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Tribokemijske spremembe med jeklom in keramiko v fretinških razmerah

Tribochemical Changes in Steel and Ceramics under Fretting Conditions

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Tribokemijske reakcije med keramiko in kovinami so se mnogokrat izkazale kot ključni dejavnik pri določanju obrabnih in tornih značilnosti v različnih drsnih in fretinških razmerah. Tudi v naši raziskavi fretinške obrabe med jeklom in keramiko iz silicijevega nitrida, se je potrdilo, da so bile tribokemijske reakcije odločujoče za odziv sistema tako v suhih kakor z oljem mazanih razmerah. Posledica tega so povsem spremenjene tribološke lastnosti površin, ki pa hkrati določajo obrabne in torne lastnosti. V tem prispevku obravnavamo različne vplive na novo nastale tribološke površine na temelju eksperimentalnih rezultatov o mikrostrukturnih spremembah, faznih premenah, različnih termodinamičnih izračunih in izračunih trenutnih temperatur ter preskusih statičnih spojev materialov, v katerih smo izolirali kemijsko obrabo pri nadzorovanih mehanskih in termičnih parametrih. Izkazalo se je, da so lahko ekstremno visoke temperature odločilne za tribokemijske reakcije tudi v primerih zelo majhnih relativnih hitrosti, za katere običajno menimo, da dosegajo le nizke temperature. V prispevku tudi pojasnjujemo, zakaj prihaja do razlik med opažanji pojavov na površinah z makro in mikro vidika.

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(Ključne besede: freting, jekla, keramika, temperature, tribokemija)

Tribochemical reactions between ceramics and metals under various sliding or fretting conditions have been reported many times to be critical in determining wear and friction behaviour. In our comprehensive study of fretting wear between steel and silicon-nitride ceramics tribochemical reactions were also determined to play the critical role under both dry and oil-lubricated conditions. As a consequence, the new properties of the changed tribological interfaces were very different than the original and govern the wear and friction behaviour. In this paper various possible effects on the resulting tribological interfaces are discussed based on the experimental evidence of microstructural changes, phase transformations, various thermodynamic and flash-temperature calculations and interaction couple experiments in which the chemical wear was isolated by controlled mechanical and thermal parameters. It is shown that extremely high temperatures must be considered as a key governing factor in tribochemical reactions, even under conditions that are usually considered as a low-speed low-temperature conditions. Furthermore, discrepancies in the macro-scale evidence including the most advanced contact-temperature measurement techniques and the micro-scale changes of the tribological interfaces are explained.

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(Keywords: fretting, steels, ceramics, temperatures, tribochemistry)

0 UVOD

Znano je, da tribokemijske reakcije določajo obrabo v različnih drsnih in fretinških razmerah keramike iz silicijevega nitrida ([1] do [10]) ter da se pri tem običajno tvori plast SiO_2. Kljub temu podrobnosti o mehanizmih in kemijskih reakcijah niso poznane. Obstajajo namreč velike razlike v predpostavljenih kontaktnih temperaturah ter pri razlagi vpliva mehanskih in termičnih

0 INTRODUCTION

It has already been recognised that tribochemical reactions determine the sliding and fretting wear behaviour of silicon-nitride ceramics under various conditions ([1] to [10]), usually resulting in the formation of a SiO_2 layer. Nevertheless, the details of the mechanisms and the chemical reactions are still not well understood. There exists a large discrepancy between the reported contact temperatures and in the interpretation of dejavnikov na nastale fazne premene. Odgovor na ta vprašanja lahko dajo le zanesljive meritve kontaktnih temperatur. Na žalost današnje metode ([11] do [13]) ne omogočajo dovolj zanesljivega zaznavanja temperatur na dotikih vršičkov, torej prav tam, kjer naj bi bile temperature dovolj visoke, da lahko pride do lokalnih faznih premen ([5], [10], [14] in [15]). Zato se vedno uporabljajo le posredni dokazi, ki nakazujejo na možne temperature, kar pa hkrati pomeni dodatne negotovosti pri sklepih.

Temeljna nasprotja o možnostih visokih temperatur pri fretingu slonijo na majhnih relativnih hitrostih, ki običajno pomenijo nizke temperature. Pri poskusih drsne obrabe se celo velikokrat izberejo majhne relativne hitrosti z namenom, da se izločijo možne termične vplive. Podobno temu včasih poskuse izvajamo pri določeni okoliški temperaturi, pri čemer predpostavimo, da je tudi kontaktna temperatura tej enaka. Vendar pa v obeh teh primerih predpostavke držijo zgolj za masno temperaturo materiala, medtem ko natančne razmere na kontaktnih površinah (temperature na vršičkih, vpliv obrabnih delcev – vpliv tretjih teles, lokalni tlaki na vršičkih itn.) niso enake in tudi ne poznane. Lahko rečemo, da je na podlagi takih predpostavk težko določiti najvišje mogoče temperature pri fretingu, kar pa je trenutno ena od pomembnejših neznank v teoriji o fretinški obrabi.

Po drugi strani pa so tribokemijske spremembe običajno podobne ali enake kemijskim reakcijam, ki so veliko bolj verjetne pri visokih temperaturah ([10], [14] do [17]) ali pa jih je vsaj vedno mogoče dokazati, ko so visoke temperature nedvoumne, četudi so hitrosti majhne ([2], [3], [18] in [19]). To nakazuje, da so temperature pomemben dejavnik, ki pospešuje nastanek tribokemijskih plasti in jih je treba analizirati bolj natančno.

Ker vsi posredni dokazi vsebujejo določeno mero negotovosti, je zelo težko ali celo nemogoče podati dokončen in nedvoumen odgovor o tem, kateri so ključni dejavniki za nastanek tribokemijskih reakcij in kolikšne so najvišje mogoče kontaktne temperature, ki lahko do teh reakcij privedejo, če v kontaktih sočasno delujejo mehanski in termični vplivi. Zatorej je treba posamične vplive ločiti in sistematično raziskati ter tako priti do temeljnih zakonitosti. V tem prispevku podajamo nekatere jasne dokaze o obstoju visokih temperatur v režimu popolnega zdrsa pri fretingu, podprte z literaturnim pregledom, izračuni trenutnih temperatur in različnimi termodinamičnimi izračuni ter s poskusi statičnih spojev materialov z nadzorovanimi mehanskimi in termičnimi vplivi. Dva zelo različna materiala v kontaktu (jeklo in keramika) ter zelo različne kontaktne razmere (suho in mazano z

the influence of mechanical and thermal effects on the observed phase transformations. Surface temperature measurements could provide the definitive answer on this subject, unfortunately however, today's wide variety of measurement techniques ([11] to [13]) still does not allow to make accurate and reliable measurements of the temperature of the asperity contacts, which have many times been suggested to be responsible for phase transformations ([5], [10], [14] and [15]). As a result, it is necessary for us to use indirect evidence for obtaining asperity contact temperatures, however, this always adds an additional uncertainty to the issue.

The main contradictions that surround the possibility of high temperatures under fretting conditions are based on the typical low relative velocity, which usually implies low temperatures. Furthermore, it is quite common that in sliding experiments the speed is preset to a "low" value in order to exclude any thermal effects. Similarly, sometimes experiments are performed at various ambient temperatures and thus it is concluded that the contact temperature was the same as the preselected temperature. However, in both cases the assumptions only hold for the overall (bulk) contact conditions, while the exact contact conditions (spot-to-spot temperatures, influence of entrapped wear particles - third body effects, local pressures at the asperities, etc.) in such situations are actually not known. Based on such assumptions it is very difficult to predict the maximum spot-to-spot temperatures in fretting, which seem to be one of the critical unknowns in fretting wear.

On the other hand, the observed tribochemical changes at the interface are often the same as in the chemical reactions that tend to occur at high temperatures ([10], [14] to [17]). At least, such transformations are commonly observed when high temperatures are indisputably present ([2], [3], [18] and [19]), although the relative velocity is low. This suggests that the temperature is an important factor, which enhances the creation of tribolayers and should therefore be examined more carefully.

