Nastanek in rast utrujenostne razpoke v korozijskem mediju

Occurrence and Growth of Fatigue Cracks in Corrosion Environment

L. Kosec*, F. Kosel**

UDK: 620.193.01
ASM/SLA: R1h, R1e, R2j, Q26p

V prispevku obravnavamo nastanek in ravzoj poškodbe kovinskih materialov v obliki klinov iz korozijskih produktov. Analizirali smo pogoje rasti in motenj v rasti klinov, vpliv števila in velikosti klinov na intenzivnost napetosti v sistemu kovina-klin. Rezultate analize smo posplošili s tremi primeri poškodb delov orodij in naprav.

1. UVOD

V kemično aktivnih okoljih nastanejo na površini kovin korozijski produkti, ki so različno trdno povezani s kovinsko osnovo. Temperaturne ali mehanske napetosti lahko poškodujejo plasti korozijskih produktov. Tesno oprijete in goste plasti korozijskih produktov upočasnijo ali povsem zavro potek korozijskih procesov. Poškodovane plasti pa te zaščite ne nudijo ali pa zgolj v omejenem obsegu. Poškodbe so različne: razpoke, luščenje korozijskih produktov na posameznih delih površine ob meji s kovino ali znotraj korozijskih produktov.

V prispevku obravnavamo vplive temperaturnih napetosti in oksidacije kovine na razvoj in obliko poškodb, ki pripeljejo do porušitve. Analiziran je primer, ko se je zaradi mehanske nestabilnosti porušila oksidna plast na površini in je skozi nastale razpoke prišel korozijski medij v stik s kovino. Na takih mestih je prišlo do pospešene oksidacije. Zaradi posebnega načina dostopa oksidanta so na teh mestih korozijski produkti zrasli v obliki klinov. Korozijski produkti se v fizikalnih in mehanskih lastnostih bistveno razlikujejo od kovine. Zato pride pri temperaturnih spremembah do napetostno deformacijskih stanj, ki vplivajo na morfologijo ter deformacijo korozijskega produkta in kovine.

Rezultate analize modela ilustriramo s tremi primeri: z elementom orodja za tlačno litje medi, cevmi pregrevalnika pare iz termoelektrarne in anodnimi palicami akumulatorja, ki naj pokažejo relativno razširjenost pojava.

O pojavu oksidnega klina in njegovem vplivu na porušitev kovine je malo strokovnih referenc. Vpliv oksidnega klina na širjenje razpok je analiziral P. T. Heald[1] in ugotovil, da razpoka samo zaradi oksidnega klina ne more preiti v nestabilno rast, če sistem ni obremenjen. Razprave o pomenu oksidnega klina na razvoj poškodb strojnih delov in naprav pa najdemo tudi v naši strokovni literaturi[2, 3, 4, 5, 6].

The contribution treats the occurrence and growth of defects in metal materials in the form of corrosion product wedges. The conditions of wedge growth and crack growth retardation, and the effect of the number and size of wedges on the stress intensity in the metal/oxide system were analyzed. The results of the analysis were illustrated by three examples of this kind of defects on certain tool parts and equipment components.

1. INTRODUCTION

In chemically active environment metal surfaces get covered by corrosion product coatings whose adhesion to the base metal is variously firm. High thermal or mechanical loads of metal/oxide systems can impair corrosion product coatings. Firmly adhered and thick corrosion product coatings can slow down or even completely stop the progress of corrosion, whereas the injured layers can no longer protect against corrosion or can do this only to a certain extent. The defects of the injured coatings can be of various kind like cracks, splitting of corrosion products on some areas of the surface, on the boundary to the base metal, inside the corrosion product layer etc.

This contribution treats the effects of thermal stresses and metal oxidation on the occurrence and development of defects leading to failure. An analysis is made of a case where due to mechanical instability, the oxide surface coating broke, and through the created cracks the corrosion medium came into contact with the metal. On such places an intensified oxidation took place. Due to the special way of transfer of the oxidizing agent through the broken oxide layer, on these places the oxides grew in the form of wedges. Corrosion products differ essentially from metals so by their physical as well as their mechanical properties. As a result the properties inside such a system are very non-uniform, so the stress-strain states which occur at temperature changes, cause the deformation of the corrosion products, and change their geometric characteristics.

