at 600 °C.

Moreover, the difference between the Raman spectra of the tribofilms (Fig. 16b, d, f, h) and those of the thermally grown scale outside the wear traces (Fig. 16a, c, e, g) were again consistent with the distinction between tribologically induced oxidation and spontaneous oxidation. The tribofilms were structurally homogeneous: all Raman spectra for a given sample were basically the same. Their elemental composition, shown in the Supplementary Material, contained a mix of all coating constituents, like at 400 °C: this is shown e.g. by Fig. S3c – spectrum 2 for the AlCuMo10 + TiC sample and Fig. S4c for the AlCuMo13 + TiC

sample, but analogous observations are also true for the other samples. By contrast, the Raman spectra of the thermally grown scales showed point-to-point variability (Fig. 16a, c, e, g), with multiple oxide species reflecting the oxidation of distinct phases. Compared with the thermally grown oxide scales formed at 400 °C, the Raman signal from the scales formed at 600 °C was more intense, indicating higher thickness. The scales at 600 °C contained variable proportions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (particularly in the AlMo+TiC sample) and spinel oxides, primarily due to oxidation of Fe; in addition, they exhibited the rutile and, sometimes, anatase polymorphs of TiO<sub>2</sub>, and the Cu-containing compositions also formed some CuO. There were also Raman peaks belonging to titanates (Fig. 16a, c, e, g), which did not exist in the scales formed at 400 °C (Fig. 15a, c, e, g). Thus, the oxides formed on distinct microstructural constituents started to interact spontaneously with each other at 600 °C to produce mixed compounds even without tribologically induced effects. The XRD signal from the thermally grown oxide scales was still weak at 600 °C (Fig. 3a–d), but a few diffraction peaks indicate the presence of rutile, anatase, MTiO<sub>3</sub>-type titanates, CuO, spinels and hematite, the latter two being especially predominant on the AlMo+TiC sample. Thus, they corroborated the interpretation of the Raman spectra.

The tribologically induced oxides were also identifiable on the ball (Fig. 7b, f, j, n, r for the tests at 400 °C; Fig. 7c, g, k, o, s for the tests at 600 °C), in most cases building up as compacted debris along the leading





**Fig. 14.** Raman spectra acquired in the wear trace produced after ball-on-disc tests at room temperature on the AlCu+TiC (a), AlMo+TiC (b), AlCuMo10 + TiC (c), and AlCuMo13 + TiC (d) coatings. Some of the acquisition areas are shown through the optical micrographs at 1000 $\times$  magnification. In each case, the spectrum came from the centre of the image.

contact edge. The balls retained their curvature and never developed measurable wear traces at 400  $^{\circ}\text{C}$  and 600  $^{\circ}\text{C}$ , indicating a negligible wear loss, as anticipated in Section 3.2 and Fig. 4b. The contact therefore produced a curved, ellipsoidal trace as the sphere penetrated the worn surface of the sample.

At 800  $^{\circ}\text{C}$ , the wear traces were covered by a thick oxide layer (Fig. 12a–h). Cross-sectional views (Fig. 13) show that, in this case, the oxide layer in the wear track was not a tribologically induced film, distinct from the thermally grown oxide outside the wear track. The entire coating was indeed covered by a thermally grown oxide scale several micrometres thick, as seen especially in Fig. 13c, e. The same micrographs showed that sliding contact resulted in the removal of the outer portion of the scale. The mechanisms were mild abrasion and contact fatigue-induced delamination, as seen e.g. in Fig. 12a, c (circled areas with corresponding details in Fig. 12b, d), and in Fig. 12f. A sub-surface delamination crack and a spallation event were also visible in the cross-sectional view of Fig. 13d, and a smaller one appeared in Fig. 13f.

