NRC Publications Archive Archives des publications du CNRC

Third body behavior during dry sliding of cold-sprayed Al-Al₂O₃ composites : in situ tribometry and microanalysis

Shockley, J. Michael; Descartes, S.; Irissou, É.; Legoux, J.-G.; Chromik, R. R.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1007/s11249-014-0326-z>

Tribology Letters, 54, 2, pp. 191-206, 2014-04-08

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=52c576a4-a5a0-4c17-8a7c-60842df22ebf>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=52c576a4-a5a0-4c17-8a7c-60842df22ebf>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Third body behavior during dry sliding of Al-Al₂O₃ composite coatings: In situ tribometry and microanalysis

J. Michael Shockley,^a S. Descartes,^{a,b} E. Irissou,^c J.-G. Legoux,^c R.R. Chromik^{a*}

a. Department of Mining and Materials Engineering McGill University
M.H. Wong Building, Rm 2100 3610 University Street Montreal, QC H3A 0C5 Canada

b. Université de Lyon, CNRS
INSA-Lyon, LaMCoS
UMR5259 F-69621
Villeurbanne France

c. National Research Council Canada
75, boul. de Mortagne Boucherville, QC J4B 6Y4 Canada

*Corresponding Author: Prof. Richard R. Chromik
Email: richard.chromik@mcgill.ca
Phone: 1-514-398-5686
Fax: 514-398-4492

Abstract

Reciprocating sliding wear experiments were conducted on cold sprayed pure aluminum and Al - 22.6 wt.% Al₂O₃ coatings using a custom-built *in situ* tribometer. By using a transparent sapphire counterface for the wear tests, the dynamic behavior of third body material in the contact was optically observed. The presence of Al₂O₃ particles led to greater stability of the transfer films adhering to the sapphire counterface, as well as greater stability of the friction coefficient and lower wear rates. Ex situ microanalysis of material in the wear tracks and transfer films suggests that the presence of Al₂O₃ particles promoted strain localization during sliding. This produced more uniform third body microstructures and protected the underlying aluminum matrix from deformation, both of which slowed the rate of transfer to the counterface.

1 Introduction

While aluminum and its alloys are highly valued for their corrosion resistance, low density, and high thermal conductivity, their poor tribological behavior limits their use in many applications. For pure

1
2
3
4 aluminum, the lack of alloying elements is a benefit for corrosion resistance, but a significant detriment to
5
6 mechanical and tribological properties [1]. A popular compromise for applications requiring both
7
8 corrosion and wear resistance are aluminum matrix composite (Al-MMC) materials, which utilize
9
10 secondary phases, commonly based on SiC or Al₂O₃, to provide mechanical reinforcement of the
11
12 aluminum matrix [2]. Reinforcing phases may be continuous (long fibers) or discontinuous (particles and
13
14 short fibers), depending on the application and processing route. Al-MMC materials can have corrosion
15
16 resistance comparable to un-reinforced pure aluminum but substantially lower wear rates in most wear
17
18 regimes [3 - 6].
19
20

21
22
23 Classical processing of discontinuously reinforced Al-MMC materials includes bulk casting, spray
24
25 casting, sintered powder metallurgy, or thermal spray processing routes [2, 7]. More recently, cold gas
26
27 dynamic spray, more often known as cold spray, has been utilized for routine deposition of Al-MMC
28
29 coatings and bulk materials [6, 8 - 10]. The cold spray process operates by accelerating feedstock powders
30
31 through a preheated inert gas stream that is passed through a Laval-type nozzle. The gas and powders
32
33 attain supersonic velocities, and upon impact with a substrate, extensive plastic deformation is induced
34
35 and metallurgical bonding takes place by way of an adiabatic shear instability [11 - 15]. Hard phases such
36
37 as SiC and Al₂O₃ may be incorporated into the coatings by admixing them into the feedstock powders [6,
38
39 8]. Coatings deposited using the cold spray process undergo very little oxidation or chemical reaction
40
41 compared to conventional thermal spray techniques. Cold spray of pure aluminum and Al-MMC materials
42
43 has become a primary mode of repair and corrosion protection for magnesium aerospace gearbox
44
45 components [10, 16]. With the growing popularity of cold sprayed Al and Al-MMC materials in structural
46
47 and surface engineering applications, it is of interest that their tribological behavior be well understood
48
49 and characterized.
50
51
52
53
54

55 In Al-MMC materials, a shift toward lower wear rates with increasing hard particle content has
56
57 been documented. Microanalysis of worn aluminum and other pure metal surfaces typically reveals
58
59 evidence of adhesion and extensive plastic deformation, resulting in surface grain refinement and material
60
61
62
63
64
65

transfer between surfaces [17 - 21]. For Al MMCs prepared by traditional methods, two groups have shown that lower wear rates may be correlated to the formation of mechanically mixed layers with constrained grain refinement [3, 22]. For the case of cold sprayed Al MMCs, specifically Al-Al₂O₃, reduction in wear rates have been observed, but connections between this reduction to the nature of the mechanically mixed layer have not been made as clear as for traditional Al MMCs. [8, 23].

For the tribology of most materials, including aluminum and Al-MMCs, “third bodies” at the sliding interface ultimately dictate the tribological behavior [24, 25]. Third bodies develop due to deformation-induced physical, chemical, and microstructural changes of material at the sliding interface, and often exhibit distinct properties compared to the unworn first bodies [26, 27]. The phenomena of material transfer, mechanical mixing, and wear debris formation are largely third body material flows, and the magnitude of these flows influences the overall performance of the sliding system in terms of friction and wear [24]. In the large body of literature on the tribology of Al and Al MMCs, assignment of mechanisms is most often done solely with *ex situ* characterization of worn surfaces occurs *ex situ*, i.e., after the test, which provide only static details from which the behavior of third bodies during the test must be inferred.

The technique of *in situ* tribometry allows for real-time observation of third body behavior through the use of a transparent sliding counterface. This technique has been frequently used for tribology of advanced coatings such as solid lubricants and diamond-like carbon coatings [28 - 32], but its use on metallic systems has considerably less precedent. In a short previous work by the authors, coatings of cold sprayed pure Al and Al-Al₂O₃ were subjected to sliding wear tests using an *in situ* tribometer [23]. This study was largely limited to a discussion of *in situ* tribometry results. In the present work, we combine *in situ* tribometry with *ex situ* methods to develop a more complete understanding in terms of third body flows and velocity accommodation [33]. The observed *in situ* behavior of third bodies, primarily transfer films, are correlated to observations from complementary *ex situ* microanalysis of the worn coatings and transfer film material using focused ion beam (FIB) cross-sectioning. By pairing *in situ* observations with

1
2
3
4 *ex situ* analysis of the structural and chemical contrasts in the third body material, a full understanding of
5
6 the tribological flows and velocity accommodation modes for the cold sprayed Al and Al-Al₂O₃ samples
7
8 will be developed.
9