The results of a general analysis of the model representing the discussed system are illustrated by three examples: an element of tool for die casting of brass, pipes of a steam superheater from a thermal power plant, and anode rods of a car battery. These examples

---

* Univerza Edvarda Kardelja v Ljubljani, FNT, VTOZD Montanistika
** Univerza Edvarda Kardelja v Ljubljani, Fakulteta za strojništvo

* E. Kardelj University of Ljubljana, Faculty of Natural Sciences, Dept. of Metallur.
** E. Kardelj University of Ljubljana, Faculty of Mechanical Engineering

Visokotemperaturna oksidacija je eden od pogostih načinov korozije kovin (suha korozija). Povišane in visoke temperature in nihanje temperature še dodatno močno obremenjujejo kovino, zato so poškodbe v takih okoljih še bolj pogoste in usodne. Take pogoje bomo upoštevali pri nastanku in rasti oksidnega klina.

2. NASTANEK IN RAST OKSIDNEGA KLINA

Nastanek oksidnega klina sledi predhodni enakomerni oksidaciji površine kovine na primerno visoki temperaturi. Na površini nastali oksid ima različen temperaturni razteznostni koeficient od kovine. Prav tako je pomembno, da ima nastali korozijski produkt tudi znatno večji specifični volumen. Fizikalne in mehanske lastnosti oksida in kovine se s temperaturo spreminjajo. Na obravnavani pojav pa vpliva tudi trdnost vezi med oksidom in kovino.

2.1 **Nastanek oksidnega klina**

Obravnavali bomo primer, kjer sta nastanek in širjenje oksidnega klina možna zaradi menjajočih se temperaturnih obremenitev. Na primerno visoki temperaturi nastane na površini kovine v določenem času zvezna plast oksida. Pri ohlajanju sistema kovina — oksid se zaradi različnih temperaturnih razteznostnih koeficientov v oksidu pojavijo tlačne napetosti. Zaradi njih se pri višjih temperaturah kovina in oksid plastificirata; ko pa se temperatura zniža in preide sistem iz plastičnega v elastično območje, začno v oksidu naraščati tlačne napetosti. Oksidni sloj na površini se elastično deformira. Z ohlajanjem lahko tlačne napetosti v oksidu dosežejo mejo plastičnosti. Če je trdnost vezi s kovino dovolj velika, prične oksid ponovno plastično teči. Drugače pa se lahko lokalno ukloni ali pa lušči, če je zrušilna strižna trdnost na meji s kovino manjša od tangencialnih napetosti. Ponavadi potekata oba pojava istočasno.

Pri ponovnem segrevanju sistema se pri določeni temperaturi eventuelne preostale tlačne napetosti v oksidu izničijo zaradi različnega širjenja kovine in oksida. Nato se s segrevanjem v oksidu pojavi in narašča natezna napetost. Zaradi mehanskih poškodb, ki so nastale med ohlajanjem, se v oksidu pojavijo koncentracije napetosti. Na teh mestih se pri nadaljnem segrevanju še razmeroma krhek oksid lahko poruši z razpoko, ki je pravokotna na površino kovine. Nastane lahko več takih razpok. Te razpoke omogočajo prost in hiter dostop zraka do kovine, zaradi česar pride do omejene, lokalne oksidacije. Ta drobna oksidna zajeda je začetek oz. zarodek oksidnega klina.

2.2 **Rast oksidnega klina**

Nastali oksid ima znatno večjo prostornino od kovine. Volumska deformacija zaradi oksidacije je tolikšna, da bi napetostno stanje daleč preseglo porušno trdnost kovine in oksida. Zato se oba (sistem) plastificirata. Napetostno stanje je v oksidni zajedi (zarodku klina) enako manjši meji tečenja ene od obeh sestavin sistema $\sigma_{T\,min}$, kot je:

$$\sigma_{T\,min} = \min\,(\sigma^{OK}_{T\,min}, \sigma^{M}_{T\,min})$$

Pri ohlajanjih s T_{max} bi se v oksidu pojavile tlačne napetosti, zaradi katerih sistem plastično teče. Plastično tečenje poteka vse do temperature prehoda sistema v elastično stanje pri T_p (temperatura prehoda sistema v

should point to the relative frequency of the phenomenon. In literature very few references can be found about the phenomenon of an oxide wedge. The effect of the oxide wedge on crack propagation was analysed by P. T. Heald (1) who proved that a crack cannot start growing unstably only because of an oxide wedge if no load is applied. Some investigations about the importance of an oxide wedge for the development of defects on various machine parts can also be found in our professional literature[2, 3, 5, 6].