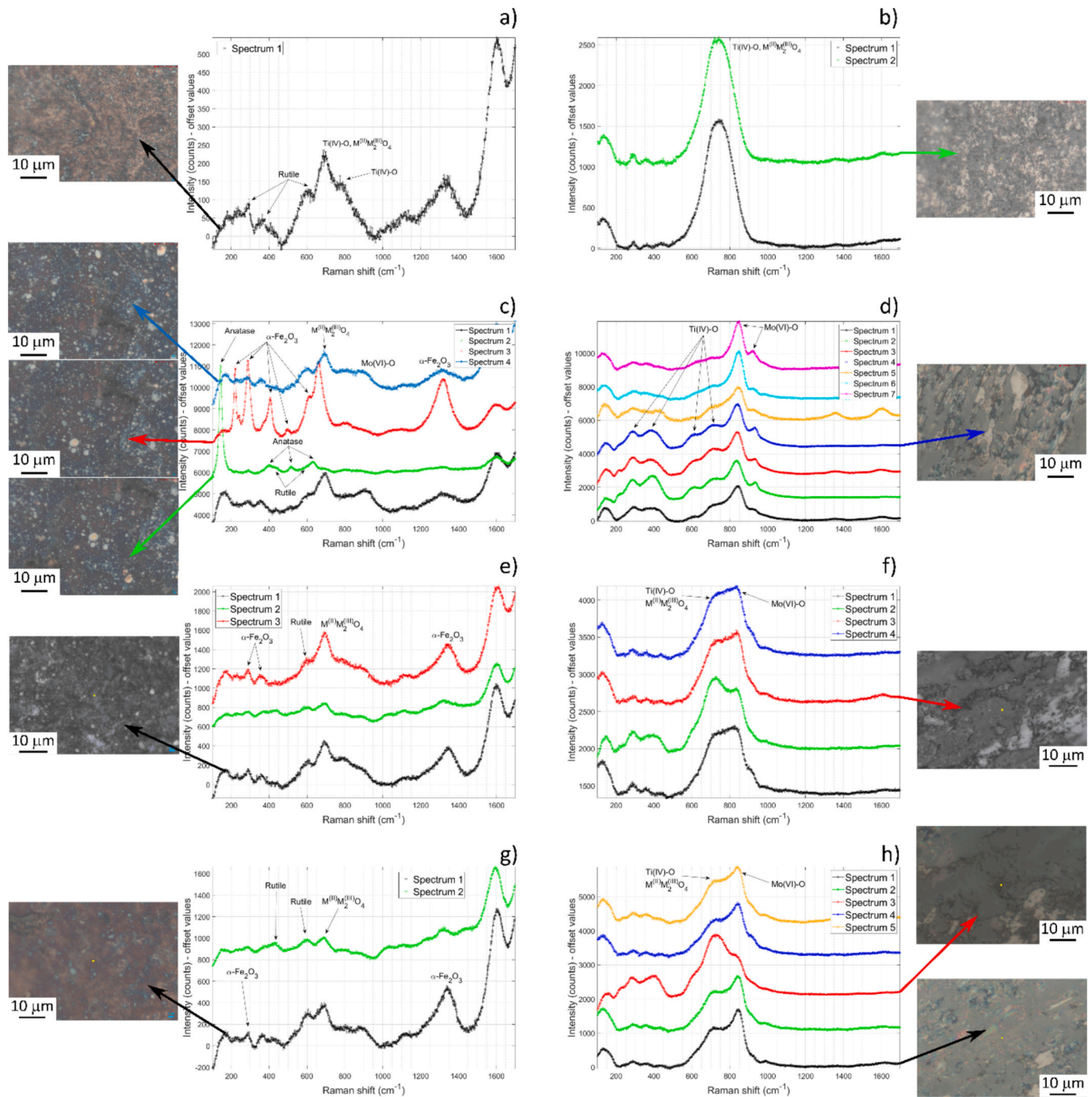
Therefore, in the samples tested at 800  $^{\circ}\text{C}$ , the difference between the Raman spectra acquired inside (Fig. 17b, d, f, h) and outside the wear tracks (Fig. 17a, c, e, g) was not due to the distinction between tribologically-induced and spontaneously grown oxides, but to the removal of the outer portion of the thermally grown oxide during sliding.