10 11 12 **2 Experimental Methods and Theory**

13 14 15 **2.1 Cold Spray Deposition**

16
17
18 Feedstock powders for cold spray were prepared by admixing commercially available spherical
19
20 Al powder (Alfa-Aesar, $H = 26 \pm 2 \text{ HV}_{10}$, $d_m = 36.2 \text{ }\mu\text{m}$) with varying percentages of Al₂O₃ powder
21
22 (Plasmatec, $H = 2019 \pm 426 \text{ HV}_{10}$, $d_m = 25.5 \text{ }\mu\text{m}$) [6]. Coatings were deposited onto mild steel substrates
23
24 using a Centerline SST cold spray system, achieving a thickness of 500-600 μm [6]. Other details of
25
26 coating deposition, including inlet gas temperature, spray velocity, deposition efficiency, etc. are provided
27
28 in an earlier work [6]. The concentration of Al₂O₃ recovered in each coating was determined by image
29
30 analysis, during which ten random images of polished cross-sections were taken in a scanning electron
31
32 microscope (SEM) and analyzed by pixel count to calculate the Al₂O₃ content. Previous studies on cold
33
34 sprayed Al-Al₂O₃ have shown that tribological behavior shifts as a function of Al₂O₃ content toward
35
36 lower sliding wear rates and more stable friction [8, 23]; the coatings used in this study were chosen to
37
38 highlight the contrast of this behavior. The coatings selected for the present study contained 0 wt.% and
39
40 $22.6 \pm 2.9 \text{ wt.\% Al}_2\text{O}_3$, which were assigned the designations of CS0 and CS22, respectively (see Figure
41
42 1). Prior to wear testing, the coating surfaces were polished to a root mean square roughness of less than
43
44 600 nm and cleaned with acetone. Aluminum grain sizes in the initial coatings were between 0.3 and 5
45
46 μm , while initial Al₂O₃ particle sizes fell between 2 and 30 μm .
47
48
49
50
51

52 53 54 **2.2 Wear Test Conditions**

55
56 Sliding wear tests on the polished coatings were performed in dry air (below 2% relative
57
58 humidity) at room temperature (21-24° C). All wear tests were conducted at a sliding speed of 3 mm/s, a
59
60 track length of 10 mm, and normal load of 1 N. Transparent monocrystalline $\alpha\text{-Al}_2\text{O}_3$ (sapphire) was used
61
62
63
64
65

as the counterface material in the form of 6.35 mm diameter hemispheres. Wear tests were run to 500 and 2000 sliding cycles, corresponding to total sliding distances of 5 and 20 m, respectively.

2.3 *In Situ* Analysis

Friction forces were measured at a sampling rate of 800 Hz using a piezoelectric sensor mounted underneath the sample stage. Microscopic observation of the contact region was carried out *in situ* through the transparent counterface using an optical microscope. The microscope was mounted above the transparent counterface and was equipped with a 10x objective lens and a commercially available camcorder.

2.4 *Ex Situ* Analysis

After wear testing, the wear tracks and counterface transfer material were analyzed *ex situ*. Using a Philips XL-30 scanning electron microscope (SEM), wear track surface features were observed and elemental contrast was revealed by energy dispersive x-ray spectroscopy (EDXS). Surface macrostructures of the wear tracks and counterface transfer material were extracted using a Wyko NT8000 non-contact optical profiler. Wear rates were calculated in accordance with ASTM Standard G99 by first integrating height profiles across the wear track above and below the original surface height to calculate a net worn cross-sectional area. This was then multiplied by the wear track length to obtain a net volume of material removed from the surface. 30-40 surface profile measurements per wear track were obtained.

Sub-surface regions of the worn surfaces were studied by both conventional metallurgical preparation of cross-sections and by focused ion beam (FIB) cross-sectioning. For the conventional cross-sectioning, wear tracks were cut transverse to the sliding direction using a lubricated slow-speed abrasive cutting wheel, followed by cold mounting in epoxy and mechanical polishing. For FIB cross-sections, a Zeiss NVision 40 dual beam FIB/SEM was used with a gallium ion source. Samples were coated with a layer of gold prior to analysis, and then cross-sections were cut parallel and transverse to the original

sliding direction. No shielding material was deposited as the specimens were not prepared for TEM cross-sections. For images collected in the FIB/SEM, grain contrast was revealed by ion channeling contrast.

Nanoindentation was performed on mechanically polished surfaces using a Hysitron Triboindenter equipped with a Berkovich diamond indenter with a tip defect radius of approximately 125 nm. Indents were performed using a 5 second linear loading time to a maximum force of 400 μN , 5 second hold time at maximum load, and 5 second linear unloading time. Each hardness value reported was calculated using the Oliver and Pharr method [34], and represents the average of at least 12 indents.

2.5 Theory and Nomenclature

The material flow in a sliding system may be described using the tribological circuit (see Figure 2a) [24]. The first bodies are contacting and are in relative motion to one another; third bodies form at the sliding interface. The source flow, Q_s , represents detachment or transformation of first body material to become the third bodies; the internal flow Q_i is movement of material across the interface; the ejection flow Q_e is material ejected from the interface; the re-circulation flow Q_r is ejected material that has been re-introduced to the interface; and the wear flow Q_w is material permanently removed from the sliding system. When applied to metallic systems, the phenomena of third body formation, mechanical mixing, and wear debris formation [19, 20, 35] may be readily assigned theoretical counterparts in the tribological circuit. In the present ball-on-flat sliding system, third bodies are formed in the wear track and as transfer film adhering to the hemispherical counterface (see Figure 2b). Ejection flow occurs as material is deposited at the ends of the wear track or pushed to the sides of the wear track. This material become wear flow unless it somehow recirculates into the contact, for instance as the wear track widens.

The surface adaptation to relative motion during dry sliding may be classified according the so-called Velocity Accommodation Modes (VAM) [36]. This analysis permits description of the locations and mechanisms by which relative motion is manifested at the sliding interface. Classically, the mechanisms of elastic deformation, fracture, shear, and/or rolling may take place in some combination of

the first bodies, third bodies, and the interfaces in between; each combination represents a VAM [36]. A shift in VAM may influence the material flows in the tribological circuit and hence the friction and wear of the sliding system.

3 Results and Discussion

3.1 Friction Coefficient (COF)

The friction coefficient throughout the tests to 500 and 2000 cycles are plotted in Figure 3. Sample CS0 exhibited a friction coefficient that fluctuated between 0.6 and 1.3, with many spikes and temporary shifts to varying plateau values. For each case, the friction coefficient started with an initial spike above 1.0, then gradually decreased over the initial 250 cycles. Meanwhile, after initial fluctuations during roughly the first 300 cycles, the friction coefficient of sample CS22 settled to around 0.7. The friction behavior of sample CS22 was considerably more stable than that of CS0, and as a whole, lower. Spencer et al observed similar friction stabilization for dry sliding wear of Al and Al-Al₂O₃ coatings slid against steel [8]. These had been cold sprayed using helium as carrier gas on an Inovati Kinetic Metallization (KM) cold spray system [8]. In our previous study, this reduction and stabilization in friction was also observed on separate specimens from the same coating [23]. A similar reduction and stabilization of friction was observed in a previous study by Wang et al., on dry sliding wear of bulk 6092 aluminum alloy and composites of 6092/15% Ni₃Al against steel [37].