All indirect evidence is, however, subjected to a certain degree of uncertainty. It is therefore clear that it is extremely difficult—or impossible—to be completely sure about the key governing factors in tribochemical reactions or about the possible maximum contact temperatures, which can result in the tribochemical changes at the interface if both mechanical and thermal effects can influence the result. Therefore, single effects should be isolated and studied systematically in order to develop some basic laws, and in this way try to unravel the puzzle piece by piece. In this paper some convincing evidence for high temperatures in the gross-slip fretting regime is presented, it is supported by a multidisciplinary literature survey, flash-temperature and various thermodynamic calculations and by the interaction of a couple of experiments in which chemical wear was isolated by controlled mechanical and thermal parameters. Two very different countermaterials (ceramic and steel) and contact conditions (air-dry, oil-lubricated) oljem) so omogočili pogled na problematiko z različnih zornih kotov, saj so nastali reakcijski produkti tudi zelo različni.

1 EKSPERIMENTALNE RAZMERE

Za namen tega prispevka so podane le osnovne informacije glede materialov, preskusnih postopkov in analiznih tehnik, saj so številne podrobnosti obsežno predstavljene za fretinške poskuse ([7] do [10]) ter za statične spoje ([10], [24] in [25]) v literaturi.

1.1 Fretinški poskusi

Vsi fretinški poskusi so bili izvedeni na tržno dostopni testni napravi, ki omogoča poskuse pri visokih frekvencah s kontaktno geometrijsko obliko kroglice na ravni ploščici. Spodnji ravni preskušanci so bili izdelani iz ležajnega kromovega jekla (DIN 100Cr6) in so bili nepomično vpeti, zgornji preskušanci pa so bile standardne ležajne kroglice iz keramike iz silicijevega nitrida (NBD-200), vpete v nihajoče vpenjalo.

Preskusi so bili izvedeni v nemazanih razmerah (sobna temperatura, relativna vlažnost približno 50 %) in z oljem mazanih razmerah. Mazanje je bilo izvedeno samo s kapljico mineralnega olja (ISO VG 220), ki smo jo nanesli na ploščico pred vsakim poskusom. Med samim preskušanjem nismo dovajali dodatnega svežega olja. Frekvenca nihanja zgornjega vpenjala je bila nespremenljiva, 210 Hz, sila v normalni smeri, ki smo jo dovedli prek obremenitvene enote pa 88 N. Amplitude pomika smo spreminjali v petih stopnjah med 5 in 50 μm. Zaradi nespremenljive frekvence nihanja se je pri tem relativna hitrost v dotiku povečevala od 0,0042 do 0,042 m/s. Pred vsakim poskusim in po njem smo vzorce očistili z alkoholom v ultrazvočni napravi.

Obrabne površine so bile analizirane z optičnim, elektronskim in transmisijskim mikroskopom, mehanskim merilnikom hrapavosti, metodo elektronske razpršilne spektroskopije ter spektroskopijo Augerjevih elektronov.

1.2 Poskusi s statičnimi spoji

Materiali, ki smo jih uporabili pri statičnih spojih, so bili enaki kakor pri fretinških poskusih, izdelani s postopki elektroerozije in izrezov z diamantno žago iz izvirnih vzorcev za fretinške teste.

Poskusi statičnih spojev so bili izvedeni s statičnim pritiskom dveh jeklenih ploščic, pri čemer je bila med njima ploščica iz keramike. Pred vsakim poskusom so bili vsi vzorci očiščeni v ultrazvočni napravi ter pripravljeni v obliki “sendviča”, kar prikazuje slika 1.

Za primerjavo fretinških testov v celotnem območju možnih kontaktnih razmer z

give quite a variety of different features according to which the key governing factors for the tribochemical reactions can be investigated.

1 EXPERIMENTAL CONDITIONS

For the purposes of this paper only basic information on the materials, experimental procedures, and analysing techniques are given, the details are comprehensively presented in [7] to [10] and [10], [24] and [25] for the fretting experiments and the interaction-couple experiments, respectively.

1.1 Fretting-wear experiments

All fretting-wear experiments were performed using a commercially available high-frequency fretting machine with a ball-on-flat testing contact geometry. The lower, flat specimens were made from bearing steel (DIN100Cr6) and fixed in the base, while the upper specimens, i.e., silicon-nitride balls (NBD-100), were fixed in the oscillating holder.

Experiments were performed under unlubricated (ambient, RH about 50%) and lubricated conditions. A small amount of mineral oil (ISO VG 220) was spread on the surface of the flat specimen for the lubricated conditions. During the test no additional oil was supplied to the contact. A normal force of 88 N was applied through the loading cell at each contact. The frequency of oscillation was constant for all experiments at 210 Hz. The displacement amplitude was increased in five levels from 5 to 50 μm. Due to the constant frequency of the oscillation, the mean sliding velocity increased with increasing amplitude from 0.0042 to 0.042 m/sec. Before and after the test the specimens were ultrasonically cleaned.

The worn surfaces of the flat and the ball were examined by means of light microscopy, stylus-tip profilometry, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), Auger-electron spectroscopy (AES) and transmission electron microscopy (TEM).

1.2 Interaction-couple experiments

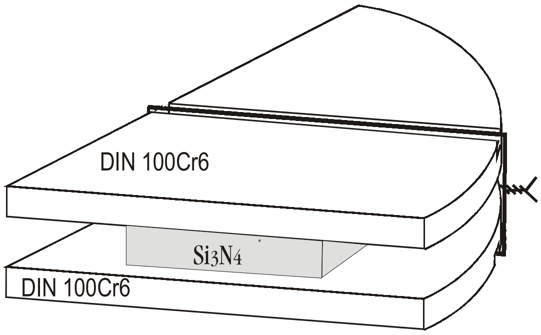
The materials for the static interaction couples were the same as those used in the fretting wear experiments, they were prepared by electrical discharge machining (EDM) and cut from the original specimens used in the fretting experiments.

The interaction-couple experiments were performed by pressing together polished slices of steel and ceramic. Before putting the specimens into the pressing apparatus, they were ultrasonically cleaned and prepared as a sandwich-type specimen with the ceramic between two pieces of steel, as shown in Figure 1.

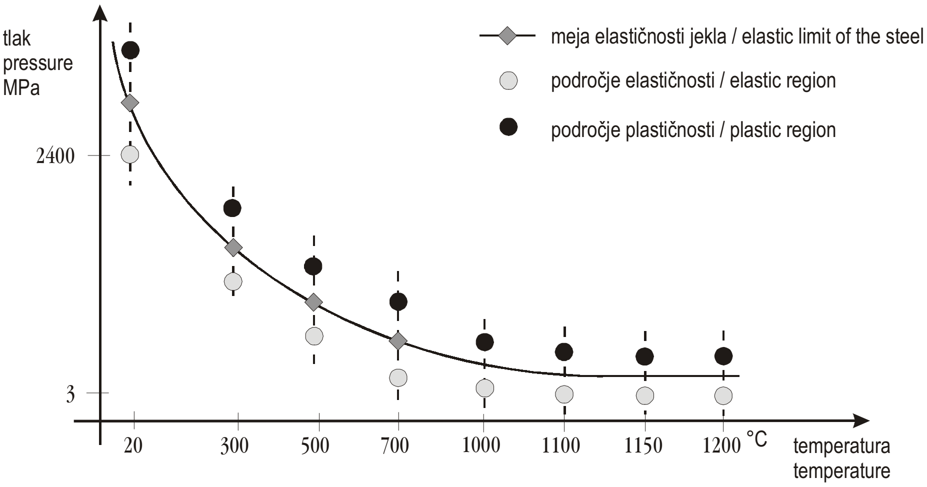
In order to compare the fretting-wear results over the whole range of possible testing conditions with

Preglednica 1. *Načrt preskusov statičnih spojev z izbranimi pogoji*
Table 1. *Plan of the experiments with selected test conditions for static interaction couples*

Temperatura / Temperature °C		20	300	500	700	1000	1100	1150	1200
Tlak / Pressure MPa	Elastično / Elastic	2400	1414	613	97	3,6	3,5	4	4
	Plastično / Plastic	4000	3000	750	120	360	130	145	123
Preskuševališče / Testing machine		nizke temperature - veliki tlaki low-temperature high-pressure				visoke temperature - majhni tlaki high-temperature low-pressure			



Sl. 1. *Sestav preskušancev v obliki »sendviča«*
Fig. 1. *Sandwich-type interaction-couple set up*



Sl. 2. *Shematična predstavitev preskusnih razmer statičnih spojev*
Fig. 2. *Schematic representation of the experimental test conditions for the static steel-Si$_3$N$_4$*

rezultati statičnih spojev, smo za preskušanje statičnih spojev izbrali široko območje tlakov in temperatur. Ker je plastična deformacija tudi eden izmed pomembnih dejavnikov, ki lahko vplivajo na tribokemijske reakcije, smo statične poskuse izvedli v elastičnem in plastičnem območju jekla. Podrobne preskusne razmere in shema preskusov so prikazani v preglednici 1 in na sliki 2.