The spontaneously grown oxide scale, indeed, had a layered structure, as could be seen through backscattered electron imaging (Supplementary Material, Fig. S5b, d). On the AlCuMo10 + TiC and AlCuMo13 + TiC coatings, the outer layer of the scale comprised CuO and molybdates (Raman spectra in Fig. 17f, h), and indeed, EDX spectra in the Supplementary Material showed that the outer layer on the AlCuMo13 + TiC coating was very rich in Cu and Mo: spectrum 1 in Fig. S5d was presumably a Cu oxide; spectrum 2 was a Cu molybdate. On the AlMo+TiC and AlCu+TiC coatings, the outer layer was especially rich in  $\alpha\text{-Fe}_2\text{O}_3$  and Fe-containing spinels (Raman spectra in Fig. 17a, c), with EDX spectra accordingly showing a high concentration of Fe (Fig. S5b: spectrum 1). Because the scale was a spontaneously grown one, formed at a very high temperature, the Raman peaks were sharp, as opposed to the broad peaks seen in the tribofilms formed at lower temperatures. This was particularly apparent with the molybdate species, which, when formed through a tribologically-induced reaction at

lower temperatures, exhibited very broad Raman bands (panels d, f, h in Fig. 14, Fig. 15, and Fig. 16), while, in the oxide scale formed at 800  $^{\circ}\text{C}$ , they displayed very narrow peaks (Fig. 17c, e, g), consistent with the known spectra of highly crystalline molybdates [63]. The XRD patterns, which returned rather clear diffraction signals from the thick thermally grown scales, consistently showed intense and narrow peaks of molybdates as the main constituents of the scales on AlCuMo10 + TiC (Fig. 3c) and AlCuMo13 + TiC (Fig. 3d), while spinel peaks were the most intense ones on the AlCu+TiC coating (Fig. 3a), and  $\alpha\text{-Fe}_2\text{O}_3$  and spinels prevailed on the AlMo+TiC sample (Fig. 3b).

When the outer layer of the thermally grown scale was removed during wear, the underlying layer, with a different chemical composition, was exposed. For example, titanates and  $\alpha\text{-Fe}_2\text{O}_3$  were the prevailing species in the wear scar of the AlCu+TiC (Fig. 17b) and AlMo+TiC coatings (Fig. 17d). Indeed, both the EDX spectrum 2 in Fig. S5b, which refers to the bottom layer of the outer scale of the AlMo+TiC coating, and the spectra 1–2 in Fig. S5a, which refer to the wear track on the same sample, showed a much higher content of Ti, while spectrum 3 in Fig. S5a presumably corresponded to an  $\alpha\text{-Fe}_2\text{O}_3$  area. Titanates and spinel oxides were the main constituents of the wear scar of the AlCuMo10 + TiC (Fig. 17f) and AlCuMo13 + TiC (Fig. 17h) coatings, and indeed, both the bottom layer of the outer scale of the AlCuMo13 + TiC coating (spectra 4–8 in Fig. S5d) and the wear scar of the same sample (spectra 1–4 in Fig. S5c) showed the co-existence of Ti and various transition metal elements (Cr, Ni, Fe, and Cu).

Because the wear scars formed at 800  $^{\circ}\text{C}$  consisted mainly of the uncovered underlying layers of the respective thermally grown scales, rather than of tribologically induced oxides, they produced narrower Raman peaks than the lower-temperature wear scars (compare the spectra in Fig. 17b, d, f, h to those in the same panels of Fig. 14, Fig. 15, and Fig. 16). Narrowing of the Raman peaks may have been further assisted by healing of any structural defects immediately after the end of the test, when the sample remained in static conditions at high temperature in the initial stages of cooling. In the same stage, the areas where the underlying hardmetal surface may have been directly exposed by complete fracture of the oxide scale could be re-oxidized very quickly. This was especially visible in Fig. 12h, where some coarse-faceted grains appeared along an otherwise smooth wear scar. These faceted grains were similar to those seen outside the wear trace (e.g., see



**Fig. 15.** Raman spectra acquired after ball-on-disc tests at 400 °C, inside the wear trace (a, c, e, g) and on the unworn surface (b, d, f, h), on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), and AlCuMo13 + TiC (g, h) coatings. Some of the acquisition areas are shown through the optical micrographs at 1000× magnification. In each case, the spectrum came from the centre of the image.

