



Load dependence of oxidative wear in metal/ceramic tribocouples in fretting environment

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ABSTRACT

For a large number of non-oxide ceramic/metal as well as for non-oxide particulate reinforced composite/metal tribocouples, oxidative wear is reported to play a major role in the overall damage and material removal process. The designing of new materials with improved resistance to oxidative wear requires understanding of the combined effect of the material properties and operating parameters on the wear resistance. In this paper, an analytical model to predict the dependence of the oxidative wear volume on load and sliding velocity is presented. The model is developed using basic chemical kinetics and Hertzian contact mechanics, and is valid for the case of a stable oxide layer. Exponential dependence of wear volume on operating parameters (load, sliding velocity) is predicted in the proposed model. It has been shown to successfully explain the qualitative experimental load dependence of the wear volume for five ceramic/metal tribocouples (Al_2O_3 /steel, WC–TiC–Co/steel, TiB_2 – MoSi_2 /steel, ASP23 steel/alumina and Ti6Al4V/alumina) that exhibit oxidative wear. The activation energy of the oxidation of metallic counter bodies under fretting conditions was also calculated using the model, which turns out to be significantly lower than in the static conditions.

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1. Introduction

The friction and wear properties of any tribosystem critically depend on two independent set of parameters: (a) operating parameters (load, velocity) and (b) material parameters (hardness, elastic modulus, fracture toughness) [1,2]. In addition, the tribological properties are also influenced by the surrounding environment (humidity, gaseous environment, lubricants, liquid medium) and the contact configuration (ball-on-flat, pin-on-disc, cylinder-on-cylinder etc.). Overall, the wear mechanisms of ceramics can be broadly divided into two categories: tribochemical and tribomechanical wear [1,3]. In assessing the tribological performance of new materials as well as to compare with competing materials, the researchers carry out tests under different operating conditions mostly with variation in sliding speed or load [4–6]. While the quantification of friction and wear resistance is of importance to tribologists/engineers in designing new material composition, the understanding of the wear mechanisms as a result of micromechanical interaction among the asperities of

two mating surfaces in a given tribological environment is of scientific importance.

In the absence of widely applicable analytical models, the tribological properties of a material are evaluated experimentally under different operating conditions/environments. Even for preliminary wear assessment of a material, wide range of standard tribological tests and experiments need to be conducted, which require a lot of time and effort. In an effort to develop analytical models for assessment of tribological properties of materials, we proposed a new model to explain the tribomechanical wear of brittle ceramics by considering the interaction of Hertzian cone cracks [7]. This model provided simple expressions for wear volume and transition load from mild to severe wear in terms of operating parameters as well as material properties. A good correlation between experimental results and model predictions in case of tribosystems with widely varying material parameters indicates reasonable potential of our model in predicting tribomechanical wear of brittle ceramics.

In this study, we focus on the oxidative wear occurring at the ceramic/metal fretting contacts. Fretting wear is the repeated reciprocatory rubbing between two surfaces, with low displacement amplitude ($\leq 200 \mu\text{m}$). Fretting is characterised by relatively low sliding speeds and consequently, high temperatures are not generated over the entire nominal contact area [8–12]. It is reported that the tribochemical transformations/reactions take place mostly at the asperity/spot-to-spot contacts due to high

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flash temperatures at these points [11–15]. It has been generally recognised that tribochemical reactions, occurring under dynamic and complex contact conditions, need to be considered as result of the simultaneous mechanical and chemical phenomena [16]. Therefore, the determination of wear rate/volume as a function of load/velocity becomes an important task for better understanding of this phenomenon.

2. Characteristics of tribochemical wear

The chemical reactions initiated by the friction process relate to the tribochemistry, which can be described as the stimulation of chemical reactions at frictional surfaces due to the influence of mechanical energy [17]. In particular, the tribochemical wear is defined as the material removal or formation of the tribochemical layer at the interface of two contacting surfaces as a result of these reactions at the interface. In the cases where tribochemical reaction happens to be the oxidation of one of the counter bodies, tribochemical wear is also referred to as oxidative wear. The oxidation reactions have been observed to play an important role in determining the wear behaviour of various metal reinforced ceramics as well as non-oxide ceramics under both dry [18–20] and oil lubricated conditions [21–23]. Under these conditions, reaction products are formed and they may increase or decrease the wear resistance of the material depending on the stability and the wear resistance of the reaction products.

It has been suggested in the previous studies that prevailing thermal severity influence the tribochemical reactions that occur at frictional interfaces under moderate to high speed sliding conditions [11,12]. However, the importance of the mechanical stimulation for the feasibility of tribochemical reaction at lower speed, via generation of surface active sites on the disrupted surface, has been highlighted in fretting wear studies, where the contact temperature is lower [3,15,16,24,25]. Experimental [21,22,24] as well as computational [26,27] studies have observed a significant (6–8 times) [21] decrease in the activation energy of the tribochemical reactions, making these reactions feasible at low contact temperatures.

Models for oxide layer formation were proposed by Kitaoka et al. [23], Quinn [28] and Xu and Kato [21], which provided the analytical expression for wear volume calculation for non-oxide ceramics in water. The analytical models take into account the delamination of the oxide layer after it grows to a certain thickness. The analytical expressions were formulated to calculate the oxidative wear volume in terms of flash temperature and kinetics as well as material parameters. A multiscale fretting wear simulation technique was developed by Ding et al. [29] combining a plasticity enhanced oxidation model and an incremental wear technique. The method simulates the evolution of oxide debris–substrate interface and shows potential to simulate complex debris and wear scar profiles. However, the explicit functional dependence of the oxidative wear volume/rate on the operating parameters (load, velocity) has not been established in the previously existing models, which can be a very useful tool for preliminary assessment of the oxidative wear properties of a tribocouple.