3.2 In Situ Observations of Transfer Film Behavior

CS0 transfer film behavior

During the opening cycles of the CS0 wear tests, extensive plowing was observed. During the first sliding cycle, the initial plowed material adhered to the slider and accumulated steadily to form a prow (see Figure 4). Prow formation behavior, where material accumulates ahead of the slider, was documented in aluminum and other metals in early studies on metallic transfer [20], and was found to be

cyclic and largely observed early in the sliding process [38]. This early transfer process is the initial activation of the source flow, Q_s , and for CS0 it corresponded to the period of highest friction coefficient. For CS0, the prow grew steadily until it reached a length of roughly 215 μm (measured parallel to the sliding direction) and width of 150 μm (see Figure 4, far right), after which it detached from the contact (as ejection flow, Q_e) and was left on the wear track. A new prow started to form immediately after, and upon the return pass, the first prow was recirculated back into the contact (Q_r). As this process continued, some ejected prow material was left at the ends of the wear track as wear flow (Q_w) as were smaller pieces of wear debris.

After the initial few sliding cycles, the formation and detachment of several prows left permanent transfer film on the slider (see CS0 in Figure 5). Throughout roughly the first 100 cycles, this transfer film was highly unstable. The instability during this period was characterized by observable plastic internal flow (Q_i) of the transfer film, and frequent detachment of material from the contact (Q_e) leaving holes that were quickly filled in with new material (Q_s). The transfer film continued to grow throughout the test, as did the observable width of the wear track, and both eventually became larger than the field of view of the microscope. While visible, the apparent transfer film remained roughly circular and grew in diameter; for instance, it grew from roughly 730 μm at 50 cycles to 1060 μm at 500 cycles. Later in the test, streaks running parallel to the sliding direction were formed, indicating internal flow of the transfer film (Q_i) or material removal (Q_e).

At several points where the COF underwent large shifts from one steady-state value to another, the transfer film showed corresponding detachments of large patches of material (for example, see a and b in Figure 6). In both cases, patches of transfer film material appeared to loosen over the course of several cycles prior to detachment (outlined regions in a1 and b1). As each patch of transfer film loosened from the sapphire, narrow air gap was created between the two, which caused optical interference fringes to form. The fringes were visible *in situ* as rapidly fluctuating rainbow colors, indicating that the gap rapidly fluctuated in height while the transfer film passed over the uneven wear track topography. This

phenomena of optical interference fringes is similar to that observed for solid lubricants [39], but does not provide a straightforward method for analysis that could measure the transfer film thickness. However, the appearance of the fringes does provide evidence of gradual detachment between the transfer film and sapphire.

After the fringes were visible for about 5 cycles, the loosened material was ejected from the contact (a2 and b2), and the hole was quickly filled in with new material as internal (Q_i) or source flow (Q_s) from the wear track (a3 and b3). Although dynamic friction events occurred throughout testing for CS0 (see Figure 3), many of them did not easily correlate with events easily visible *in situ* such as this. One possible explanation is that as the transfer film grew beyond the microscope's field of view, such events occurred there. A second explanation is that not all of the events resulted from an adhesive failure at the interface of the transfer film and sapphire, with the failure instead occurring cohesively within the transfer film.

CS22 transfer film behavior

The initial CS22 transfer film formed through prow formation very similar to that of CS0, and for the initial few cycles, transfer film instability comparable to CS0 was observed as internal flow (Q_i). However, after just a few sliding cycles, the observable internal flow essentially ceased and the transfer film remained stable throughout opening several hundred cycles (see Figure 5), taking the form of an oval roughly 600 μm in length and 200 μm wide. In this stable state, none of the behaviors observed in the CS0 transfer film, such as obvious internal and ejection flows, were present – and neither were the corresponding jumps in COF. At higher cycle numbers the wear track widened, as did the transfer film, but far less than CS0 (see Figure 5 at 500 and 2000 cycles). The enhanced stability of the CS22 transfer film when observed *in situ* may be interpreted as lower magnitudes and less frequent activation of internal, ejection, and source flows.

3.3 Ex Situ Observations of CS0 Third Bodies

Morphology of CS0 Transfer Film and Wear Track

Viewed *ex situ*, the CS0 transfer film after 500 sliding cycles was patchy and mostly consisted of material less than 20 μm thick (see Figure 7). However, near the center was a prominent patch of material roughly 150-200 μm in width and 400-500 μm in length and generally greater than 40 μm thick. At the top of this patch of material was a prow of similar length and width as those prows observed *in situ* early in sliding (see Figure 4). This prow reached a maximum thickness of roughly 75 micrometers. The streaks of material correspond strongly to the scoring marks visible in the transfer film in Figure 5. In the regions of thin transfer material, the underlying sapphire counterface was frequently visible (see 7d). Flake-shaped wear debris were visible adhering to the transfer film as well.

The *ex situ* observations in Figure 7 suggest that the *in situ* appearance of the CS0 transfer film, nominally greater than 1 mm in diameter, as in Figure 5, is misleading in terms of the volume of third body material attached to the sapphire. Much of the CS0 transfer film after 500 sliding cycles consisted of very thin, smeared material. This thick region of transfer film may have been the main area of contact, which is supported by the observation of a prow at its leading edge, as it is evidence of source flow that occurred just prior to stopping the test.

Features in the CS0 wear track were characteristic of adhesive wear, similar to that seen in previous dry sliding wear studies of pure bulk [40] and cold-sprayed aluminum [8]. Layered structures of adhesively smeared material were present (see Figure 8a and c). Wear debris was also visible in flake morphologies 5-20 μm wide. Some amount of scoring in the direction of sliding was also evident. Wear rates after 500 and 2000 sliding cycles are reported in Table 1. These wear rate values are of a similar order of magnitude as those measured in previous studies when sliding against balls made of Al_2O_3 [23] and 100Cr6 steel [8] with similar loading conditions as in the present study.