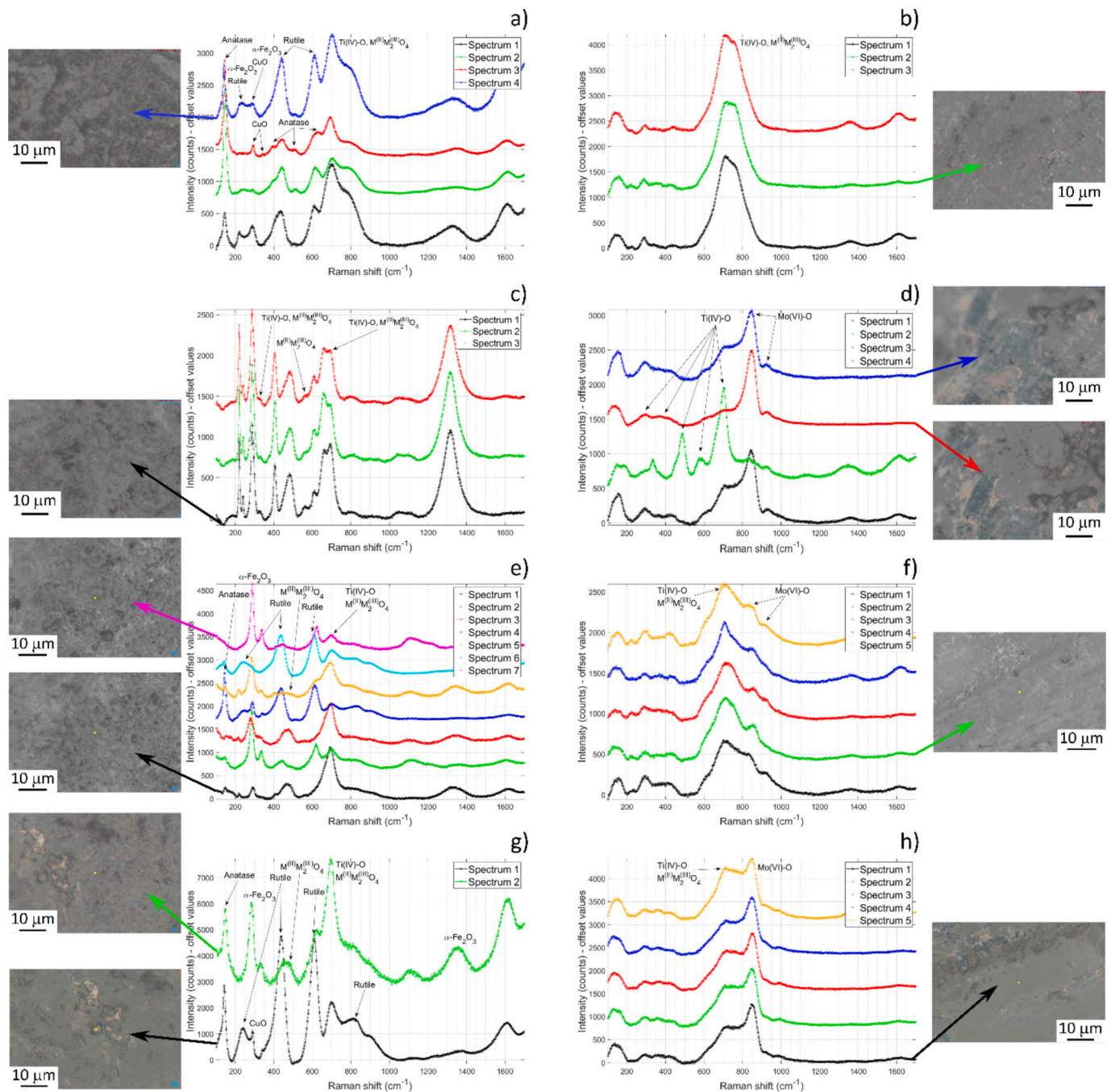
the optical images in Fig. 17). Thus, the faceted grains inside the wear track probably corresponded to a secondary oxidation process, i.e., the growth of new oxide scale immediately after the end of the test, in an area where the pre-existing scale had entirely been spalled off. Therefore, the overall extent of oxide scale delamination during the test may have been greater than it would seem from the SEM micrographs acquired at the end. On the other hand, it can be inferred that at 800 °C, the oxide scale could self-heal quite rapidly. The Raman spectrum 3 in Fig. 17h, also taken on a rougher area in the wear scar (see the associated optical micrograph), showed sharp molybdate peaks similar to those seen on the outer scale (Fig. 17g). This confirmed that the rough

area was a re-growth of the scale immediately after the end of the test, presumably on an uncovered portion of hardmetal surface.