In the present work, an analytical model is proposed to quantify the wear resistance of materials, experiencing oxidative wear at ceramic/metal tribological contacts. The case of the formation of a stable oxide layer at the interface is analysed, which has been frequently observed for many tribocouples fretted in ambient environment and at very low sliding velocities ($\sim 10^{-3}$ m/s) [18–20]. The dependence of wear volume on operating parameters (load/velocity) has been formulated and a very basic model has been proposed for stable oxide layer formation

during the fretting wear. In the model, the exponential dependence of the oxidative wear volume on load has been derived using basic chemical kinetics and Hertzian contact mechanics. The exponential dependence of the oxidative wear volume on load has been validated with experimental data for five tribocouples. Activation energy of the oxidation of metallic counter bodies in fretting conditions is also calculated. The simplicity and the agreement with the experiments of our model for five different tribocouples make it potentially useful for the preliminary assessment of the oxidative wear properties of ceramic/metal tribocouples in fretting conditions.

3. Oxidative wear model

List of symbols

V	oxidative wear volume
V_0	initial tribomechanical wear volume
A_0	asperity contact area
t	sliding duration
Δr_c	critical oxide layer thickness before it delaminates from the metallic surface
ρ	density of oxide product
k_0	pre-exponential constant for oxidation reaction
Q	activation energy for oxidation reaction
R	universal gas constant in SI units
T_a	ambient temperature
μ	coefficient of friction between the surfaces
P	normal load
E^*	composite elastic modulus of the tribocouple
R^*	composite radius of the tribocouple
v	sliding speed
k	thermal conductivity of the flat
T_f	flash temperature at the contacting surface
T_a	ambient temperature

3.1. Assumptions

The analytical model has been developed under the following assumptions:

- Oxidation takes place only at the asperity–asperity contacts.
- Oxidative wear is caused only by the oxidation during the steady-state running-in process.
- The model is valid only for the case of stable oxide layer formation.
- Only ball-on-flat type of contact configuration has been considered.
- The velocity variation at the ends of a displacement stroke in reciprocatory motion has been neglected, because the distance over which the velocity varies is of the order of 5% of the total stroke length. Therefore, in the model, constant sliding velocity is assumed.

3.2. Model description

It is known that when two contacting surfaces are in relative motion against each other, heat is generated at the interface due to the conversion of frictional energy to heat energy. The heat generated at the interface results in the elevation of the interface temperature. In this context, the contact thermal conditions are characterised by two types of contacts: nominal contact and asperity contact [1,2]. In order to characterize the thermal

severity of tribocontacts two parameters are used, bulk temperature and flash temperature, respectively for nominal and asperity contacts. Since the asperity contact area is much smaller than the nominal contact area, the flash temperature at the asperity contacts is much higher than the bulk temperature. It needs to be emphasised here that the oxidation takes place at the asperity contacts only, due to high temperature and severe wear conditions [13–15]. This is specifically true for the case of fretting wear. As a result, the tribological interface is covered with oxide layer. The rate of oxide layer formation depends on two simultaneously occurring phenomena:

- Rate of wear of oxide layer (w)
- Rate of formation of oxide layer (r)

Based on these two rates, two limiting conditions can be proposed as far as the stability of the oxide layer is concerned:

- Oxide layer is stable, i.e. the oxidative wear is effective to reduce the wear loss. This condition occurs when $r \gg w$.
- Oxide layer is unstable, i.e. the oxidative wear leads to accelerated wear loss. This condition occurs when $r \ll w$.

In this paper, we present a model for the case of stable oxide layer formation, i.e. the wear of oxide layer is neglected during the running in process, which has also been found experimentally [21]. In the following, we describe the analytical model under the set of assumptions mentioned in Section 3.1.

During the initial running-in-period, the mechanical interlocking of asperities occurs and under an external load, the asperity deformation or fracture leads to initial wear. As a result of reduction in contact pressure and smoothing of the friction surface, the wear mode changes from mechanically dominated wear to oxidation dominated as the sliding distance increases [21,24]. Thereafter, a wear scar is formed until the oxidative wear takes over. Oxidation reaction takes place at the asperity contacts on the metal surface (either the ball or the flat disc). Initially, small zones are formed at the metal surface. After some time, these small zones grow in size and oxidative layer spreads over the entire contact zone. The schematic diagram of the run in process of the oxide layer formation in this case is shown in Fig. 1. Due to prevailing thermal conditions at the tribological interface, the oxidation of the mating surfaces leads to oxidative reaction, when the tests are carried out in ambient atmospheric conditions.

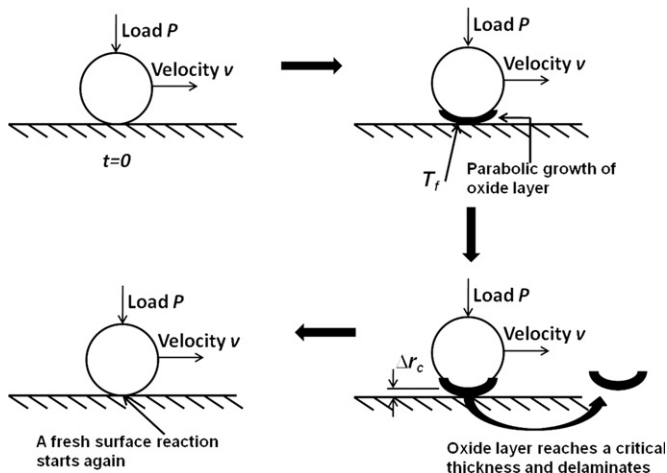


Fig. 1. Schematic diagram of the oxidative wear model in case of ceramic/metal tribocouple (ball is assumed to be metallic in the diagram).