Izbrane razmere preskušanja smo dosegli z uporabo dveh testnih naprav. Z eno smo lahko izvajali teste v območju velikih tlakov, a razmeroma nizkih temperatur, z drugo pa je mogoče doseči zelo visoke temperature, a pri

the results of the interaction couples, a broad range of pressures and temperatures had to be selected for the static interaction-couple experiments. Plastic deformation is another factor influencing the tribo chemical reactions. Tests were performed in both the elastic and plastic regions of the steel. The experimental data and a schematic of the conditions are presented in Table 1 and Figure 2, respectively.

The selected temperature-pressure test conditions were achieved by using two different testing machines, one with the ability to apply very high loads at relatively low temperatures and another with which high temperatures could be obtained at low loads. Further-majhnih tlakih. Ker smo želeli raziskovati tudi vpliv kisika na kemijsko aktivnost izbranih materialov, smo izvedli statične poskuse tudi ob navzočnosti kisika v kontaktu. Kisik smo dovedli v kontakt med jeklom in keramiko s predoksidacijo jekla, saj obe napravi delujeta le v zaščitni atmosferi. Jeklo smo predoksidirali pri isti temperaturi, kakor so bili kasneje izvedeni statični testi.

2 REZULTATI

2.1 Fretinški testi

Primerjava diagramov obrabe v odvisnosti od amplitude zdrsa pri mazanih in nemazanih razmerah kaže na precejšnjo razliko v obrabni odpornosti (sl. 3). Medtem ko se obraba povečuje skoraj linearno z amplitudo v nemazanih razmerah, dobimo v mazanih razmerah izrazito največjo vrednost pri amplitudi 25 μm. Razvidno je tudi, da je obraba v mazanih razmerah za dva velikostna razreda manjša kakor v nemazanih ([7] in [10]).

V mazanih razmerah je bil koeficient trenja visok le v začetni fazi (0,6 do 0,85), a se je, razen pri amplitudi 5 μm (sl. 4a), kasneje zmanjšal na precej nižjo vrednost, približno 0,2. Čas, potreben za omenjeni padec, je bil pri višjih amplitudah krajši. V nemazanih razmerah je bil koeficient trenja pri amplitudah 25 in 50 μm višji ves čas preskusa, tudi že v začetnem obdobju, in sicer med 1,0 in 1,3 (sl. 4b). Nekoliko nižji (0,7), a nespremenljiv koeficient trenja je bil izmerjen samo pri amplitudi 5 μm.

Iz diagrama na sliki 3 je razvidno, da je prišlo v mazanih razmerah pri amplitudi 25 μm do spremembe obrabnega mehanizma. To spremembo je mogoče razložiti tudi s slikami z elektronskega mikroskopa, na katerih je jasno vidno, da je pri

more, in order to gain the effect of oxygen on the chemical reactivity of the selected materials and to compare it with the fretting results, the interaction-couple experiments were performed with oxygen introduced into the interaction zone. Both the furnaces used for the static experiments only operate under vacuum or inert-gas conditions and so the oxygen was introduced by pre-oxidation of the steel. The steel was oxidised in air at the same temperature as used in the interaction-couple experiment.

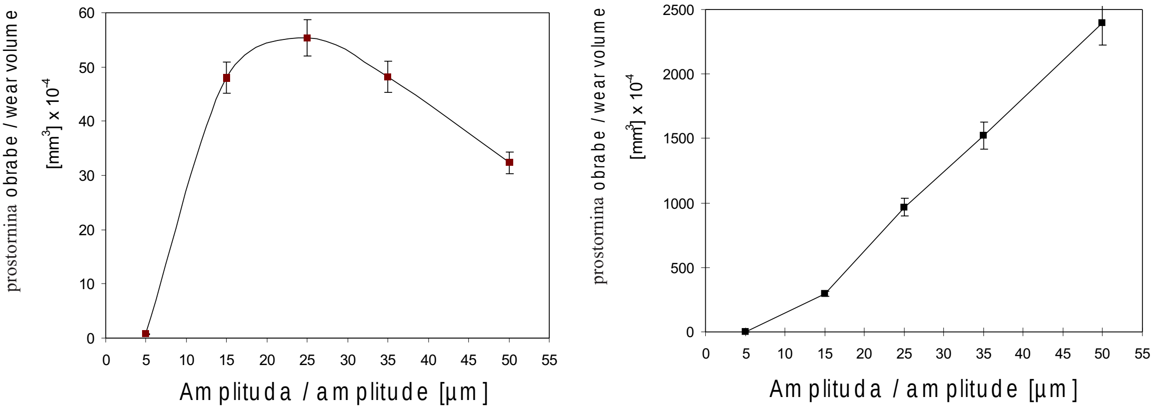
2 RESULTS

2.1 Fretting-wear experiments

A comparison of the diagrams for wear loss as a function of amplitude for lubricated and unlubricated conditions indicates significantly different wear behaviour, Figure 3. While the wear volume increased almost linearly with increasing amplitude for the unlubricated conditions, an obvious peak value at an amplitude of 25 μm was detected for lubricated fretting. Lower and higher amplitudes resulted in a lower wear volume. Also, it must be pointed out that the wear volume in the unlubricated conditions is about two orders of magnitude higher than in the lubricated conditions ([7] and [10]).

In lubricated conditions the coefficient of friction was high (0.6 to 0.85) in the first stage of fretting but remained high only for an amplitude of 5 μm (Figure 4a). At higher amplitudes it decreased sharply to a value of approximately 0.2. The time needed to reach this low value decreased with increasing amplitude. In the unlubricated conditions at 25 and 50-μm displacement amplitudes the coefficient of friction was higher, even at the beginning of the test, i.e. 1.0 to 1.3, and remained high throughout the test, Figure 4b. A somewhat lower, but still constant, value throughout the test (0.7) was obtained only at an amplitude of 5 μm.

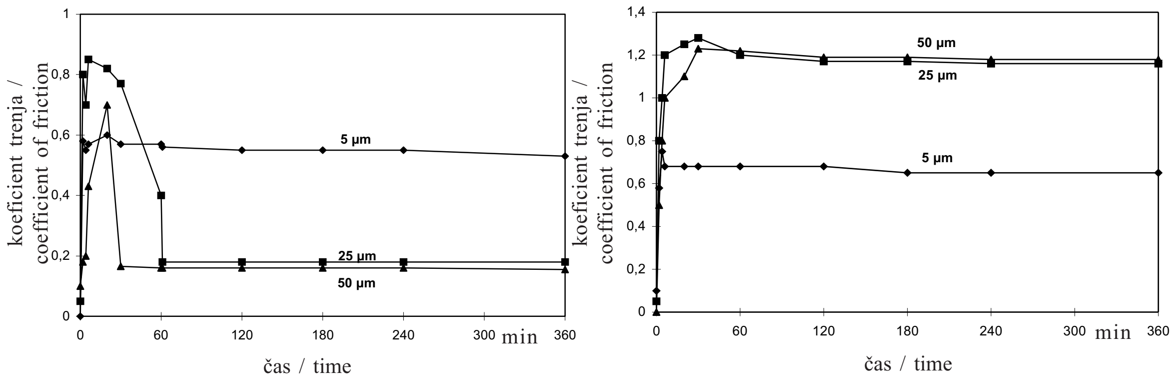
From the wear diagrams in Figure 3 we can see that for lubricated fretting a transition occurred at the 25 μm displacement amplitude. This could be ex-



(a) (b)

Sl. 3. Obrabna prostornina v odvisnosti od amplitude pomika v (a) mazanih, (b) nemazanih razmerah

Fig. 3. *Wear volume as a function of amplitude under (a) lubricated, (b) unlubricated conditions*



(a) (b)