Thus, at 800 °C, the wear behaviour of the coatings was controlled by that of their thermally grown scale. Probably because of the faceted morphology that the scale initially exhibited, coupled with a loss of hardness even of Al<sub>2</sub>O<sub>3</sub> at this temperature, the ball suffered some more wear than at 400 °C and 600 °C, developing a flattened scar by the end of the test (Fig. 7d, h, l, p). For this reason, a specific wear rate could be quantified again for the ball at 800 °C (Fig. 4b).

Clearly, the increasing coverage of the wear tracks with oxides, due to tribologically induced oxidation at 400 °C and 600 °C or to the thick





**Fig. 16.** Raman spectra acquired after ball-on-disc tests at 600 °C, inside the wear trace (a, c, e, g) and on the unworn surface (b, d, f, h), on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), and AlCuMo13 + TiC (g, h) coatings. Some of the acquisition areas are shown through the optical micrographs at 1000× magnification. In each case, the spectrum came from the centre of the image. In panel (c), all unlabelled peaks belong to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

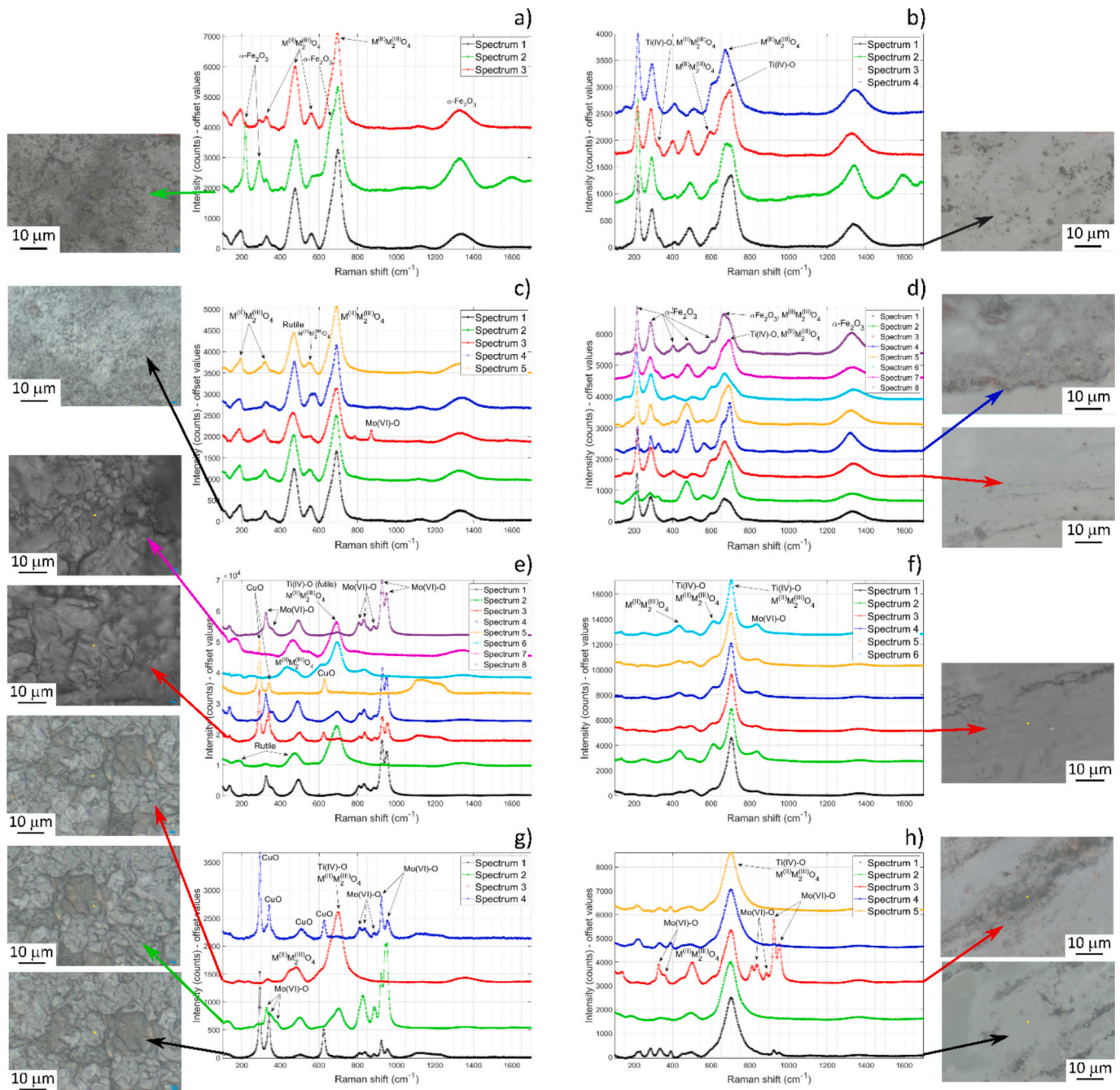
thermally grown scale at 800 °C, was the cause of the continuous decrease of the friction coefficient (Fig. 4c).