Although the oxidation of metals at low temperature (\sim room temperature) is known to follow logarithmic growth law in static conditions, in tribological experiments it has been shown to follow parabolic growth law even at room temperature [24,30]. Therefore, growth law of oxide layer can be written as

$$m = k_p \sqrt{t} \quad (1)$$

where m is the mass gain of the oxide layer per unit area in total time t and k_p is the reaction constant. Quasi-static removal of the oxide layer is the fundamental mechanism of oxidative wear in metal/ceramic tribocouples [21,24]. Therefore, when the oxide layer reaches a critical thickness, it delaminates from the reacting surface as wear debris. The quasi-periodic removal of oxide layer from the ball surface enhances the oxide layer formation because it repeatedly exposes fresh surface for further oxidation. If Δr_c is the critical thickness at which the oxide layer delaminates from the surface of the metal and gets transferred to the ceramic surface, the mass of the oxide formed at a single asperity contact will be

$$m' = \rho A_0 \Delta r_c = k_p \sqrt{t_c} A_0 \quad (2)$$

where t_c is the time taken to form the critical thickness of the oxide layer, A_0 is the asperity contact area, and ρ is the density of oxide product. From the above equation, one can write

$$t_c = \left(\frac{\Delta r_c \rho}{k_p} \right)^2 \quad (3)$$

Total mass of oxide formed on the interface in time t is given by

$$m(t) = (k_p \sqrt{t_c} A_0) t / t_c \quad (4)$$

At any time t , oxide volume formed at the interface ($V(t)$) can be derived by combining Eqs.(3) and (4) and is given by

$$V(t) = \frac{k_p^2 A_0 t}{\Delta r_c \rho^2} \quad (5)$$

Typically, the reaction constant, k_p , follows Arrhenius type of relationship, i.e. depends exponentially on the temperature, as $k_p = k_0 \exp(-Q/RT)$. Therefore, Eq. (5) can be written as

$$V = \frac{A_0 t}{\rho^2 \Delta r_c} k_0^2 \exp(-2Q/RT_f) \quad (6)$$

where Q is the activation energy for the oxidation reactions occurring at $T=T_f$ (flash temperature), k_0 is the pre-exponential constant and R is the universal gas constant. In this process, reaction takes place at the flash temperature (T_f), which depends on the load and sliding velocity, according to the Archard's relationship [9]:

$$T_f = T_a + 1.67 \mu \frac{(\pi P_m)^{1/2}}{8k} P^{1/2} v \quad (7)$$

where μ is the coefficient of friction; P_m is the Hertzian contact stress; P is the applied load; v is the sliding velocity; T_a is the absolute ambient temperature and k is the thermal conductivity of the flat. From Hertzian analysis for elastic contacts, P_m can be expressed as following [31]:

$$P_m = \left(\frac{6PE^*2}{\pi^3 R^*2} \right)^{1/3} \quad (8)$$

where E^* and R^* are the composite elastic modulus and composite radius of individual asperity respectively. The above formulation holds true for interaction of loaded single asperity against a nominally flat surface [1].

Now substituting expressions for T_f and P_m from Eqs. (7) and (8), the final expression for oxidative wear volume can be obtained as

$$V = \frac{A_0 t}{\Delta r_c \rho^2} k_0^2 \exp\left(\frac{-2Q}{R(T_a + 2.25\mu P^{2/3}(E^*/R^*)^{1/3}v/8k)}\right) \quad (9)$$

Δr_c is the only unknown parameter in Eq. (9). But, an approximate critical thickness (> 1 nm) [24] can be assumed for preliminary oxidative wear volume prediction. For further precision, the experiments can be conducted at different loads keeping all other parameters constant. Δr_c can be fitted to match the experimental values of the oxidative wear volume at different loads with the predicted values.

3.3. Model implications

Derived expression for oxidative wear volume depends on materials properties (hardness, density) as well as kinetic (activation energy, pre-exponential constant) and operational parameters (load, velocity). The thermodynamic feasibility and rate of the reaction both are strongly dependent upon the temperature. Oxidative wear volume increases exponentially with the temperature. However, since the reaction only takes place at the asperity contacts and the bulk temperature being low, it is the flash temperature not the bulk temperature, which is of importance.

Operational wear parameters are important due to their effect on the flash temperature. Different models for the calculation of flash temperatures have been proposed in the previous works [9,10]. But the functional dependence on wear parameters, such as load and sliding velocity, remains more or less same in all the models. Due to its simplicity and explicit load dependence, we have used Archard's model [9] to calculate the flash temperature. The effect of flash temperature model on the load dependence of the oxidative wear volume has been discussed in detail in the next section. According to Eq. (9), wear volume increases with increasing load and/or sliding velocity. Fig. 2 shows the variation of the wear volume with load for oxidative as well as fracture/tribomechanical wear. In arriving at different data points in Fig. 2, a combination of different parameters values was assumed i.e., $Q=25$ KJ/mole, $\mu=0.5$, $E^*=150$ GPa, $R^*=10$ mm, $v=0.5$ m/s, $k=25$ W/m K. The estimated wear volume was normalised using the wear volume value at 2 N load. This figure highlights the key difference between oxidative and tribomechanical wear. For oxidative wear, with stable oxide layer, the wear volume increases exponentially as load increases (Fig. 2a), while

for tribomechanical wear, it increases linearly with the load (Fig. 2b) [7].