Microstructures of CS0 Transfer Film and Wear Track

1
2
3
4 In the CS0 transfer film, the regions selected for further microstructural observation were the top
5
6 of the thick patch of transfer film, which is roughly 45 μm thick, and a region of thinner transfer film 5-10
7
8 μm thick (see Figure 7a). In both cases, the microstructures cut transverse to the sliding direction in the
9
10 CS0 transfer film show three main features (see Figure 9). The first feature is nanostructured aluminum
11
12 grains (labeled as “NS Al”), which are present in bands 1-5 μm thick. Given the imaging technique used
13
14 in this study it is difficult to quantify the size and morphology of the nanostructured grains, but they
15
16 appear to be on the order of 20-50 nm in diameter. Grain refinement is a consequence of the mechanical
17
18 mixing processes and severe plastic deformation occurring during sliding [38, 41]. Also visible in the
19
20 microstructures are bands of relatively larger aluminum grains (“LG Al”), showing grain sizes on the
21
22 order of 200 nm to 2 μm . These larger grain sizes indicate that these regions have gone through less
23
24 plastic deformation than the nanocrystalline regions. Finally, thin cracks exist between adjacent patches
25
26 within the microstructures. Cracks between these regions indicate that the transfer film consists of patches
27
28 of material, some subjected to more mechanical mixing than others, pushed together but not necessarily
29
30 bonded. The grain refinement visible in material just next to the cracks (e.g., Figure 9b) may have
31
32 originated from contact and deformation between these regions during sliding. Microstructures from the
33
34 thin regions of CS0 transfer film (see Figure 9c) show similar features as those in the thicker regions. The
35
36 sapphire is apparent under a region of transfer film 4-5 μm in thickness, similar to the interferometry
37
38 measurements in Figure 7a. In this region and others observed, the only material observable at the
39
40 interface with the sapphire was nanostructured aluminum.
41
42
43
44
45
46

47 For comparison, the edge of a piece of adhesively smeared material in the bottom of the CS0
48
49 wear track was selected for microstructural analysis, and a FIB cut was performed transverse to the
50
51 sliding direction (see Figure 8e). In the microstructure, aluminum with grain sizes up to the 3-5 μm is
52
53 visible 5-10 μm below the surface. Above this and closer to the wear interface, the bulk aluminum
54
55 exhibits grain refinement down to roughly 100 nm, at which point a distinct crack separates the first body
56
57 from the smeared third body material above it. The microstructure of the third body region shows highly
58
59
60
61
62
63
64
65

1
2
3
4 refined aluminum grains and cracks existing in the material, which are both evidence of plastic
5 deformation and mechanical mixing as part of the internal flow (Q_i) that occurred during the adhesive
6 smearing behavior. The gradient of grain size in the first body is evidence that strain extended 5-10 μm
7 below the third body material. As strain would continue to accumulate in this layer, eventually material
8 would detach and become third body material as source flow (Q_s).
9
10

11 12 13 14 15 16 **3.4 Ex Situ Observations of CS22 Third Bodies**

17 18 19 ***Morphology of CS22 Transfer Film and Wear Track***

20
21
22 When viewed *ex situ*, the CS22 counterface after 500 sliding cycles appeared to include one
23 primary patch of transfer film, the thickness of which never exceeded 40 μm (see Figure 10). Its length
24 was between 300 and 400 μm and its width remained between 100 and 250 μm . The length scale of this
25 transfer film is relatively similar to the most prominent patch of the CS0 transfer film in Figure 7, without
26 the large prows and the streaks of transferred material. Furthermore, the transfer film size viewed *ex situ*
27 is strongly comparable to its appearance *in situ*, unlike CS0. The highest point of the transfer film is
28 shown and is relatively flat, with scoring marks parallel to the sliding direction. The lack of a prominent
29 prow as was observed in CS0 suggests that less source flow (Q_s) was activated at the time that the test
30 was stopped, and this compares well with the *in situ* observations that less source flow and internal flow
31 was activated for CS22. Fine wear debris, on the length scale of 1-10 μm , was observed adhering to the
32 transfer film.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

48 The CS22 wear tracks showed more uniformity than CS0 when run to similar numbers of cycles
49 (see Figure 8b and d). The wear track shows evidence of the development of a relatively smooth, coherent
50 film, with no Al_2O_3 particles visible in top-down views. Cracking is visible in the wear track and there is
51 extensive scoring of the surface in the direction of sliding, indicative of micro-plowing. Wear rates after
52 500 and 2000 sliding cycles are reported in Table 1; the wear flow rate of CS22 was nearly an order of
53 magnitude less than CS0, again in agreement with wear rates measured in previous studies [8, 23].
54
55
56
57
58
59
60
61
62
63
64
65

Microstructures of CS22 Transfer Film and Wear Track

Microstructural features in the CS22 transfer film mostly consisted of nanocrystalline aluminum (labelled “NS Al” in Figure 11), along with several patches of relatively larger aluminum grains (“LG Al”). Also present were refined particles of Al_2O_3 . The depth of the FIB cuts did not exceed the thickness of the CS22 transfer film, so the sapphire counterface is not visible, but in each case it would run parallel with the bottom of the image. The mixed material is present in layers 1-3 μm thick which run roughly parallel to the transfer film surface.

Subsurface microstructures in the CS22 wear track were revealed transverse and longitudinal in relation to the sliding direction (see Figure 8d). A clearly distinguishable layer, containing nanocrystalline aluminum and Al_2O_3 particles, is present at the surface of the wear track and is generally 1-3 μm in thickness. In cross-section, some particles were clearly evident just under the subsurface layer. These particles were roughly 1-5 μm in diameter, showing considerable size reduction from the initial Al_2O_3 particles in the feedstock and unworn microstructure. The nanocrystalline mechanically mixed layer, with grain sizes on the order of 20-100 nm, is relatively evenly distributed, but it appears thinner in areas surrounding Al_2O_3 particles. In Figure 8f, the cracks observed in the CS22 wear track penetrated this layer, appearing on a length scale similar to the size of wear debris observed in Figure 10 adhering to the transfer film. Below the mechanically mixed layer, the matrix appears relatively un-deformed as indicated by the aluminum grain size. This is in contrast to that seen in the CS0 wear track, where below the adhesively smeared third body, the first body grain size showed a gradient of size indicating penetration of strain (see Figure 9).

3.5 Ex Situ Measurements of Third Body Mechanical Properties and Elemental Composition

In the unworn microstructures, the average hardness measured by nanoindentation of the pure aluminum phases of CS0 and CS22 was 0.85 ± 0.07 GPa, while for the Al_2O_3 particles it was 21.1 ± 0.96 GPa. The third body regions of CS0 had a hardness of 1.46 ± 0.23 GPa, while the hardness of the CS22

third body was 3.72 ± 0.42 GPa (see Figure 12). Representative load-displacement curves from the nanoindentation tests showed pronounced pop-in behavior during the loading curve for the unworn Al regions, and to a lesser extent on the CS0 third body region. No pop-in behavior was visible for the CS22 third body material, nor for the Al_2O_3 particles. Electron images of indents from the tested regions are shown in Figure 13. Several previous studies have shown similar elevated MML hardness. Venkatamrman and Sundararajan found that for in dry sliding wear of Al-SiC composites against steel, the third body microhardness was roughly six times that of the undeformed material, whereas measurements on third bodies of an unreinforced Al alloy showed considerably less hardening [42]. Another study by Farhat et al. of dry sliding wear of pure bulk aluminum against steel found hardening at the surface layer as high as 1.6 times that of the undeformed bulk [43]. This is similar to the degree of hardening of the CS0 third body compared to the undeformed aluminum, which was approximately 1.7 times harder, whereas the CS22 third body was approximately 4.4 times harder than the undeformed aluminum.