High temperature corrosion is one of the most frequently found types of metal corrosion (dry corrosion). High temperatures, raised temperatures and high temperature cycles represent an additional load for metal, making the deffects in these environments even more frequent and fatal. These very conditions will be considered in our investigation of the occurrence and growth of an oxide wedge.

2. OCCURRENCE AND GROWTH OF OXIDE WEDGE

And oxide wedge occurs after a previous uniform oxidation of a metal surface at a correspondingly high temperature. The newly formed oxide has a different thermal expansion coefficient than the metal. It is also important that this new corrosion product has a considerably larger specific volume than the metal. The physical and mechanical properties of the oxide and the metal are changing with temperature. Besides this, the discussed phenomenon is affected also by the strenght of the oxide adhesion to the metal.

2.1. **Oxide Wedge Occurrence**

We will discuss a case where the occurrence and growth of the oxide wedge are possible because of changing thermal loads. At a correspondingly high temperature and within a certain time a continuous oxide layer occurs on the metal surface. During the cooling process of the metal/oxide system compressive stresses arise in the oxide due to the different thermal expansion coefficients. At higher temperatures the oxide and the metal become plastic because of the compressive stresses, but when the temperature lowers, and the system passes from the plastic into elastic region, the compressive stresses in the oxide start increasing. Now, the oxide layer on the surface undergoes elastic deformation. During the process of cooling the compressive stresses in the oxide can reach the plastic limit. If the strength of the adhesion to the metal is strong enough, the oxide starts flowing plastically. Otherwise, it can bend locally or split in case that the breaking shear strength on the metal boundary is smaller than the tangential stresses. Generally, however, both these two processes are going on simultaneously.

During reheating of the system, at a certain temperature the possible remaining compressive stresses in the oxide become eliminated because of the different expansion of the metal and the oxide. If heating is continued, tensile stresses appear and increase in the oxide. Due to mechanical defects that occurred in the oxide during the process of cooling, different stress concentration areas can be found. With continued heating on these areas, a relatively brittle oxide can break with a crack running rectangularly to the metal surface. Several such cracks might occur. These cracks enable a free and fast transfer of the oxidant (air) to the metal, induelastično stanje pri tlaku). Napetostno stanje v oksidni zajedi je pri tej temperaturi enako:

$$\sigma_{T\,\min}\,(T_p = \sigma_{\min}\,(\sigma_T^{OK}\,(T_p),\ \sigma_T^{M}\,(T_p))$$

Z ohlajenjem pa tlačne napetosti naraščajo. Če dosežejo mejo tečenja $\sigma_{T\,\min}$, pride do ponovnega plastičnega tečenja sistema.

Naslednja stopnja v spremenljivem temperaturnem režimu je segrevanje sistema od $T_{\min}$ na $T_{\max}$. Pri tem se v začetku tlačne napetosti, nastale pri ohlajanju, zmanjšujejo in pri določeni temperaturi je sistem brez napetosti. S segrevanjem se v zajedi pojavijo natezne napetosti, ki s temperaturo rastejo. Če napetost preseže trdnost zajede pod temperaturo prehoda iz elastičnega v plastično področje (T_p^+ — pri natezni obremenitvi), se zajeda poruši. Razpoka je nadaljevanje razpoke v zvezni površinski plasti oksida. S tem se ponovno odpre hitra pot za dostop oksidanta do kovine ter se tako pospeši rast zajede v smeri razpoke. Po večkratni ponovitvi temperaturnega cikla ($T_{\max} - T_{\min} - T_{\max}$) se zajeda izoblikuje v obliko klina mikroskopskih razsežnosti.