From Eq. (9), it is clear that the coefficient of friction μ and the composite elastic modulus E^* are the only mechanical properties, which directly influence the oxidative wear volume. E^* is given as following:

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad (10)$$

where ν_1 , E_1 and ν_2 , E_2 are the Poisson's ratio and elastic modulus of the ball and flat respectively. For wear experiments with the same ball material, the oxidative wear volume will increase with increasing elastic modulus of the flat (E_2). Therefore, materials with higher elastic modulus are expected to exhibit higher oxidative wear. Wear volume also depends on the contact area of a single asperity, A_0 , which depends on the applied load and the hardness (H) of the material [32]. Asperity contact area decreases with increasing hardness. Therefore, the oxidative wear will decrease with increasing hardness.

4. Results and discussion

4.1. Validation methodology

The proposed model results have been compared with the experimental wear data obtained with Al_2O_3 /steel [18], WC-TiC-Co/steel [19] and TiB_2 -MoSi₂/steel [20], Ti6Al4V/alumina [33] and ASP23 steel/alumina [34] tribocouples, where oxidative wear has been reported during fretting wear experiments in earlier studies. In first three tribocouples, the flat ceramic discs were fretted against steel balls, while for the last two tribocouples the metallic flat was fretted against a ceramic ball. The wear scar depth measurement technique was used to measure the wear volume in all the experimental cases. In this method, the wear volume is calculated by measuring the diameter and the depth of the wear scar created on the flat disc or the ball. The details of the experimental method can be found in the respective references.

Before discussing the validation of the model with the experimental values, it is important to note a point about the specific method of wear scar depth measurement for wear volume calculation. As mentioned earlier, the wear process starts with the tribomechanical wear of the tribocouple causing a wear scar on the contacting surfaces (Fig. 3a). After the initial running in

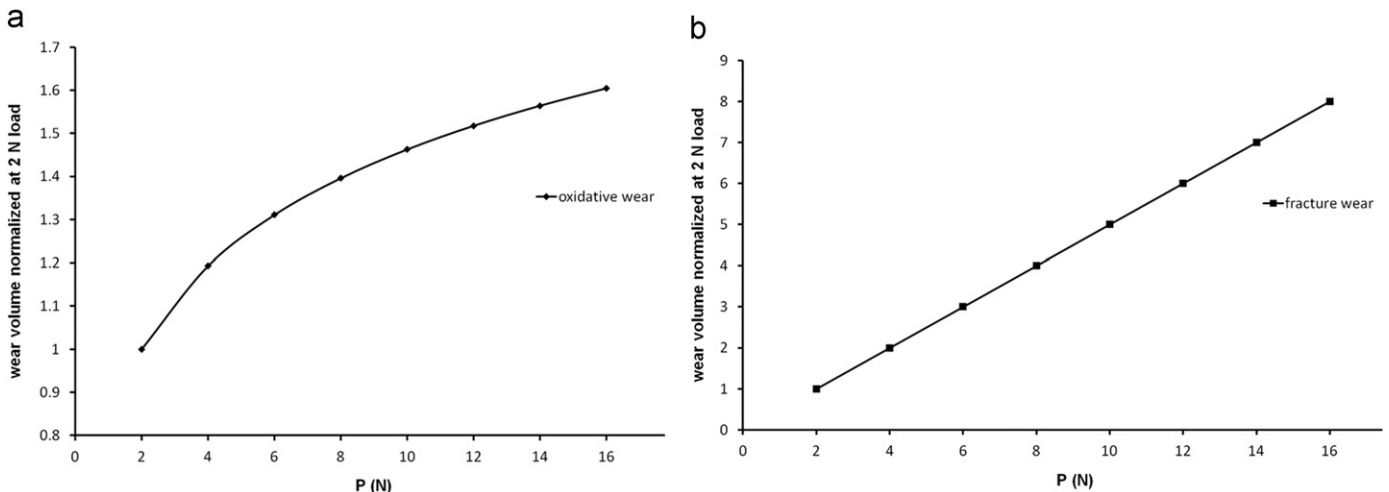


Fig. 2. Comparison of functional load dependence of (a) oxidative wear, and (b) fracture wear volume (P is load in N).

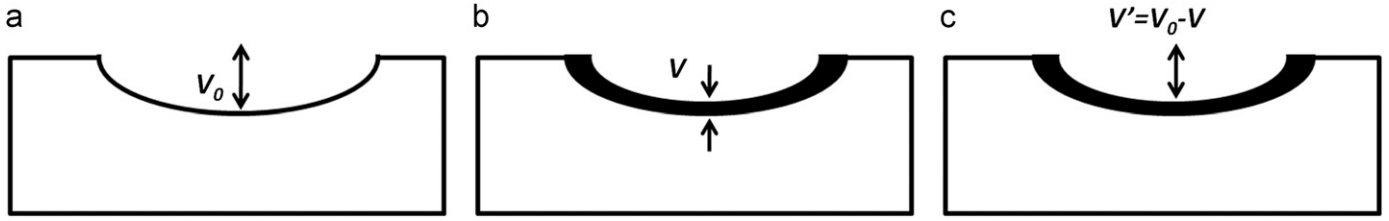


Fig. 3. Illustrative diagram of the experimental measurement of the oxidative wear volume using wear scar depth measurement technique. (a) Initial tribomechanical wear during running in period (V_0), (b) oxide layer formed in the wear cavity (V), (c) experimental wear volume (V') measured using wear scar depth measurement technique.