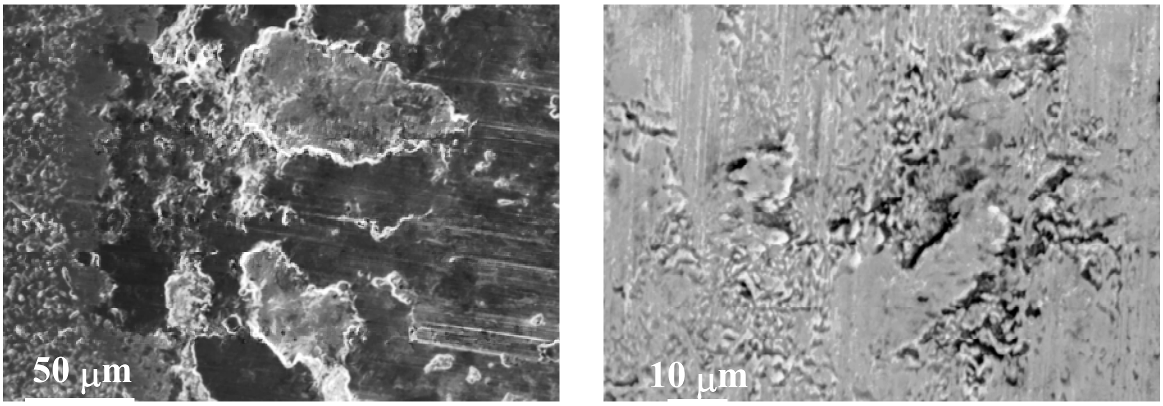
Sl. 4. *Koeficient trenja v odvisnosti od časa v (a) mazanih, (b) nemazanih razmerah*
Fig. 4. *Coefficient of friction as a function of time under (a) lubricated, and (b) unlubricated conditions*

nižjih amplitudah prevladovala mehanska obraba z lomi na kontaktni ploskvi (sl. 5a), medtem ko je prišlo pri višjih amplitudah do nastajanja tribokemijske plasti ter predvsem njene plastične deformacije, kakršna je značilna tudi za končno obdobje preskušanja pri amplitudi 25 µm (sl. 5b). Analiza z Augerjevimi elektroni in transmisijskim mikroskopom je potrdila nastanek tribokemijske plasti [9]. Najpomembnejši dokaz je bil pridobljen z elementno analizo prereza vzorca pod obrabno površino, kjer je bila ugotovljena izjemno visoka koncentracija ogljika, ki izvira iz olja (sl. 6). Ti rezultati kažejo 200 do 300 nm tanko plast v bližini površine (zanemarjajoč prvih 150 nm zaradi “čiščenja” površine), v kateri je koncentracija ogljika večja od 10 utežnih %. Rezultati s transmisijskega mikroskopa pa dokazujejo nastanek karbidov Fe_3C. Prostega ogljika ali razpok nismo našli, kar potrjuje tribokemijski in ne mehanski proces pri nastanku plasti.

Tudi v nemazanih razmerah je prišlo do tribokemijske reakcije in nastanka tribokemijske plasti, ki pa je bila, v nasprotju z opažanji pri nemazanih

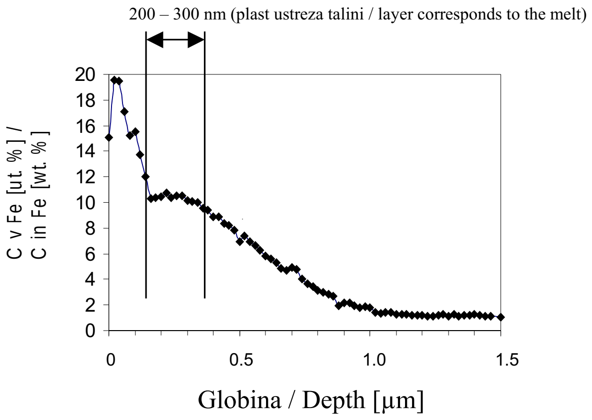
plained by SEM analysis, where a mechanically dominated wear by fracture of the interface layer was observed in the beginning of the test at a 25 µm displacement amplitude (Figure 5a), while at the end of the test at 25 µm and throughout the test at a 50 µm amplitude, a more viscous type of layer with plastic deformation and smearing can be seen, Figure 5b. AES and TEM analysis confirmed that a tribochemical reaction took place under these conditions [9]. The most important feature observed in the AES spectra of a depth profile across the layer created on the steel specimen is a very high concentration of carbon which originates from the oil, Figure 6.The results show that there is a 200 to 300 nm thick layer close to the surface (neglecting the first 150 nm due to “cleaning” of the surface) in which the concentration of carbon is about 10 wt. %. TEM analysis revealed that the broadly prevailing phase in the carbon diffusion layer is Fe_3C. No free carbon and no microcracks were found in the layer, which excluded the possibility that the layer is a tribomechanical mixture.

In contrast to the lubricated fretting, under unlubricated conditions the wear occurred primarily



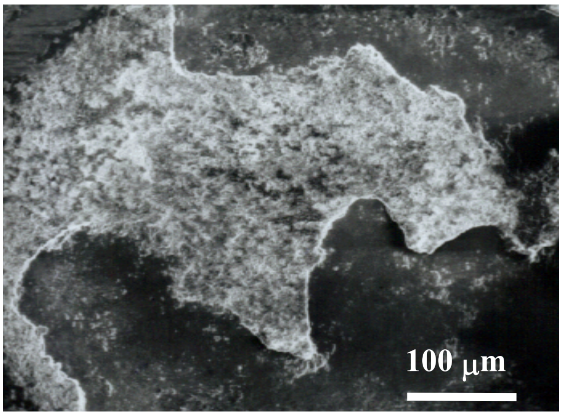
(a) (b)

Sl. 5. *Tribokemijske plasti, nastale v mazanih razmerah pri amplitudi 25 µm po (a) 10min, (b) 360min*
Fig. 5. *Tribolayers created during lubricated fretting at 25-µm amplitude after (a) 10 min, (b) 360 min*



Sl. 6. *Koncentracija C v Fe v odvisnosti od globine plasti na jeklenem vzorcu, testiranem pri amplitudi 50 µm in 360 min*

Fig. 6. *C concentration in Fe, obtained from the AES spectra across the tribolayer created on a steel plate during lubricated fretting for 360 min at 50 µm*



Sl. 7. *Posnetek krhke oksidne plasti SiO_2 z elektronskim mikroskopom na Si_3N_4 vzorcu*

Fig. 7. *SEM micrograph of the brittle oxide layer of SiO_2 on Si_3N_4 ball*

razmerah, oksidna in krhka in se je kasneje intenzivno luščila (sl. 7) ter tako povzročila znatno večjo obrabo, kar je razvidno na sliki 3. Analize z Augerjevimi elektroni in transmisijskim mikroskopom so potrdile oksidacijo silicijevega nitrida, kar je povzročilo nastanek 2 µm debele plasti silicijevega oksida (SiO_2), v katerem so bili precipitati različnih železovih oksidov okrogle oblike in velikosti 5 do 20 nm [7]. Poleg tega v plasti nismo našli dušika ali delcev Si_3N_4. Te ugotovitve še dodatno dokazujejo tribokemijsko naravo nastanka plasti.

2.2 Poskusi s statičnimi spoji

Vpliv tlaka in temperature

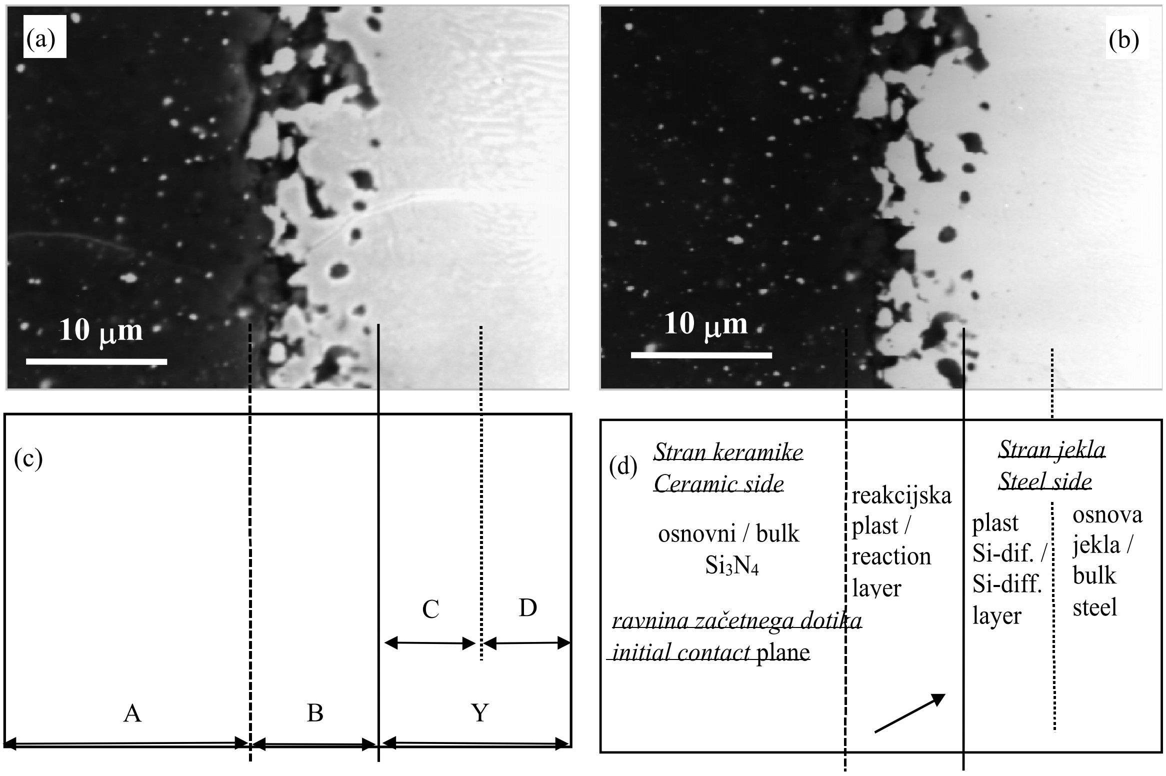
Slika 8 prikazuje morfologijo prereza spoja med jeklom in silicijevim nitridom po preskusu pri temperaturi 1200 °C v elastičnih razmerah (preglednica 1). Na sliki 8a lahko jasno razločimo tri področja: A, B in Y. Vendar se je izkazalo, da je področje Y sestavljeno iz dveh različnih področij, ki sta označeni s C in D.