There are several possible contributions to the higher hardness in the CS22 third bodies. As the wear track material in CS22 was more homogeneous in microstructure and showed finer grain sizes than what was observed for the CS0 (compare Figures 8 e and f), one contribution to the higher hardness could be Hall-Petch strengthening. As the velocity accommodation occurred in a smaller volume of material in CS22 versus CS0, the material in that layer would more highly strained and work hardened. The lack of pop-in behavior in CS22 may be further evidence of this, as the greater dislocation densities and smaller grain sizes would prevent the homogeneous dislocation nucleation events associated with pop-in [44].

Elemental microanalysis of the unworn and third body microstructures revealed elevated oxygen in the third body material. EDXS mapping showing the region of interest, oxygen and aluminum Ka peaks, and representative spectra from the regions of interest are shown in Figure 13. While a formal quantitative elemental analysis was not carried out, the relative intensities of Ka peaks of oxygen and aluminum, centered at 0.53 and 1.48 keV, respectively, reveal the different oxygen concentrations of the

CS0 and CS22 third body material. In the unworn aluminum, the aluminum peak entirely dominates, while in the pure Al_2O_3 particle, a characteristic ratio is developed with oxygen slightly higher than aluminum. In the CS22 mechanically mixed layer, roughly equal intensities of oxygen and aluminum were measured, while the CS0 third body showed a smaller but significant presence of oxygen. There are several possible explanations for the oxygen content. First, the mechanical mixing exposes clean aluminum surfaces which spontaneously oxidize to form amorphous Al_2O_3 [1]; Kim and Rigney suggested that a mechanical mixing induces solid solution dissolution of oxygen into the aluminum matrix [17]. As the CS22 third body material has been demonstrated to highly localized, it is possible that it took up greater concentrations of oxygen. Second, refined Al_2O_3 particles were observed in the CS22 third body material, contributing to the oxygen signal as well.

4 Relationship Between Third Body Flows and Microstructural Changes

The opening cycles of transfer film formation for both CS0 and CS22 were nearly identical when observed *in situ* – initial formation and flow of the transfer film occurred because of the low levels of strain. This initial high source flow, Q_s , corresponded to the initial friction spikes for both coatings and were quite similar (see Figure 14). After this point, the behavior of CS0 and CS22 third bodies took different directions.

In CS0, considerable amounts of dynamic recrystallization occurred due to severe plastic deformation. Strain penetrated far into the first body and the bulk of the transfer film, as shown through the grain size gradient beneath the third body material (see Figure 8). The source flow therefore remained high throughout testing for CS0 (see Figure 14), as new third body material was constantly being generated below the wear track. Some amount of oxygen uptake occurred in the CS0 third bodies as well as new surfaces were generated and exposed to the atmosphere, but it was spread among a relatively large volume of material. The higher internal flows and ejection flows prevented formation of a uniform, dynamically recrystallized and chemically passivated layer, as it was removed from the contact very

frequently. Thus, the third body material contained material subjected to differing degrees of grain refinement and work hardening.

The high internal and ejection flows visible in the CS0 transfer film are partly due to the structural instability. The causes of this instability could be among the following. First, the thicker the transfer film, the greater the mechanical moment induced from the friction force. Second, the more material that accumulates as part of the transfer film, the greater chance that defects or incomplete bonding will provide a location for failure. And finally, should the contact pressure on the prow of transfer film be lost due to ejection flow of third body material, the hydrostatic pressure preventing crack propagation would be lost. Thus, the catastrophic detachment of transfer film observed in Figure 3 should not be surprising in this scenario, and such an internal flow is likely to originate at the sapphire-transfer film counterface as no localized welding could occur there. Velocity accommodation in the form of shear occurred throughout the third body and into the coating first body.

In CS22, after initial transfer film formation, dynamic recrystallization occurred due to strain localization in the vicinity of the Al_2O_3 particles. This led to stable nanocrystalline microstructures in the transfer film and wear track. Strain localization then prevented deformation in the underlying microstructure and decreased the source flows considerably (see Figure 14). As the mechanically mixed layers in CS22 became uniform and hardened, transfer was less likely to occur for several reasons. First, higher hardness led to a greater resistance to conformal adhesion. Second, fewer instances of micro-welding could occur because of passivation through uniform and high levels of oxygen. The layered microstructures structures in the CS22 transfer film indicate that either bands of mechanically mixed material were transferred directly to the counterface, but this seems unlikely due to their demonstrated stability. A more likely scenario is that after a piece of third body material detaches from the wear track, un-deformed aluminum is exposed and readily transferred to the counterface. Then, the same deformation process could occur there as in the wear track. The resulting internal and ejection flows were very low compared to CS0, and correspondingly the wear flow was lower by roughly an order of magnitude . The

VAMs are three in this scenario: shear in the third body, which is constrained to a thin layer, tensile cracking in the wear track third body, and elastic deformation of the third body and underlying material. The presence of the tensile cracks permits elastic deformation through flexing of the third body material [36].

The contrasting tribological behavior of CS0 and CS22, manifested in terms of the friction, wear rates, and behavior observed *in situ*, was driven by microstructural evolution of third body microstructure. As these microstructural changes are induced through deformation, some understanding may be drawn from literature on severe plastic deformation (SPD) processes. Various SPD processes, such as high pressure torsion (HPT) and equal channel angular processing (ECAP), are employed to induce high shear strains into materials at low temperatures to create very fine grain structures [45]. Accumulated strains in excess of 10 may be readily induced using these methods, progressively forcing grains to subdivide at finer and finer length scales through the formation of high angle grain boundaries [46]. Eventually, the high angle grain boundary spacing converges with the subgrain size and the process saturates at grain/subgrain sizes on the order of 100-200 nm [46, 47]. SPD processes operate at high degrees of hydrostatic pressure and shear stress, and hence, they bear similar conditions to tribological contacts [47, 48]. Frequently, the crystallite sizes observed in third body microstructures are considerably smaller than what typically arises from SPD processes on Al and its alloys [46]. Mahato attributed this to the higher strain rates in sliding wear compared to SPD processing [47].

For both CS0 and CS22, third body microstructures showed crystallite sizes as low as 30 nm (see Figures 9 and 11). Yet the finest nanostructured regions within the CS0 third bodies were mixed very closely with less highly deformed grains; this was particularly clear in Figure 9 where the gradient of grain sizes and turbulent microstructures demonstrate the disorder of this process. The contrasting uniformity in the CS22 third body microstructures arises from the higher strain gradients and shear localization of the Al matrix around the Al_2O_3 particles. A study by Apps et al. compared the SPD-processed microstructures of a single-phase Al alloy and an alloy containing micron-scale hard $\text{Al}_{13}\text{Fe}_4$

particles, finding that grain refinement occurred much more rapidly in the particle-containing alloy [46]. Similar findings in an SPD-processed Al-Si alloy were attributed to enhanced dislocation formation around Si particles [49, 50]. Geometrically necessary dislocations, which form due the strain gradient surrounding the nondeforming Si particles, cause a higher local rate of dislocation formation and hence accelerate the dynamic recrystallization process [49, 51]. Such models have been incorporated into tribological studies as well, as several studies in aluminum tribology have demonstrated smaller grain sizes in the vicinity of stiff reinforcement phases [41, 47, 52]. Fragmentation of hard particles is commonly observed in SPD and tribology studies alike [3, 5, 47, 49, 53], further contributing to a higher strain gradient.