period, the oxidative wear sets in and the metallic ball/flat starts oxidising as a result of the reduction in pressure and smoothening of the metallic surface. The oxidation product delaminates from the metallic surface at a critical thickness and gets deposited on the ceramic disc/ball forming a protective oxide layer on both the contacting surfaces (Fig. 3b). Therefore, experimentally measured wear volume (V') using wear scar depth measurement technique is the difference of initial tribomechanical wear (V_0) and oxide wear (V) as shown in Fig. 3c, i.e. $V' = V_0 - V$, which can be written as following, using the expression for oxidative wear volume (V) from Eq. (9):

$$V' = V_0 - \frac{A_0 t k_0^2}{\rho^2 \Delta r_c} \exp\left(\frac{-2Q}{R(T_a + 2.25 \mu P^{2/3} (E^*/R^*)^{1/3} v/8k)}\right) \quad (11)$$

In SEM/EDX analysis in these studies, the oxide layer consisting of metal oxide was found in the wear cavity of the discs as well as the ball surfaces. Another direct evidence for the dominance of oxidative wear in these cases comes from the fact that the wear scar depth of the flat ceramic decreases with increasing load in all the cases, in contrast to the tribomechanically dominated wear process [7]. Since oxidative wear of the metallic surface increases with the increasing load, thicker protective oxide layer is deposited in the wear cavity of the flat/ball and hence, the wear scar depth decreases with the load.

The dependence of wear volume on asperity contact temperature has been reported in previous studies [8,11,12] as well as in the present model. The asperity contact temperature is determined by the operating parameters (load and velocity) and material properties. In general, the wear experiments are conducted with varying load and/or velocity. In order to evaluate the validity of the model, experimental results on the effect of load on the oxidative wear volume were compared to model predictions. A comparison of the absolute wear volume could not be performed due to the unavailability of the required thermodynamic and kinetic parameters for the experimental cases considered in the present study. Eq. (11) can be rewritten as

$$V' = V_0 - K_1 \exp\left(\frac{-2Q}{K_2 + K_3 P^{2/3}}\right) \quad (12)$$

where K_1 , K_2 , K_3 are the respective load independent parameters in Eq. (11). Eq. (12) can be written in the following form:

$$\frac{-2Q}{\ln((V_0 - V')/K_1)} = K_2 + K_3 P^{2/3} \quad (13)$$

Now, if $[\ln((V_0 - V')/K_1)]^{-1}$ is plotted against $P^{2/3}$, it should be a straight line. The y -intercept of the straight line can be used to calculate the activation energy of the oxidation reaction in fretting conditions. To validate the model with the experimental data, the values of V_0 and K_1 need to be calculated. As mentioned earlier, V_0 is the tribomechanical wear of the contacting surfaces in the initial stage of the running in process. It was calculated

Table 1

Values of system parameters used for the calculation of tribomechanical wear volume (V_0) during the initial running in period.

Material	β	χ	H (GPa)	K_c (MPa m ^{1/2})	E_{flat} (GPa)	E_{ball} (GPa)
Alumina [18]	1.2	3.0	17.6 ± 1.6	3.9 ± 0.6	378	210
WC-TiC-Co [19]	1.2	3.0	11.9 ± 0.2	14.0 ± 1.3	409	210
TiB ₂ -MoSi ₂ [20]	1.2	3.0	24.7 ± 1.3	5.2 ± 0.8	504	210
ASP23 steel [43]	1.2	3.5	1.96	13.9	223	378

Table 2

Values of the parameters of the metallic counter body used for the calculation of $K_1 = A_0 t k_0^2 / \rho^2 \Delta r_c$.

Material	H (GPa)	k_0 (Kg ² m ⁻⁴ s ⁻¹)	ρ (Kg/m ³)	Δr_c (nm)
SAE 52100 steel	8.316 [44]	0.015 [36]	5242	1.00 [24]
ASP 23 steel	1.96 [38]	0.015 [36]	5242	1.00 [24]
Ti6Al4V	3.5 [33]	124.82 [37]	4230	1.00 [24]

using the tribomechanical wear model proposed in our earlier work [7]

$$V_0 = \frac{\pi s \beta^2}{3} \left(\frac{3PR_i}{4E^*}\right)^{2/3} \sqrt{\left(\left(\frac{4\chi^2 E^* P}{3\beta^3 K_c^2 R_i}\right)^{2/3} - 1\right)} \quad (14)$$

where s is the amplitude of the fretting motion, R_i is the radius of the ball, K_c is the fracture toughness of the ceramic flat, and β is a constant which is equal to 1.2 in case of ceramics and χ is a fitting parameter. All other symbols have their usual meanings as mentioned earlier. The values of the mechanical parameters of the tribocouples used in the calculations are listed in Table 1. To calculate the pre-oxidation tribomechanical wear of Ti6Al4V/alumina tribocouple, the mechanical properties of commercially pure (99.5%) alumina were taken from Ref. [18].