by the creation and spalling of a brittle tribochemical layer, Figure 7. AES and TEM analyses revealed severe silicon-nitride oxidation, resulting in a 2 µm thick amorphous SiO_2 rich phase with small precipitates of iron oxides, which were between 5 and 20 nm in diameter and had an almost circular shape [7]. This implies that these are indeed precipitates and not wear debris. Furthermore, neither nitrogen nor Si_3N_4 were found in the layer. This again confirms that the layer is a tribochemical reaction product and not a tribomechanical mixture.

2.2 Interaction-couple experiments

The effect of temperature and pressure

Figure 8 shows the morphology of a cross-section of the steel and silicon-nitride couple tested at the highest investigated temperature, i.e. 1200°C, under elastic conditions (Table 1). Three regions can be clearly distinguished from Figure 8, i.e. A, B and Y, however, it was found that the Y region is actually composed



Sl. 8. *Prerez statičnega spoja po 5 urah testiranja pri 1200 °C in tlaku 4Mpa, (a) slika sekundarnih elektronov, (b) slika odbitih elektronov (isti del prereza kakor na sliki (a)), (c) shematična predstavitev področij s slik a) in b), (d) shematična predstavitev morfologije prereza spoja*

Fig. 8. *Interaction-couple cross-section after 5 hours at 1200 °C and 4 MPa, (a) secondary electron SEM image, (b) back-scattered electron SEM image (same cross-section as in (a)), (c) schematic drawing of regions in the cross-section from Fig. a and Fig. b, (d) schematic of the morphology of the interaction couple*

Področje A pomeni izvirno Si_3N_4 keramiko. Področje B je reakcijska plast spoja na strani keramike, ki vključuje še nekatere reakcijske produkte ([10] in [25]), medtem ko se področje Y nanaša na stran jekla v spoju. Dotikalna ravnina med področjem B in Y je začetna dotikalna ravnina pred preskusom, ki je bila določena z uporabo inertnega materiala, kakor je podrobno opisano v literaturi ([25] in [26]).

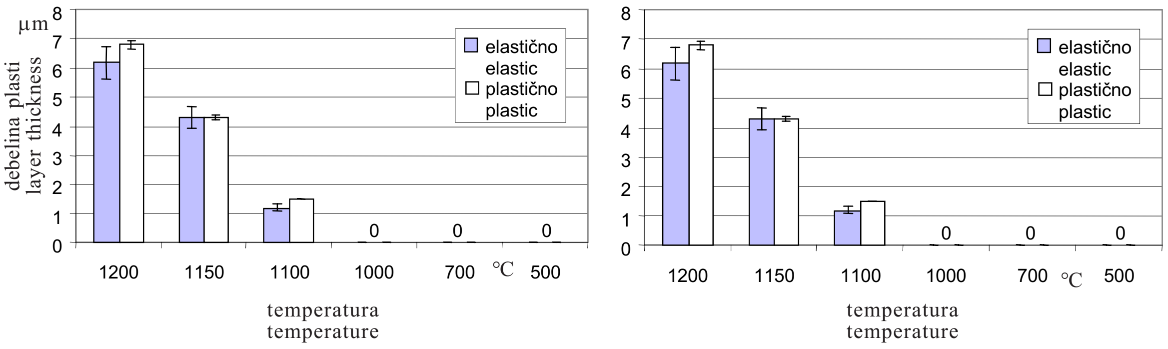
Elementna analiza z ektronskim mikroskopom je pokazala, da je v področju Y blizu področja B (začetni kontakt) poleg pričakovano velike količine Fe in Cr, tudi veliko Si. Ta ugotovitev je zahtevala nadaljnje preiskave po prerezu v področju Y. V ta namen smo naredili črtne profile koncentracije Si skozi področje Y. Področje, kjer je bila koncentracija Si višja od izvirne, smo označili kot področje C. Širino reakcijske plasti na strani keramike (B) in difuzijske plasti Si na strani jekla (C) smo nato sistematično merili pri vseh temperaturah in tlakih, pa tudi v obeh deformacijskih (el in pl.) območjih jekla. Rezultati so prikazani na sliki 9.

Za elastično in plastično območje je bilo ugotovljeno, da pride do močne vezi med jeklom in keramiko samo pri temperaturah 1100°C in več. Pri nižjih temperaturah je spoj vedno razpadel na posamezne sestavne dele, to je osnovne vzorce jekla

of two regions, denoted as C and D. Region A represents the original Si_3N_4 ceramic. Region B is the reaction layer on the ceramic side of the interaction couple incorporating a few reaction products ([10] and [25]), whereas region Y refers to the steel side of the interaction couple. The contact plane between region B and Y is the initial ceramic-steel interface, which was determined by the inert ZrO_2 marker, as reported elsewhere ([25] and [26]).

EDS inspection of the steel material in region Y, close to the region B (initial ceramic/steel interface) revealed besides the expected presence of Fe and Cr, a high Si content. This finding suggested a more detailed analysis of the Y region and Si concentration line-profiles were determined across the Y region. The layer that incorporates Si on the steel side was therefore determined as the C region. The width of the reaction layer (region B) on the ceramic side and the Si-diffusion layer on the steel side (region C) were systematically measured for all temperatures and pressures used under both elastic and plastic conditions. The results are presented in Figure 9.

For both the elastic and plastic regions it was found that the strong bond between the steel and the ceramics was formed only at 1100°C or higher. At lower temperatures the interaction couple always fell apart. Additionally, the thickness of the reaction



(a) (b)

Sl. 9. *Debeline (a) reakcijske plasti in (b) plasti Si-difuzije v elastičnem in plastičnem področju jekla*
Fig. 9. *Overall results for the elastic and plastic contacts of the (a) reaction-layer thickness, (b) Si-diffusion-layer thickness*

in keramike. Poleg tega pa se debelina reakcijske plasti in s tem kemijska reaktivnost manjšata z nižanjem temperature, kar kaže na izrazito prevladujoč vpliv temperature (sl. 9a).

Podobno smo ugotovili tudi pri analizi debeline difuzijske plasti Si v jeklu. Debelina se manjša z nižanjem temperature in kar je zelo pomembno, pod 700 °C znakov kemijske povezave nismo več našli (sl. 9b). Analiza debelin plasti pri velikih in majhnih tlakih, oziroma v plastičnem in elastičnem območju je pokazala, da razlik med njimi praktično ni [10].

Ti eksperimentalni rezultati se odlično ujemajo tudi s termodinamičnimi izračuni ([10] in [26]), saj je bilo izračunano, da reakcijska plast prične nastajati pri 1033°C (eksperiment: 1100°C), difuzija Si v jeklo pa nastopi pri 636°C (preskus 700°C). Pri nižjih temperaturah te plasti ne nastajajo.