5 Conclusions

Dry sliding tribology experiments showed that dry sliding friction of sapphire against cold sprayed Al- 22 wt.% Al₂O₃ (sample CS22) was generally lower and more stable than the cold sprayed pure aluminum (sample CS0). In situ tribometry revealed strong contrasts between the two samples in terms of the behavior of the third body material adhering to the sapphire counterface. The CS0 transfer films exhibited instability marked by visible plastic flow, debris detachment, and subsequent plowing of new material, and some of these events corresponded with shifts in the friction coefficient. The CS22 transfer films remained stable throughout testing, correlating with the more steady friction behavior. This behavior remained true after 500 and 2000 sliding cycles.

Subsequent *ex situ* analysis after 500 sliding cycles revealed further contrasts between CS0 and CS22 in terms of third body morphology, flow, and microstructure. The wear track and transfer film of CS0 showed evidence of bulk flow of third body material. The near-surface microstructures of CS0 were highly inhomogeneous and revealed that plastic deformation extended deeply into the first body microstructures. The CS22 wear track and transfer film were comparatively more homogeneous, with the microstructures being largely constrained to a thin layer and consisting of nanostructured aluminum and

1
2
3
4 fragmented Al_2O_3 particles. Nanoindentation revealed that the CS22 third body was considerably harder
5
6 than that of CS0. The volumetric wear rate of CS22 was lower by roughly an order of magnitude
7
8 compared to CS0 after 500 and 2000 sliding cycles. Many of the *ex situ* observations are similar to
9
10 previous dry sliding wear investigations of Al and Al-MMC materials, both cold sprayed and prepared by
11
12 other processing routes.
13
14
15

16 The use of *in situ* and *ex situ* techniques in this study proved particularly powerful as the
17
18 combination of the two permitted a more complete analysis of the tribological circuit for CS0 and CS22.
19
20 This revealed that the strain localization caused by the presence of Al_2O_3 particles forced the internal
21
22 flows (Q_i) to be constrained to a thin layer. This promoted greater work hardening and oxidation of the
23
24 CS22 third body, preventing deformation deeper in the first body. By constraining velocity accommodation
25
26 to the third body material, the CS22 source flow (Q_s) was greatly reduced, which slowed the rate of
27
28 transfer to the counterface. With no strain localization, the source flow remained activated for CS0
29
30 throughout testing.
31
32
33
34

35 **6 Acknowledgments**

36
37
38 The authors gratefully acknowledge the financial support from the Canadian Foundation for
39
40 Innovation (CFI) project No. 8246 for the cold spray equipment, the CFI Leader's Opportunity Fund
41
42 project No. 13029 for the *in situ* tribometer and nanoindentation equipment, and the Natural Sciences and
43
44 Engineering Research Council (NSERC) Discovery Grants Program for the operational funding of this
45
46 project. JMS acknowledges partial financial support from the McGill Engineering Doctoral Award
47
48 (MEDA) program. Thanks are also due to the CLYM (Centre Lyonnais de Microscopie, [http://clym.insa-](http://clym.insa-lyon.fr)
49
50 [lyon.fr](http://clym.insa-lyon.fr)) for the access to the FIB/SEM (Zeiss NVision 40) and to N. Blanchard, A. Descamps-Mandine,
51
52 Th. Douillard, and B. Van De Moortèle for the technical help. CLYM is supported by CNRS, le Grand
53
54 Lyon and le Conseil Régional Rhône-Alpes.
55
56
57
58

59 **7 References**

60
61
62
63
64
65

- [1] J.R. Davis, editor. Aluminum and Aluminum Alloys, chapter Corrosion Behavior, pages 579– 622. ASM Specialty Handbook. ASM International, 1993.
- [2] T.W. Clyne and P.J. Withers. An Introduction to Metal Matrix Composites, chapter 9: Fabrication Processes, pages 318–360. Cambridge University Press, Cambridge, 1993.
- [3] R.L. Deuis, C. Subramanian, and J.M. Yellup. Dry Sliding Wear of Aluminium Composites - A Review. *Composites Science and Technology*, 57:415–435, 1997.
- [4] B. Venkataraman and G. Sundararajan. The sliding wear behaviour of Al-SiC particulate composites - I. Macrobehaviour. *Acta Materialia*, 44(2):451–460, 1996.
- [5] A.T. Alpas and J. Zhang. Effect of Microstructure (Particulate Size and Volume Fraction) and Counterface Material on the Sliding Wear Resistance of Particulate-Reinforced Aluminum Matrix Composites. *Metallurgical and Materials Transactions A*, 25A:969–983, 1994.
- [6] Eric Irissou, Jean-Gabriel Legoux, Bernard Arsenault, and Christian Moreau. Investigation of Al- Al_2O_3 Cold Spray Coating Formation and Properties. *Journal of Thermal Spray Technology*, 16(5-6):661–668, 2007.
- [7] Alexander Evans, Christopher San Marchi, and Andreas Mortensen. *Metal Matrix Composites*, pages 9–38. Kluwer Academic Publishers, Dordrecht, 2003.
- [8] K. Spencer, D.M. Fabijanic, and M.-X. Zhang. The use of Al- Al_2O_3 cold spray coatings to improve the surface properties of magnesium alloys. *Surface & Coatings Technology*, 204:336–344, 2009.
- [9] Yongshan Tao, Tianying Xiong, Chao Sun, Huazi Jin, Hao Du, and Tiefan Li. Effect of Al- Al_2O_3 on the properties of cold sprayed Al- Al_2O_3 composite coatings on AZ91D magnesium alloy. *Applied Surface Science*, 256(1):261 – 266, 2009.
- [10] U.S. Department Of Defense Manufacturing Process Standard MIL-STD-3021, “Materials Deposition, Cold Spray,” 2008.
- [11] Hamid Assadi, Frank Gärtner, Thorsten Stoltenhoff, and Heinrich Kreye. Bonding mechanism in cold gas spraying. *Acta Materialia*, 51:4379–4394, 2003.