Values of the parameters of the metallic materials used to calculate $K_1 = A_0 t k_0^2 / \rho^2 \Delta r_c$ with the source references are listed in Table 2. The asperity contact area was calculated using the expression $A_0 = P^{0.25}/H$, which holds true at nominal loads for the real surfaces having roughness on many length scales [35]. The value of pre-exponential constant (k_0) for the oxidation of carbon steel [36] and Ti6Al4V [37] (Table 2) was extracted from the parabolic rate constants measured in the temperature range of 773–973 K and 1050–1340 K respectively. Fe₂O₃ and TiO₂ have been reported to be the major oxidation products [18,33] of steel and Ti6Al4V respectively; hence their theoretical densities were taken for the calculations. Since the exact value of critical oxide layer thickness for various metal oxides of the present case was not available, a minimum critical oxide layer thickness of 1 nm was assumed as suggested by Fisher [24].

4.2. Validation of the exponential load dependence of the oxidative wear volume

Fig. 4a–e shows the plots of $[\ln((V_0 - V')/K_1)]^{-1}$ vs. $P^{2/3}$ for all the tribocouples. A linear fit was plotted for the experimental data. R -squared values for the linear fit were calculated to check the precise functional dependence of the model. R -squared value is a statistical parameter which refers to the fraction of variance explained by a model. It provides a measure of how well future outcomes are likely to be predicted by the model. It can vary between 0 and 1, 1 meaning 100% accurate prediction capability of a model. For all the cases, experimental data fits the model very well (see Fig. 4). R -squared values of the straight line fit of the experimental data vary from 0.89 to 0.96 for different tribocouples (Table 3, $n=2/3$). Although the exponential dependence of the oxidative wear volume on load is valid for all

the considered cases, the developed model requires further verification using experimental results obtained with additional tribocouples, where the oxidative wear results into stable oxide layer formation. This will establish wider applicability of the model. Also, the quantitative accuracy of the model needs to be validated by doing well designed experiments to measure all required kinetic and material parameters.

It can be observed that the exact functional dependence of the oxidative wear volume on load and other wear parameters depends on the flash temperature expression. Archard's model for the flash temperature calculation has been used for the formulation in the present case, which gives a specific expression for wear volume in terms of load and other parameters. Although the exponential dependence of the wear volume on the load has been verified for all the cases, the expression inside the exponential part can be different, depending on the