Vpliv kisika

Slika 10 prikazuje detajl prereza statičnega spoja, preskušanega pri 1200°C ob navzočnosti kisika. Elementna analiza z elektronsko disperzno spektroskopijo je razkrila številne različne faze v reakcijski plasti, ki so podrobneje predstavljene drugje ([10] in [24]). Med temi je tudi 5 do 10 µm debela plast silicijevega oksida (sl. 10). Manjše količine železa, ki smo jih tudi našli v tej oksidni plasti, bi lahko izvirale iz okolne jeklene matrice ali pa železovih oksidov, podobno kakor so bili najdeni pri fretinških poskusih. To bi lahko pomenilo še bolj neposredno povezavo z rezultati fretinških testov, a podrobnejša razsikava v tej smeri ni bila izvedena.

Z nižanjem temperature se je manjšala tudi kemijska reaktivnost in, podobno kakor pri preskusih brez kisika, pri 500°C ni bilo nobene sledi reakcije več. Še več, pri temperaturi 1000°C ali nižje silicijev oksid ni več nastajal, medtem ko je bila njegova navzočnost pri višjih temperaturah izrazita

layer, and thus the chemical reactivity, decrease with decreasing temperature, revealing the dominating effect of the temperature, Figure 9a.

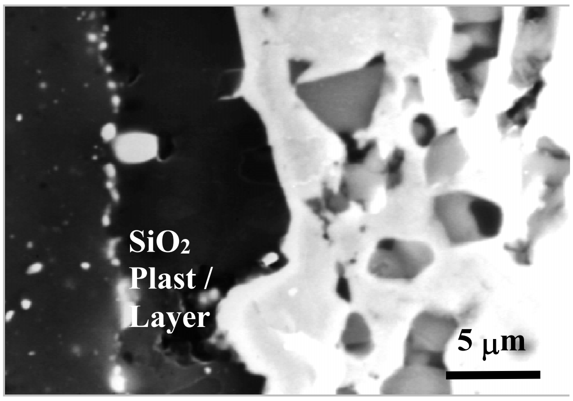
A similar situation was found when measuring the depth of Si diffusion into the steel. The depth is smaller with lower temperatures and, it is very important to note, that at temperatures below 700°C, there was no Si diffusion observed, Figure 9b. A quantitative evaluation of the thicknesses obtained at high and low pressures, i.e. under elastic and plastic conditions, showed that they are practically the same since there is no relevant difference between the two conditions [10].

These experimental results are also in excellent agreement with thermodynamic predictions ([10] and [26]). That is to say, the reaction layer was calculated to form at 1033°C (experiment: 1100°C) and the Si diffusion layer at 636°C (experiment: 700°C). At temperatures lower than those calculated, the layers were not formed.

The effect of oxygen

Figure 10 shows a detail of a cross-section of the interaction couple tested at 1200°C with the presence of oxygen in the contact. The EDS analysis revealed a number of different phases in the reaction layer, details are reported elsewhere ([10] and [24]). Among others, a 5 to 10 µm thick SiO_2 rich layer was found at the reaction front, as shown in Figure 10. A limited amount of iron was also found in some regions of the SiO_2 rich layer, which could originate either from the matrix surrounding the layer or from iron oxides, similar to those that were determined using TEM analysis on the fretting specimens. This would suggest an even more direct correlation between both types of experiments, but this was not investigated further and is therefore not confirmed.

With a decrease in the temperature the chemical reactivity also decreased and, exactly as with the absence of oxygen, at 500°C there are no traces of any chemical interaction between the contacting materials. Furthermore, at 1000°C or below, there is no SiO_2 layer formed in the contact, while at higher temperatures, clear



Sl. 10. *Prerez statičnega spoja pri 1200 °C ob navzočnosti kisika, ki prikazuje SiO_2 plast*
Fig. 10. *Interaction-couple cross-section at 1200 °C in the presence of oxygen, showing the SiO_2 layer*

[24]. To ponovno potrjuje odločilno vlogo temperatur pri nastanku silicijevega oksida.

3 OBRAVNAVA

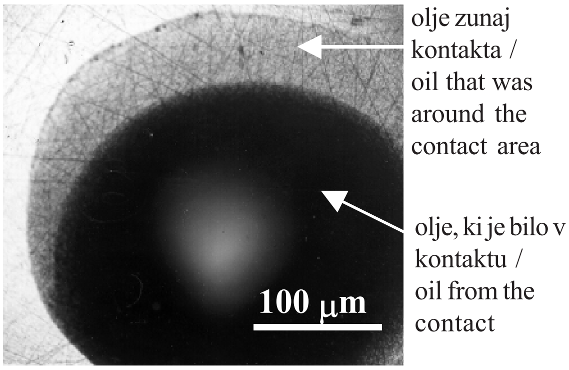
3.1 Fretinški testi

Mazane razmere

Glede na dobljene rezultate menimo, da je prišlo do prehoda v mehanizmu obrabe zaradi povečanja drsnih hitrosti in s tem kontaktnih temperatur. To je povzročilo fazne premene in nastanek tribokemijske plasti na površini, ki je vplivala na zmanjšanje koeficienta trenja in obrabe.

Ključne informacije o največjih mogočih kontaktnih temperaturah so bile pridobljene z analizami s transmisijskim mikroskopom in spektroskopijo z Augerjevimi elektroni, pri katerih se je izkazalo, da je nastala plast tribokemijska. Poleg tega približno 10,5 utežnih % ogljika v 200 do 300 nm tanki plasti pod površino presega vsako ravnotežno sestavo v faznem diagramu Fe-C, razen taline, kar nakazuje možnost za temperature nad 1145°C [10]. Taka razlaga je v skladu z veljavnimi termodinamičnimi zakoni in se ujema z nizkim koeficientom trenja, izmerjenim v teh razmerah.

Poleg tega je zgornjim navedbam pomembna podpora tudi dejstvo, da je olje med preskusom toplotno razpadlo, saj je ogljik iz olja rabil za ogljičenje jekla. Potrebna temperatura za razcep ogljikovih vezi v olju je približno 400°C [27]. Le-ta torej definira spodnjo mejo temperatur, ki je morala biti dosežena, da je do ogljičenja sploh prišlo. Jasno je, da je ogljičenje potekalo pri še višji temperaturi. Toplotni razpad olja smo zaznali že optično ob koncu preskusov, saj je



Sl. 11. *Slika z optičnega mikroskopa, ki nakazuje toplotni razpad olja v kontaktu*
Fig. 11. *Optical micrograph revealing the thermal break-down of the oil after the test*

and well-defined layers were always observed [24]. This again confirms the critical influence of temperature on the formation of the SiO_2 layer on silicon nitride.

3 DISCUSSION

3.1 Fretting wear

Lubricated conditions

According to the results, we suggest that the wear transition occurs due to the higher sliding speed and the consequent higher contact temperature, resulting in a tribochemical transformation of the interface that has much more beneficial properties in terms of wear and friction behaviour than the original materials.

Critical information about the possible maximum contact temperature is obtained by the TEM and AES results which confirmed that the layer observed is not a tribomechanical, but a tribochemical, layer. Furthermore, appr. 10.5 wt. % of carbon found in 200 to 300 nm thick layer close to the surface is above any equilibrium content of all components in the binary Fe-C phase diagram except the melt, which requires a temperature of about 1145°C [10]. This was not confirmed yet but it is the subject of further investigation. However, this tentative explanation is in agreement with the thermodynamic model and the low coefficient of friction under these conditions.

Furthermore, strong support for the suggested high temperature comes from the fact that the oil broke down during the experiment and acted as a source for the carbonisation of the steel. The temperature required for thermal cracking of oil we used is about 400°C [27], and so this must represent the minimum temperature at the contact. It is clear that carbonisation must occur at much higher temperatures and thermal degradation of oil was also anticipated by visual inspection of the wear scars. When bilo olje pri višjih amplitudah vedno črno, kar je nakazovalo na omenjeno toplotno razpadanje, (sl. 11).

Izvedeni so bili tudi izračuni trenutnih kontaktnih temperatur, in sicer z osmimi različnimi teoretičnimi modeli, ki smo jih našli v literaturi. V primerih, ko so bili vhodni parametri ovrednoteni dovolj natančno so tudi temperature pri višjih amplitudah presegale 1500 °C, kar je v skladu z drugimi rezultati in njihovo razlago ([10] in [28]).