- [12] F. Gärtner, T. Stoltenhoff, T. Schmidt, and H. Kreye. The cold spray process and its potential for industrial applications. *Journal of Thermal Spray Technology*, 15(2):223–232, 2006.
- [13] Eric Irissou, Jean-Gabriel Legoux, Anatoly Ryabinin, Bertrand Jodoin, and Christian Moreau. Review on Cold Spray Process and Technology: Part I-Intellectual Property. *Journal of Thermal Spray Technology*, 17(4):495–516, 2008.
- [14] V.K. Champagne. *The Cold Spray Materials Deposition Process: Fundamentals and Applications*. Woodhead Publishing Limited, Cambridge, 2007.
- [15] A. Papyrin, V. Kosarev, K.V. Klinkov, A. Alkhimov, and V.M. Fomin. *Cold Spray Technology*. Elsevier, Oxford, 2006.
- [16] Victor K. Champagne. The Repair of Magnesium Rotorcraft Components by Cold Spray. *Journal of Failure Analysis and Prevention*, 8:164–175, 2008.
- [17] Hong Jin Kim, Wolfgang Windl, and D.A. Rigney. Structure and chemical analysis of aluminium wear debris: Experiments and ab initio simulations. *Acta Materialia*, 55:6489–6498, 2007.
- [18] Peter J. Blau. Mechanisms for Transitional Friction and Wear Behavior of Sliding Metals. *Wear*, 72:55–66, 1981.
- [19] M. Cocks. Interaction of sliding metal surfaces. *Journal of Applied Physics*, 33(7):2152–2161, 1962.
- [20] Morton Antler. Processes of Metal Transfer and Wear. *Wear*, 7:181–203, 1964.
- [21] S.V. Prasad, J.R. Michael, B.S. Majumdar, and C.C. Battaile. On the Evolution of Friction- Induced Microstructures in Single Crystal Nickel. *Microscopy and Microanalysis*, 14 (Supplement 2):906–907, 2008.
- [22] B. Venkataraman and G. Sundararajan. The sliding wear behaviour of Al-SiC particulate composites - II. The characterization of subsurface deformation and correlation with wear behaviour. *Acta Materialia*, 44(2):451–460, 1996.
- [23] J.M. Shockley, H.W. Strauss, R.R. Chromik, N. Brodus, R. Gauvin, E. Irissou, and J.- G. Legoux. In Situ Tribometry of Cold-Sprayed Al-Al₂O₃ Composite Coatings, *Surface and Coatings Technology*, 215:350–356, 2013.

- 1
2
3
4 [24] Y. Berthier. *Wear - Materials, Mechanisms and Practice*, chapter 7: Third-Body Reality -
5
6 Consequences and Use of the Third-Body Concept to Solve Friction and Wear Problems, pages
7
8 291–316. John Wiley and Sons, Ltd., 2005.
9
- 10 [25] S.K. Biswas. *Wear - Materials, Mechanisms and Practice*, chapter 3: Wear of Metals: A Material
11
12 Approach, pages 21–36. John Wiley and Sons, Ltd., 2005.
13
14
- 15 [26] Maurice Godet. The third-body approach: a mechanical view of wear. *Wear*, 100:437–452, 1984.
16
- 17 [27] Maurice Godet. Third-bodies in tribology. *Wear*, 136(1):29–45, 1990.
18
- 19 [28] S. Descartes and Y. Berthier. Rheology and flows of solid third bodies: background and application
20
21 to an MoS_{1.6} coating. *Wear*, 253:546–556, 2002.
22
23
- 24 [29] Richard R. Chromik, Colin C. Baker, Andrey A. Voevodin, and Kathryn J. Wahl. In situ tribometry
25
26 of solid lubricant nanocomposite coatings. *Wear*, 262(9):1239–1252, 2007.
27
- 28 [30] Holger W. Strauss, Richard R. Chromik, Salim Hassani, and Jolanta E. Klemberg-Sapieha. In situ
29
30 tribology of nanocomposite Ti-Si-C-H coatings prepared by PE-CVD. *Wear*, 272(1):133–148,
31
32 2011.
33
34
- 35 [31] Pantcho Stoyanov, Holger W. Strauss, and Richard R. Chromik. Scaling effects between micro- and
36
37 macro-tribology for a Ti-MoS₂ coating. *Wear*, 274-275(0):149–161, 2012.
38
- 39 [32] I.L. Singer, S.D. Dvorak, K.J. Wahl, and T.W. Scharf. Role of third bodies in friction and wear of
40
41 protective coatings. *Journal of Vacuum Science & Technology A*, 21(5):S232–S240, 2003.
42
43
- 44 [33] R. R. Chromik, H. W. Strauss, and T. W. Scharf. Materials Phenomena Revealed by In Situ
45
46 Tribometry. *JOM*, 64(1): 35–43, 2012.
47
- 48 [34] W.C. Oliver and G.M. Pharr. An improved technique for determining hardness and elastic modulus
49
50 using load and displacement sensing indentation experiments. *Journal of Materials Research*,
51
52 7(6): 1564–1586, 1992.
53
54
- 55 [35] D.A. Rigney. Transfer, mixing, and associated chemical and mechanical processes during the sliding
56
57 of ductile materials. *Wear*, 245(1):1–9, 2000.
58
59
60
61
62
63
64
65

- [36] Y. Berthier, M. Godet, and M. Brendle. Velocity Accommodation in Friction. Tribology Trans, 32:490–496, 1989.
- [37] Y. Wang, W.M. Rainforth, H. Jones, and M. Lieblisch. Dry wear behaviour and its relation to microstructure of novel 6092 aluminium alloy-Ni₃Al powder metallurgy composite. Wear, 251:1421–1432, 2001.
- [38] D.A. Rigney, L.H. Chen, M.G.S. Naylor, and A.R. Rosenfield. Wear Processes in Sliding Systems. Wear, 100:195–219, 1984.
- [39] K.J. Wahl, R.R. Chromik, and G.Y. Lee. Quantitative *in situ* measurement of transfer film thickness by a Newton's rings method. Wear, 264:731, 2008.
- [40] H.-J. Kim, A. Emge, S. Karthikeyan, and D.A. Rigney. Effects of tribooxidation on sliding behavior of aluminum. Wear, 259:501–505, 2005.
- [41] W.M. Rainforth. Microstructural evolution at the worn surface: a comparison of metals and ceramics. Wear, 245:162–177, 2000.
- [42] B. Venkataraman and G. Sundararajan. Correlation between the characteristics of the mechanically mixed layer and wear behaviour of aluminium, Al-7075 alloy and Al-MMCs. Wear, 245:22–38, 2000.
- [43] Z.N. Farhat, Y. Ding, D.O. Northwood, and A.T. Alpas. Effect of grain size on friction and wear of nanocrystalline aluminum. Materials Science and Engineering A, 206:302–313, 1996.
- [44] Afrooz Barnoush, Markus T. Welsch, and Horst Vehoff. Correlation between dislocation density and pop-in phenomena in aluminum studied by nanoindentation and electron channeling contrast imaging. Scripta Materialia, 63:465–468, 2010.
- [45] R.Z. Valiev, R.K. Islamgaliev, and I.V. Alexandrov. Bulk nanostructured materials from severe plastic deformation. Progress in Materials Science, 45:103–189, 2000.
- [46] P.J. Apps, J.R. Bowen, and P.B. Prangnell. The effect of coarse second-phase particles on the rate of grain refinement during severe deformation processing. Acta Mat, 51:2811–2822, 2003.