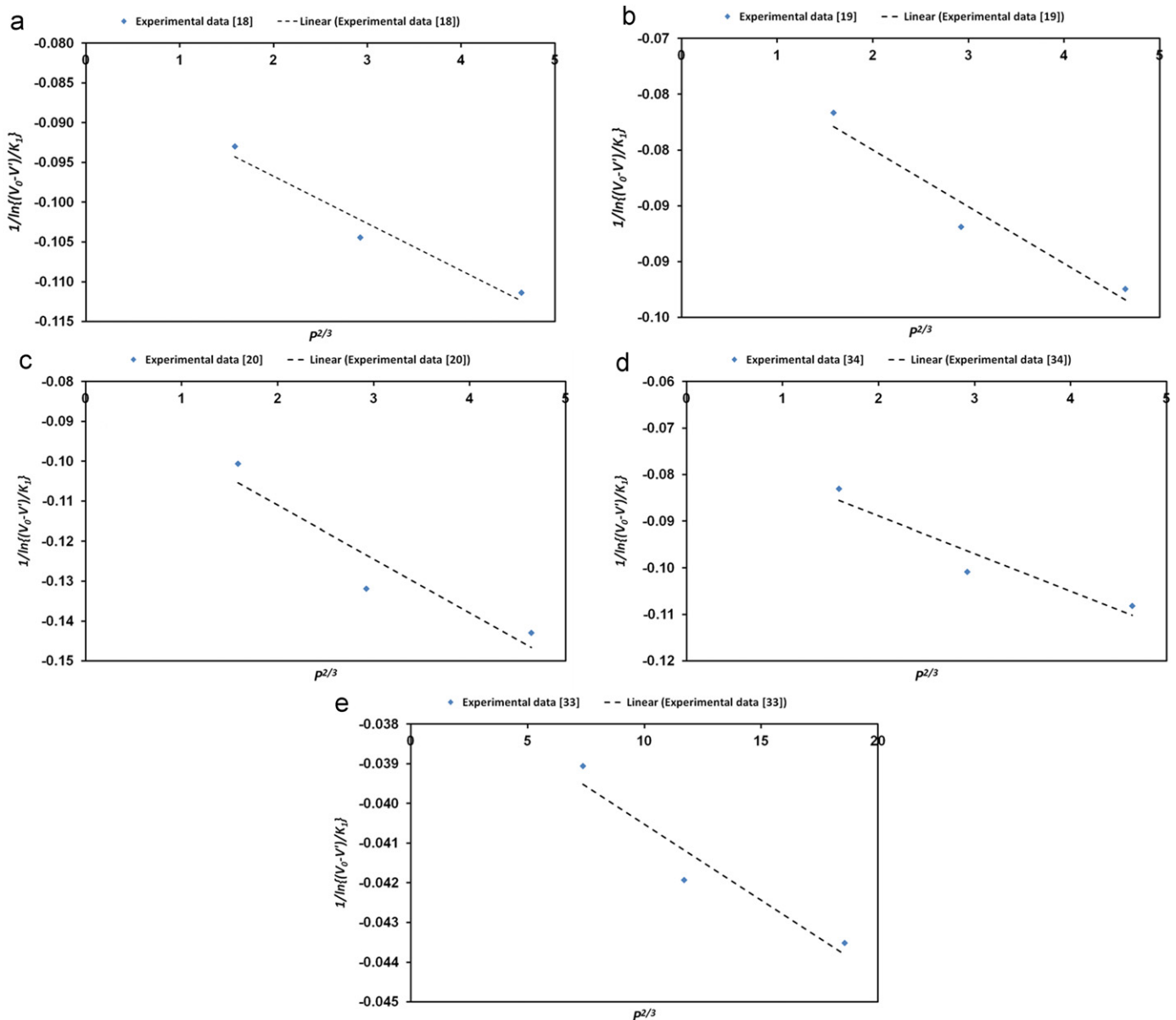


Fig. 4. $[\ln((V_0 - V)/K_1)]^{-1}$ is plotted against $P^{2/3}$ for five selected tribocouples: (a) $\text{Al}_2\text{O}_3/\text{steel}$ [18], (b) $\text{TiC-WC-Co}/\text{steel}$ [19] and (c) $\text{TiB}_2\text{-MoSi}_2/\text{steel}$ [20], (d) $\text{ASP23 steel}/\text{alumina}$ [34], and (e) $\text{Ti6Al4V}/\text{alumina}$ [33]. P is the normal load in N applied during the fretting tests, V_0 is the tribomechanical wear volume (mm^3) of the ceramic disc prior to set in of oxidative wear, V' is the wear volume of the flat (mm^3) measured by scan depth measurement. The dotted straight lines are the best fit to the experimental data points.

Table 3

R-square values of the linear fit of the experimental data for varying load dependence using $-2Q/(\ln((V_0-V)/K_1)) = K_2 + K_3P^n$.

Tribocouple	'n' Value					
	$P^{1/3}$	$P^{1/2}$	$P^{2/3}$	$P^{3/4}$	P^1	P^2
Al ₂ O ₃ /steel [18]	0.98	0.97	0.96	0.95	0.92	0.81
WC–TiC–Co/steel [19]	0.97	0.96	0.94	0.93	0.91	0.78
TiB ₂ –MoSi ₂ /steel [20]	0.93	0.91	0.89	0.88	0.84	0.70
Ti6Al4V/alumina [33]	0.95	0.93	0.91	0.91	0.88	0.77
ASP23 steel/alumina [34]	0.95	0.93	0.91	0.90	0.86	0.73

use of a specific theoretical model for the flash temperature estimation.

In order to assess various functional dependence of the wear volume on load, a sensitivity analysis was conducted, in which $[\ln((V_0-V)/K_1)]^{-1}$ is plotted against P^n for different values of n . On the basis of the flash temperature models of Archard [9], Kong and Ashby [10], Greenwood and Alliston-Greiner [38], the values of 'n' in our analysis were taken to be equal to 0.67, 0.5 and 1, respectively. In addition, a few other values of 'n' are also taken for this analysis. In each case, the R-squared values of the linear fit to the data were calculated and these are summarised in Table 3. R-squared values for powers of load less than unity are greater than 0.88 for each case, which shows a very good agreement of the linear fits of the plots. It can be seen that although R-squared values of linear fit do not vary much for the powers of load less than unity and are always > 0.88, they are comparatively very low (0.7–0.81) for power of load equal to 2. Observing that $n \leq 1$ in all the three flash temperature models [9,10,40], it can be concluded that the dependence of wear volume on load is very little sensitive to the exact value of the exponent (as long as it is < 1). Also, the exponential dependence of wear volume on load, as revealed in our analysis, is validated by the five tribocouples considered here.

4.3. Calculation of activation energy (Q)

From Eq. (13) it can be seen that the y-intercept of $[\ln((V_0-V)/K_1)]^{-1}$ versus $P^{2/3}$ plot is equal to $-K_2/2Q$, where $K_2 = RT_a$. Therefore, activation energy can be calculated as $Q = -RT_a/2y\text{-intercept}$. Thus, the activation energy of oxidation of the carbon steel and Ti6Al4V in fretting conditions was calculated using y-intercepts of the plots in Fig. 4 for all the tribocouples. All the fretting wear tests were performed at room temperature. The average activation energy for the oxidation of SAE 52100 bearing grade steel under fretting conditions calculated from the three cases (Al₂O₃/steel [18], TiC–WC–Co/steel [19], TiB₂–MoSi₂/steel [20]) comes out to be 15.95 kJ/mole. The activation energy for ASP23 steel and Ti6Al4V comes out to be 17.30 kJ/mole and 34.32 kJ/mole respectively. The activation energy for both the carbon steels (SAE 52100 and ASP23) is 5–6 times lower than the activation energy of iron and carbon steel at moderately elevated temperatures in static conditions reported earlier in the literature [39–41]. The activation energy of the Ti6Al4V under fretting conditions is also 2 times lower in comparison to the activation energy in the static conditions [36]. First principle studies have also shown that the transfer of the localised electrons into the conduction bands of solids or antibonding orbitals of molecules becomes easier under shear stress resulting in free or non-localised electrons. It greatly decreases the chemical stability of solids and molecules, and hence facilitate their mechanochemical reactions [26,27]. Macroscopically, the disrupted surfaces caused by the sliding contact generate surface-active sites promoting reactions that otherwise might not occur [22].