Vendar pa so ti dokazi o temperaturi vsaj 400°C v precejšnjem razkoraku z izračuni najvišjih kontaktnih temperatur, ki se v literaturi običajno navajajo za freting, to je okoli 100°C ali manj ([10] in [28]). To torej jasno kaže, da izračuni najvišjih trenutnih kontaktnih temperatur niso pomembni za dejanske temperature pri fretingu. Glavni razlog je verjetno v napačnih ocenah dejanske kontaktne površine in drugih potrebnih predpostavkah v modelih za izračun teh temperatur.

Nemazane razmere

Na podlagi visokega koeficienta trenja in precejšnjih količin silicijevega oksida (velika obraba), ki je nastajal med fretingom v nemazanih razmerah lahko predpostavljamo, da so bile temperature še višje kakor v mazanih razmerah. Namreč, četudi je bilo večkrat poročano, da silicijev oksid nastaja tudi pri sobni temperaturi, je treba pri teh ugotovitvah upoštevati količino in debelino teh oksidnih plasti.

V veliko raziskavah o oksidaciji silicijevega nitrida je bilo ugotovljeno, da je oksidacija pasivna. To pomeni, da nastane na površini najprej tanek oksidni sloj, potem pa ta sloj ščiti površino pred nadaljnjo oksidacijo. Prav tako je bilo v teh raziskavah ugotovljeno, da poteka taka oksidacija v suhi in vlažni atmosferi v skladu z difuzijskimi zakoni ([30] do [34]).

To pomeni, da pri sobni temperaturi sicer nastaja silicijev oksid, je pa verjetno sloj zelo tanek zaradi omejenega časa testiranja, prav tako pa je zato tudi količina razmeroma majhna. Iz literaturnih podatkov je tudi mogoče razbrati, da je oksidacijske poskuse upravičeno izvajati le več ko 100 ur pri temperaturah nad 1000°C, saj je sicer reakcijskih ostankov tako malo, da jih ni mogoče kvantitativno ovrednotiti. Ti rezultati so zato skladni tudi z rezultati zelo tankih in celo prozornih obrabnih delcev, dobljenih v nekaterih triboloških testih [35]. Torej lahko večje količine in razmeroma debele plasti silicijevega oksida pričakujemo samo pri visokih temperaturah zaradi difuzijske narave oksidacije silicijevega nitrida, ki je temperaturno in časovno pogojen.

the ball and flat were separated after the test, the black (burned) oil/carbon was spread across the clean oil, which surrounded the contact set-up (Figure 11).

Furthermore, flash-temperature calculations based on eight different ready-to-use models showed that temperatures above 1500°C are easily obtained if better approximations to the interface conditions are used ([10] and [28]).

However, these indisputable proofs of temperatures of at least 400°C show a large discrepancy with surface temperature measurements in similar fretting conditions where the measured temperatures are usually much lower, i.e. below 100°C. Furthermore, calculations of the flash temperatures using impropriate input data with a poor adjustment of the interface conditions to the real conditions also give results around or below 100°C ([10] and [28]). This, therefore, clearly shows that both measurements and the conventional use of flash-temperature equations significantly underestimate the maximum flash temperatures. The reason is primarily because of the too-large real contact area and poor interface-property corrections used.

Unlubricated conditions

Based on the high coefficient of friction and the large amounts of silica (high wear loss) produced in our experiments under unlubricated conditions, even higher temperatures are expected compared to lubricated fretting. Although silica was reported to form on silicon nitride in tribological applications even at room temperature, the amount of wear loss and the layer thickness must be considered in any interpretation of the results. According to the following explanation these two parameters seem to be the critical points of the contradictions in reported key governing factors for the tribochemical reactions with silicon nitride.

According to many isolated oxidation studies of silicon nitride it was realised that for engineering applications the silicon-nitride oxidation type is the “passive” one, which occurs at high oxygen potentials. Here, a thin protective film of SiO_2 is formed on the surface of the ceramics, which limits the rate of any further oxidation. Furthermore, it was found that in both dry and wet atmospheres, the oxidation process proceeds in a strongly diffusion-controlled manner ([30] to [34]).

This implies that in wear experiments at room temperature a silica layer can form, but its thickness is, because of the limited testing time, probably very thin and also its quantity is very low. Furthermore, a literature survey revealed that in order to obtain a quantitatively relevant amount of oxidation products, isolated oxidation experiments are typically performed at temperatures above 1000°C and for a test duration of more than 100 hours. As such, the very thin and transparent wear debris of the silica layer produced in rolling applications with almost no wear at room temperature [35] seem to be very consistent with the above results and explanations. Accordingly, the large amounts and the relatively thick layer of silica produced in our fretting experiments suggest that the temperature should be much higher because of

Poleg tega so bile za dane razmere izračunane temperature prek 1500°C, kar potrjuje zgornjo razlago ([10] in [28]). Tudi zaradi višjega koeficienta trenja v nemazanih in v mazanih razmerah, kar je sorazmerno z nastankom toplote, ter z dokazanimi temperaturami vsaj 400 °C v mazanih razmerah, lahko v nemazanih razmerah upravičeno pričakujemo temperature nad 1000°C.

3.2 Poskusi s statičnimi spoji

Ta metoda omogoča izoliranje kemijske obrabe pri hkratnem natančnem nadzoru toplotnih in mehanskih vplivov ter je tako posreden dokaz, kateri so ključni dejavniki pri tribokemijskih procesih med keramiko iz silicijevega nitrida in jeklom. Podobni poskusi so se pokazali kot zelo uspešni in uporabni tudi pri raziskavah obrabe rezilnih orodij ([36] in [37]), četudi so tam razlike med statičnimi in dinamičnimi razmerami še večje kakor pri fretingu.

Iz naših rezultatov lahko sklepamo, da so kemijske povezave med izbranimi materiali odločilno odvisne od temperature. Pod 700°C nismo zaznali nobenih znakov reakcij, medtem ko je nad 1100°C nastala močna vez med materialoma in je bila reaktivnost znatno povečana. Po drugi strani pa povečevanje tlakov in celo prehod v plastično področje praktično niso vplivali na reaktivnost v kontaktu ([10], [24] in [25]).

Ena izmed pomembnih ugotovitev, ki kaže odločilen vpliv temperature, je tudi dejstvo, da je silicijev oksid v navzočnosti kisika nastal samo pri temperaturah nad 1100°C. Čeprav je bilo trajanje statičnih poskusov precej daljše od trenutnih dotikov v fretinškem testu, pa pri nižjih temperaturah ti oksidi niso nastajali. To se ponovno odlično ujema z rezultati oksidacijskih poskusov silicijevega nitrida ([30] do [34]) in termodinamičnih izračunov na temelju proste energije (Gibbsov kriterij), potrebne za nastanek reakcij ([10] in [24]).

3.3 Splošne ugotovitve

Zelo različni materiali (jeklo in keramika) in dotikalne razmere (mazane / nemazane) so v tej raziskavi tribokemijskih reakcij omogočili upoštevanje različnih dokazov z različnih zornih kotov. Poleg tega smo v ta namen uporabili še izračune trenutnih kontaktnih temperatur ter različne termodinamične izračune.

the diffusion-controlled nature of silicon-nitride oxidation, which is a temperature–time-dependent process.

Furthermore, flash temperatures above 1500°C were calculated for the selected fretting conditions ([10] and [28]), which support the above explanations. Additionally, because of the higher coefficient of friction in unlubricated than in lubricated fretting, which is directly proportional to the frictional heat, and confirmed temperatures of order of at least 400°C under these conditions, temperatures well above 1000°C are very reasonable for unlubricated conditions.

3.2 Interaction-couple experiments

The following method gives an opportunity to isolate the chemical wear by simultaneous control of thermal and mechanical effects, thus providing indirect evidence of the governing factor in tribochemical interactions between the steel and the ceramic. Such experiments were successfully applied in cutting-tool applications. Based on the experimental results of turning, which were in good agreement with results of static interaction-couple experiments, it was confirmed that they are relevant for the simulation and correlation of the tribochemical wear of cutting tools ([36] and [37]). Because of the even larger discrepancy between static experiments and dynamic conditions in turning, compared to fretting, it is reasonable to assume that they can also be applied for studying chemical behaviour in fretting wear.

From our results it is clear that the chemical interaction of silicon nitride with steel and oxidised steel is strongly influenced by the temperature. Below 700°C, no evidence of any interaction was found, while at temperatures above 1100°C, the reactivity was strongly enhanced. On the other hand, increased high contact pressures, resulting in extensive plastic deformation of the steel, did not enhance the chemical reactivity between the selected materials at any temperature ([10], [24] and [25]).