- 1
2
3
4 [47] Anirban Mahato, Nisha Verma, Vikram Jayaram, and S.K. Biswas. Severe wear of a near eutectic
5 aluminium-silicon alloy. *Acta Materi*, 59:6069–6082, 2011.
6
7
8
9 [48] Sylvie Descartes, C. Desrayaud, and E.F. Rauch. Inhomogeneous microstructural evolution of pure
10 iron during high-pressure torsion. *Materials Science & Engineering, A*, 528:3666– 3675, 2011.
11
12
13 [49] I. Gutierrez-Urrutia, M.A. Munoz-Morris, and D.G. Morris. Contribution of microstructural
14 parameters to strengthening in an ultrafine-grained Al-7% Si alloy processed by severe
15 deformation. *Acta Materialia*, 55:1319–1330, 2007.
16
17
18 [50] I. Gutierrez-Urrutia, M.A. Munoz-Morris, I. Puertas, C. Luis, and D.G. Morris. Influence of
19 processing temperature and die angle on the grain microstructure produced by severe deformation
20 of an Al-7% Si alloy. *Materials Science and Engineering A*, 475:268–278, 2008.
21
22
23 [51] N.A. Fleck, G.M. Muller, and J.W. Hutchison. Strain gradient plasticity: Theory and experiment.
24 *Acta Metallurgica Et Materialia*, 42:475–487, 1994.
25
26
27 [52] C. Perrin and W.M. Rainforth. The effect of alumina fibre reinforcement on the wear of an Al-4.3%
28 Cu alloy. *Wear*, 181-183:312–324, 1995.
29
30
31 [53] A.P. Sannino and H.J. Rack. Dry sliding wear of discontinuously reinforced aluminum composites:
32 review and discussion. *Wear*, 189:1–19, 1995.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

List of Figures

- Fig. 1** Secondary electron (SE) images of etched unworn microstructures of CS0 (a) and CS22 (b) viewed in cross-section. Particle boundaries are visible in the etched microstructures, as are porosity and strain lines. Al₂O₃ particles in CS22 are embedded near particle boundaries.
- Fig. 2** The tribological circuit: (a) theoretical [Berthier2005] and (b) applied to the current system (not to scale). Wear and recirculation flows in (b) may be ejected longitudinally at the ends of the wear track or laterally, as indicated by the arrows.
- Fig. 3** Mean friction coefficient per cycle plotted vs. cycle number for tests run to 500 (a) and 2000 (b) cycles
- Fig. 4** In situ micrographs showing the formation of the initial CS0 transfer film during the first cycle. “SD” indicates sliding direction.
- Fig. 5** In situ micrographs of transfer films from CS0 (a) and CS22 (b) at 10, 50, 500, and 2000 cycles
- Fig. 6** Average friction coefficient vs. cycle number (left), in situ micrographs of CS0 transfer films in the vicinity of two friction events, a and b (right). Patches of interference fringes are evident just prior to the event (highlighted in a1 and b1), after which point material detached (a2 and b2) and was replaced with newly plowed material (a3 and b3).
- Fig. 7** Features of the CS0 transfer film observed ex situ after 500 sliding cycles. (a) Overall view of main features, including the location and perspective of FIB cross-sections in Figure 9; (b) height profile of the features in (a); detail images of (c) the highest prow and (d) a region of thin material

Fig. 8 Features and microstructures in the wear tracks of CS0 and CS22 viewed ex situ. (a) and (b): top-down views; (c) and (d): locations and perspectives of FIB cross-sections in (e) and (f). Image (c) was taken at a 54° tilt.

Fig. 9 Microstructures from two regions of the CS0 transfer film after 500 sliding cycles. The locations and perspectives are shown in Figure [Fig7 CS0 TF Top Down]. (a): Microstructures in the thick region of transfer film, with details highlighted in (b) and (c); (d): microstructures in the thin region of transfer film. Microstructural features of nanostructured aluminum (NS Al), relatively large-grained aluminum (LG Al), and cracks between sections are visible in each micrograph.

Fig. 10 Features of the CS22 transfer film viewed ex situ after 500 sliding cycles. (a) Overall view of main features, including the location and perspective of FIB cross-sections in Figure 10; (b): height profile of the features in (a); (c) and (d): sections of tribofilm selected for longitudinal cross-sectioning and transverse cross-sectioning, respectively

Fig. 11 Microstructures from two regions of the CS22 transfer film after 500 sliding cycles. The locations and perspectives are shown in Figure [Fig10 CS22 TF Top down]. (a) Longitudinal cross-section, with details in (b) and (c); (d): transverse cross section from a sloped part of the transfer film. Microstructural features of nanostructured aluminum (NS Al), relatively large-grained aluminum (LG Al) and Al₂O₃ particles are visible.

Fig. 12 Hardness data from nanoindentation (a) and representative load-displacement curves (b) from CS0 and CS22. Error bars show plus and minus one standard deviation of the mean value.

Fig. 13 Secondary electron images and EDXS mapping of aluminum and oxygen K α signals (left) and representative spectra (right) of the polished cross-sections of CS0 and CS22 wear tracks.

Fig. 14 Tribological flow schematics of CS0 and CS22 at the beginning of the test, where source flow dominates for both to form the initial transfer film, and later in the test after the initial run-in. The block pattern shows the schematic locations of nanocrystalline third body material, where for CS22 it was highly constrained while for CS0 it was greatly intermixed with less-refined material.

Table1 CS0 and CS22 properties
Click here to download Table: Table 1 CS0 and CS22.xlsx

Sample	Al ₂ O ₃ in Cold Spray Feedstock Powder	Al ₂ O ₃ Recovered in Cold Sprayed Coating	Hardness (HV ₂₀₀) [6]	Wear Rate after 500 cycles (10 ⁻² mm ³ N ⁻¹ m ⁻¹)	Wear Rate after 2000 cycles (10 ⁻² mm ³ N ⁻¹ m ⁻¹)
	(wt.%) [6]	(wt.%) [6]			
CS0	0	0	53.4 ± 1.7	2.815 ± 0.263	0.911 ± 0.113
CS22	50	22.6	78.9 ± 4.7	0.357 ± 0.097	0.148 ± 0.020

Figure3a COF to 500

[Click here to download Figure: Fig3a COF to 500.eps](#)

Cycle:	0
CoF:	0

Cycle:	0
CoF:	0

Cycle:	0
CoF:	0

Initial Transfer
(Prow Formation)

Prow at critical size
before detachment

500 μm

Figure 5b CS22-TF
Cycles to do load

CoF: 0.605

1000 μm

Cycle: 50
CoF: 0.649

1000 μm

Cycle: 500
CoF: 0.647

1000 μm

Cycle: 2000
CoF: 0.595

1000 μm

Figure6 TF Around Friction Event
Click here to download Figure_Fig6 CS0 TF around friction event.pptx

80.0 μm
 60.0
 50.0
 40.0
 30.0
 20.0
 10.0
 0.0

Figure12b Load-Displacement Curves
Click here to download Figure: Fig12b L-D Curves.eps

Figure13 EDX

CS0: Initial Cycles **CS22: Initial Cycles** **CS0: Steady State** **CS22: Steady State**