5. Conclusions

- In the present work, an analytical oxidative wear model, based on the major assumption of the stable oxide layer formation at ball-on-flat metal/ceramic tribocontact, is developed, using the chemical reaction kinetics in combination with Hertzian contact mechanics.
- The newly developed model provides a simple relationship between oxidative wear volume and kinetic parameters as well as material properties. The dependence of the flash temperature on the material properties and test conditions is critical in determining the wear volume.
- The dependence of wear volume on load and sliding speed is less sensitive to the model used for calculating the flash temperature. A simple expression for the dependence of the wear volume on the load has been developed in the present model. Such a model is shown to be applicable for experimental results obtained with a wide range of tribocouples, including alumina/steel, TiC–WC–Co/steel, TiB₂–MoSi₂/steel, ASP23 steel/alumina and Ti6Al4V/alumina. Thus, for the tribocouples exhibiting oxidative wear with stable oxide layer as a predominant wear mechanism, we propose the following dependence of the wear volume on the load:

$$V = K_1 \exp\left(\frac{-2Q}{K_2 + K_3P^n}\right)$$

- The value of 'n' depends on the model for determining the flash temperature. Good fits has been obtained for a range of tribocouples with 'n' less than unity.
- Activation energy for the oxidation of metals under fretting conditions was found to be significantly lower than the activation energy in static conditions.
- Major limitation of the model is the difficulty in experimental determination of the critical oxide layer thickness. Since activation energy of oxidation reaction in fretting conditions is not same as in the static conditions, fretting wear volume expression has two fitting parameters ($Q, \Delta r_c$). However, satisfactory agreement with the experiments was achieved using a constant value of Δr_c in the present cases.

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Appendix. Summary of experimental results from literature used in this paper

Al₂O₃/steel tribocouple [18]: As part of the investigation to assess whether glass infiltration can enhance the wear resistance of alumina, the hot pressed high purity alumina discs were fretted against bearing steel of diameter 10 mm using a specially designed ball-on-disc type fretting tribometer. The fretting wear experiments were carried out with varying loads (2, 5, 10 N) and varying cycles (10,000, 50,000 and 100,000) at constant frequency (8 Hz) and constant displacement stroke (100 μm) in air at room temperature (28 ± 2 °C) with relative humidity (RH) 50 ± 5%.

SEM–EDS and XRD studies confirmed the formation of various iron oxides (Fe_xO_y) depending on the temperature of the interface. Fracture toughness of the alumina samples was determined using Anstis formula [42] by measuring crack length around Vickers indents at 49 N load. Four point bending tests were done to determine the flexural strength of the ceramic.

WC–TiC–Co/steel tribocouple [19]: In a study to evaluate the wear resistance of mixed carbide cermets, a planned set of experiments was carried out on WC–TiC–Co cermets, processed from both solid solution WC/TiC powders as well as premixed WC–TiC powders. The powder compacts of WC–TiC premixed powders were sintered at 1500 °C in vacuum for 1 h to obtain a Vickers hardness of 12 GPa and toughness of 14 MPa m^{1/2} (calculated as explained in the previous case). The elastic modulus of the ceramic (409 GPa) was determined using the pulse echo technique. The tribological study was conducted using a ball-on-flat type of fretting wear tester using steel ball of 6 mm diameter as a counterbody. The operating parameters include a constant frequency (8 Hz), a constant displacement stroke (50 µm) and a large number of cycles (100,000), while load varying between 2 and 10 N. EDS compositional analysis of the wear debris and transfer layer revealed the formation of a stable oxide layer rich in iron transferred from the counterbody (bearing steel) besides the stronger presence of W, Ti, and O peaks.

TiB₂–MoSi₂/steel tribocouple [20]: In an effort to densify the boride ceramics with silicide additives, TiB₂ composites with 20% MoSi₂ sinter-aid were densified by hot pressing at 1700 °C for 1 h in vacuum to achieve close to 98% theoretical density. The hot pressed composites exhibited a hardness of 25 GPa and an indentation toughness of 5 MPa m^{1/2} (calculated as explained in the previous case). The fretting experiments were performed on TiB₂-composites against 8 mm diameter bearing grade steel balls with varying load (*P*) of 2, 5 and 10 N at 8 Hz oscillating frequency and 100 µm linear stroke for 10,000 cycles duration. Based on the results of SEM–EDS and XRD analyses, the formation of a stable oxide layer containing various oxides (Fe_xO_y , TiO₂, B₂O₃) was confirmed in case of TiB₂–MoSi₂/steel tribocouple and the oxidative wear was observed to be the major wear mechanism for the investigated material.

ASP23 steel/alumina [34]: Hardened high-speed steel ASP23 discs of 60-mm diameter with a nominal hardness of 63 HRC were fretted against commercially available corundum ball (Ceratec, The Netherlands) of diameter 10 mm and hardness 2000 HVN. Fretting tests were performed with a computer controlled fretting simulator using a ball-on-flat contact geometry. The testing temperature was kept constant at 23 °C. The normal load was varied from 1 to 10 N. The test frequency and the displacement stroke were fixed at 10 Hz and 100 µm, respectively. Oxidation of ASP23 steel was reported to be the dominating wear mechanism after a critical transition load (2 N), which resulted into a protective oxide layer of Fe₂O₃ at the interface.

Ti6Al4V/alumina [33]: The wear tests were performed using a ball-on-disc configuration in ambient conditions. High purity 99.5% commercially available α -alumina balls of 8 mm diameter and 16.5 GPa hardness were fretted against a Ti6Al4V disc (hardness 3.5 GPa). Tribological tests were conducted on a pin-on-disc tribometer over a range of loads 5–80 N and speeds 0.0625–1 m/s for a constant total sliding distance of 500 m. The reduction of alumina surface and the oxidation of Ti6Al4V were reported to be the major wear mechanisms. After a critical load (20 N) and velocity (0.25 m/s), the wear process was dominated by the oxidation of the metallic disc, which forms protective layer of titanium oxide at both the contacting surfaces.

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