### 3.3.3. Comparison to the Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark

Compared with the TiC-HEA coatings, the Cr<sub>3</sub>C<sub>2</sub>-NiCr reference exhibited more severe abrasion at room temperature (see the numerous, rather deep grooves in Fig. 5i), together with localised pitting (Fig. 5i, j). In fact, in this case part of the surface voids may even be due to adhesive wear rather than surface fatigue. The presence of bright, metallic transfer material on the Al<sub>2</sub>O<sub>3</sub> ball (Fig. 7q) indeed suggests direct seizure with material transfer, despite the lower friction coefficient (Fig. 4c). This behaviour is consistent with our previous observations for

thermally sprayed Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings [60] and is plausibly exacerbated here by the higher contact pressure, which increased the severity of both the adhesive and abrasive mechanisms, explaining the order-of-magnitude increase in specific wear rate (as discussed in Section 3.2). At first sight, adhesive wear appears inconsistent with the higher hardness of the Cr<sub>3</sub>C<sub>2</sub>-NiCr coating (Section 3.1 and Table 6), but hardness alone is not a good predictor of sliding wear behaviour. Because the chromium carbide grains in the Cr<sub>3</sub>C<sub>2</sub>-NiCr coating were much coarser than the fine and uniformly distributed TiC grains in the TiC-HEA samples, the larger matrix mean free path in Cr<sub>3</sub>C<sub>2</sub>-NiCr was likely responsible for the occurrence of adhesive wear.

At 400 °C, oxide patches formed only intermittently on the surface of



**Fig. 17.** Raman spectra acquired after ball-on-disc tests at 800 °C, inside the wear trace (a, c, e, g) and on the unworn surface (b, d, f, h), on the AlCu+TiC (a, b), AlMo+TiC (c, d), AlCuMo10 + TiC (e, f), and AlCuMo13 + TiC (g, h) coatings. Some of the acquisition areas are shown through the optical micrographs at 1000× magnification. In each case, the spectrum came from the centre of the image. In panel (a), all unlabelled peaks belong to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Cr<sub>3</sub>C<sub>2</sub>-NiCr and showed poor cohesion (Fig. 8i, j), leaving softened material exposed to adhesive wear (Fig. 8j). This mechanism was testified both by the formation of an irregular wear scar profile (Fig. 8i) and by the presence of shiny (metallic) transfer material on the ball (Fig. 7r). At 600 °C and 800 °C, a tribolayer developed but remained irregular (Fig. 9i and Fig. 12i, respectively) and prone to fracture and spallation (Fig. 9j and Fig. 12j). In our previous work, we had also noted that the tribofilm formed on Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings at 700 °C tended to spall off [10], but with a much lower severity than in the present case. Again, this was consistent with the higher contact pressure. The discontinuity of the tribofilm explained the correspondingly higher specific wear rate (as observed in Section 3.2). The markedly different morphology of the wear scars at 800 °C (Fig. 12i, j), relative to the TiC-HEA coatings

(Fig. 12a-h), was consistent with the orders-of-magnitude differences in specific wear rate and (Fig. 4a) with the generally lower friction observed for TiC-HEA at this temperature (Fig. 4c).