One of the most important facts in this paper, which strongly favours the critical influence of temperature in silicon-nitride oxidation, is, however, the observation that in the contact between steel and silicon nitride in the presence of oxygen, silica was formed only at temperatures of 1100°C and above. Although the contact times in the static interaction-couple experiments were much longer than in the contacts in the fretting experiments, no silica was formed at lower temperatures. This is again in excellent agreement with results of isolated Si_3N_4 oxidation experiments ([30] to [34]) and thermodynamic calculations based on the Gibb's free energy criteria ([10] and [24]).

3.3 General considerations

Very different materials (steel and ceramic) and contact conditions (air-dry / oil-lubricated) in this paper allowed us to use different indirect evidence from different points of view in order to investigate the observed tribochemical reactions. Additionally, flash-temperature calculations and various thermodynamic calculations were employed for this purpose.

Vsi rezultati, predstavljeni v tem prispevku in številni drugi iz ločenih analiz oksidacije silicijevega nitrida ter različni termodinamični izračuni, kažejo, da je temperatura ključni dejavnik pri oksidaciji silicijevega nitrida, vsaj ko govorimo o plasteh z debelino nekaj mikrometrov. V vseh teh študijah se je izkazalo, da taka oksidacija opazno poteka pri temperaturah nad 1000°C. Torej se zastavlja vprašanje, kateri mehanski vpliv lahko tako spremeni oksidacijski mehanizem in poveča kemijsko reaktivnost do mere, ki bi bila ustrezna temperaturi skoraj 1000°C? V prispevku smo prikazali, da v naših preskusih tlak in plastična deformacija nista vplivala na omenjene reakcije. Poleg tega je treba poudariti, da je keramika razmeroma nedeformabilen material, še posebej za obremenitve, ki so značilne za večino testov obrabe. Tudi vplivi striga so pri fretingu manj pomembni kakor pri drsenju, saj so hitrosti znatno manjše.

Poleg teh dejstev pa smo v mazanih testih, pri katerih je bila temperatura verjetno nižja kakor pri nemazanih testih, zaradi nižjega koeficienta trenja, našli jasne dokaze o obstoju temperatur vsaj 400°C. Po eni razlagi, ki je tudi v skladu s sedanjimi termodinamičnimi zakoni, bi lahko pričakovali celo temperature nad 1145°C. Vsi ti rezultati, vključno z izračuni najvišjih trenutnih temperatur ter termodinamičnimi izračuni, podpirajo možnost za izjemno visoke temperature na dotikih vršičkov (dejanski kontaktni površini) tudi pri zelo majhnih relativnih hitrostih. Model, ki te postopke podrobno razlaga, pa je predstavljen drugje ([10] in [38]).

Kljub temu pa je zelo težko ali celo nemogoče predstaviti nedvoumen dokaz o tem, kateri dejavniki najbolj vplivajo na te tribokemijske procese, saj v dinamičnih pogojih delujejo sočasno tako mehanski kakor termični vplivi in se je mogoče opirati zgolj na različne posredne dokaze.

Najbolj zanesljiv način za ugotovitev kotaktnih temperatur bi bile seveda meritve le-teh. Na žalost pa trenutno znane metode zaznavajo temperature v kontaktu med tribološkim postopkom le na območju, ki obsega med 300 in 900 (μm)^2 ([11] do [13]), kar je znatno prevelika površina v primerjavi s površino kontaktov vršičkov, ki je za en velikostni razred manjša. To je lahko tudi razlaga, zakaj so običajno izmerjene temperature tako nizke, in hkrati pomeni, da potrebujemo bolj natančne metode, ki bi lahko dale bolj zanesljiv odgovor o dejanskih najvišjih temperaturah v triboloških kontaktih.

However, all the results presented in our paper and in many other previous isolated studies on silicon-nitride oxidation, together with the thermodynamic calculations, strongly favour temperature as the key governing factor for tribo-oxidation of silicon nitride, at least for the layers which have thicknesses in the range of micrometers. In all these studies it was shown that the silica layer is likely to form only above 1000°C. So this begs a question, which mechanical factor could contribute in such a manner to completely change the oxidation mechanism and drastically increase the chemical reactivity that would be the equivalent of about 1000°C? It was shown here that pressure (compressive stress) and plastic deformation cannot affect these reactions. Besides, it must be pointed out that silicon nitride is a relatively non-deformable material, especially for the loads and stresses which are considered in most wear experiments. Furthermore, shear effects in fretting can also be considered as low, compared to the sliding conditions. Finally, there exist no indications that silica can form by any other process other than those described above, which means that its amount and thickness generated under the selected fretting action are related mainly to the contact temperature and time.

In addition to the above explanations, in lubricated fretting where the frictional heating was lower due to a much lower coefficient of friction, there exists clear evidence that the contact temperature was at least 400°C. Furthermore, a tentative explanation, which is in agreement with the thermodynamic model suggests temperatures even higher than 1145°C. These and other findings described in details in this paper, including flash-temperature calculations and all the performed thermodynamic calculations, strongly support the above suggestions that extremely high temperatures on the spot-to-spot contacts must be considered even under low-speed conditions. A model explaining these processes in detail is presented elsewhere ([10] and [38]).

Nevertheless, it is very difficult to give indisputable proof of the key governing factors for the tribochemical reactions, since in dynamic situations we have both mechanical and thermal effects acting simultaneously.

The surest way to prove the maximum contact temperature would, of course, be a contact-temperature measurement. However, today’s best measuring techniques can detect temperatures that are an average over an area of about 300 to 900 (μm)^2 ([11] to [13]). This is definitely too large an area compared to the small spot-to-spot contact areas of only few, to a few tens (μm)^2. This could explain why the experimentally obtained temperatures are usually so low and would further imply that more accurate techniques with measurements over a much smaller contact area are necessary to give the final answer on the possible maximum contact-temperature rise.

4 SKLEPI

1. Rezultati v tem prispevku kažejo, da je najbolj vplivni dejavnik za nastanek tribokemijskih reakcij v danih fretinških razmerah temperatura. Predstavljeni rezultati se tudi odlično ujemajo z različnimi teoretičnimi izračuni. Izjemno visoke temperature so torej mogoče tudi v razmerah, ki jih splošno pojmujemo kot nizko temperaturne zaradi majhnih relativnih hitrosti.
2. Samostojne in izolirane študije posameznih vplivnih dejavnikov lahko pripomorejo pri razumevanju osnovnih mehanizmov in postopkov. Tako smo v naši raziskavi statičnih spojev, pri katerih smo izolirali kemijsko obrabo materialov, odkrili, da je temperatura odločilna pri kemijskih reakcijah, medtem ko tlak in deformacja nista povečala kemijske reaktivnosti.
3. Zaradi difuzijske narave oksidacije silicijevega nitrida, ki je odvisna od temperature in časa, lahko pričakujemo večje količine in debele plasti oksidacijskih ostankov zgolj pri višjih temperaturah v kontaktu, npr. nad 1000°C.
4. Meritve dotikalnih temperatur (zaradi povprečenja na preveliki površini) pa tudi uporaba teoretičnih modelov (zaradi slabih predpostavk o dejanski površini in drugih parametrih) dajejo znatno nižje vrednosti od dejanskih na dotikalnih vršičkih. Razlike pri tem so lahko skoraj 1000°C.

4 CONCLUSIONS

1. The results reported in this paper strongly favour temperature as the key governing factor for the tribochemical reactions under selected fretting conditions. All the presented experimental evidence is in excellent agreement with the various theoretical predictions performed for the purpose of this work. Extremely high temperatures must be therefore be considered as the key governing factor in tribochemical reactions, even under conditions that are usually considered as a low-speed low-temperature conditions.
2. Isolated studies of the different influencing factors should be performed to reveal the fundamental mechanisms acting in dynamic situations. In our interaction-couple experiments under controlled temperatures and pressures we found that pressure and/or plastic deformation did not enhance the chemical reactivity between steel and Si_3N_4, while the temperature was critical to all the interactions.
3. Because of the strongly diffusion-controlled oxidation of silicon nitride (temperature-time dependence), large amounts and thick layers of silica produced in tribochemical reactions suggest temperatures well above 1000°C.
4. Surface temperature measurements (due to averaging of the temperature over too-large an area) and the conventional use of flash-temperature equations (due to poor approximation of the interface properties and real contact area) significantly and critically underestimate the maximum temperatures at the spot-to-spot contacts. The differences can be as high as 1000°C.

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