#### 4. Conclusions

This work analysed the sliding wear behaviour of four HVOF-sprayed hardmetal coatings consisting of 60 vol% TiC in high-entropy alloy (HEA) matrices based on the AlCrFeNi system with additions of Cu and/or Mo: Al<sub>0.5</sub>CuCrFeNi<sub>2</sub>, Al<sub>3</sub>Cr<sub>6</sub>Fe<sub>31</sub>Ni<sub>34</sub>Mo<sub>26</sub>, Al<sub>5</sub>Cr<sub>18</sub>Cu<sub>18</sub>Fe<sub>24</sub>Ni<sub>25</sub>Mo<sub>10</sub> or Al<sub>8</sub>Cr<sub>16</sub>Cu<sub>16</sub>Fe<sub>16</sub>Ni<sub>31</sub>Mo<sub>13</sub>. The work specifically compared the performance of the four TiC-HEA coatings under ball-on-disc testing conditions at room temperature, 400 °C, 600 °C, and 800 °C. A HVOF-



sprayed Cr<sub>3</sub>C<sub>2</sub>-NiCr coating was used as benchmark. The main findings can be summarized as follows:

- The TiC-HEA powders produced by high-energy ball-milling exhibited some inhomogeneities in the metal matrix, because of incomplete interdiffusion. However, the HEA matrices were heated above their melting point during HVOF spraying (~1900–1950 °C) and were thus fully homogenized in the liquid state.
- The high-velocity impact (~650–700 °C) of these hot particles resulted in extensive flattening and left almost no porosity in the coatings.
- Although the TiC-HEA coatings were softer than the Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark (~800–850 HV compared to 960 HV), their specific wear rates measured at room temperature against an Al<sub>2</sub>O<sub>3</sub> ball under high contact pressure conditions were one order of magnitude lower,  $\sim (1.5\text{--}2.0) \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  against  $\sim 2 \times 10^{-5} \text{ mm}^3/(\text{N}\cdot\text{m})$ . The main wear mechanisms of the TiC-HEA coatings included surface fatigue and tribo-oxidation. The Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark exhibited less tribo-oxidation; further, it experienced some adhesive wear, probably because of the greater matrix mean free path between the much coarser Cr<sub>3</sub>C<sub>2</sub> particles.
- As the temperature increased to 400 °C and 600 °C, the TiC-HEA formulations containing Mo exhibited remarkably stable specific wear rates in the  $(1\text{--}2) \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  range. This was ascribed to the formation of rather continuous and protective tribofilms based on molybdates.

At 800 °C, all TiC-HEA coatings exhibited low specific wear rates of  $(1\text{--}2) \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$  and also produced low friction (~0.3), because a thick oxide scale separated the hardmetal from the counterpart. Hence, wear was limited to the oxide scale only.

The Cr<sub>3</sub>C<sub>2</sub>-NiCr benchmark, by contrast, suffered progressively higher wear with increasing temperature. Because of the lower stability of the tribo-oxidized layer, which tended to spall off, the underlying material continued to suffer from adhesive wear.

Overall, the Mo-containing TiC-HEA coatings were shown to be promising candidates for the wear protection of components operating over a wide temperature range.

#### CRediT authorship contribution statement

**Lorenzo Miconi:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Stefania Morelli:** Writing – review & editing, Investigation, Formal analysis. **Magdalena Lassinantti Gualtieri:** Writing – review & editing, Formal analysis. **Maria Francesca Bonilauri:** Writing – review & editing, Investigation, Formal analysis. **Luca Bortolotti:** Investigation, Formal analysis. **Giovanni Bolelli:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Alvise Bianchin:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Luca Lusvarghi:** Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: All authors report financial support was provided by European Union under GA no 101092211. Alvise Bianchin reports a relationship with MBN Nanomaterialia Srl that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.surfcoat.2026.133728>.

#### Data availability

Data will be made available on request.

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