3. NAPETOSTI ZARADI OKSIDNEGA KLINA

Rast oksidnega klina v kovini uravnava predvsem hiter prenos kisika po razpoki do kovine, v smeri normalno na steno klina, pa difuzija skozi oksid. Na ta način nastane in se ohranja trikotna oblika klina. Vsaka razpoka skozi primarni oksidni sloj je lahko začetek oksidne zajede oz. klina. Zato je na kovinskih delih, ki so izpostavljeni menjajočim se temperaturam, veliko mikroskopskih poškodb v obliki oksidnih klinov.

Napetostno stanje, ki se pojavi v sistemu med rastjo oksidnega klina, raziskujemo na poenostavljenem modelu, tako da izberemo tanek sloj polprostora, ki ga predstavlja polravnina z več oksidnimi klini. Napetostno stanje je odvisno od temperaturnih obremenitev in ga bomo analizirali pri treh značilnih mejnih temperaturah.

3.1 Napetostno stanje pri najvišji temperturi, $T_{\max}$.

Pri tej temperaturi oksidni klin najhitreje raste. V njem se pojavijo tlačne napetosti, ki dosežejo minimalno mejo tečenja ene od sestavin sistema $\sigma_{T\,\min}$. Ker pa se oksid in kovina razlikujeta tudi v drugih lastnostih, se pojavijo še dodatne temperaturne napetosti. Te napetosti so v temenu klina, to je na meji polravnine razmeroma velike tlačne napetosti in so vzporedne z mejo polravnine. Pod mejo polravnine delujejo na klin znatne strižne in normalne napetosti pravokotno na smer polravnine[5]. Primerjalna napetost v sistemu kovina-oksid je znatno večja od meje tečenja, zato je hitrost plastične deformacije velika in napetostno stanje ne preseže $\sigma_{T\,\min}$. Rezultanta sil zaradi tlačne napetosti na plašču klina ($\sigma_{T\,\min}$) deluje proti meji polravnine. Zaradi nje in temperaturnih napetosti se sistem značilno deformira. Teme oksidnega klina se pri tem zoži, kovina pa s plastičnim tečenjem zavzame ta prostor. Posledica rezultirajočih napetosti je izbočitev meje polravnine okoli temena oksidnega klina **(sl. 1)**. Zelo izraziti primeri plastične deformacije sistema so takrat, ko na temenih oksidnih klinov izpade del oksida in se poruši ravnotežno napetostno stanje na tem delu polravnine **(sl. 2, 3)**.

Oksidni klin vpliva na stabilno oz. nestabilno rast razpoke v kovini zaradi tlačnih napetosti, ki so enake meji tečenja $\sigma_{T\,\min}\,(T_{\max})$. Dejanska širina korena razpoke je (2):

cing a limited local oxidation. This tiny oxide flaw represents the beginning of an oxide wedge.

2.2. **Oxide Wedge Growth**

The newly formed oxide has a much larger volume than the metal. The volume deformation due to oxidation is so extensive that the stress state exceeds by far the rupture strength of the metal and the oxide. Therefore both of them (the metal/oxide system) become plastic. The stress state in the oxide flaw (wedge embryo) is equal to the lower yield point of one of the system's components as follows:

$$\sigma_{y\,\min} = \sigma\,\min\,(\sigma_{y\,\min}^{OK},\ \sigma_{y\,\min}^{M}) \tag{1}$$

During cooling from $T_{\max}$, compressive stresses appear in the oxide due to which the system exceeds the yield point. The plastic flow continues down to the temperature of the transition of the system from the plastic into elastic state, T_p (temperature of the system's transition into elastic state under pressure). The stress state in the oxide flaw at this temperature is:

$$\sigma_{y\,\min}\,(T_p) = \sigma\,\min\,(\sigma_y^{OK}\,(T_p),\ \sigma_y^{M}\,(T_p)) \tag{2}$$

With continued cooling the compressive stresses increase. If they attain the yield point $\sigma_{y\,\min}$, this induces a repeated plastic flow of the system.

In changing temperature conditions, the next stage is heating up the system from $T_{\min}$ onto $T_{\max}$. Here, at the beginning, the compressive stresses induced by cooling, are reduced and at a certain temperature the system is free of stress. With heating up the system, tensile stresses appear in the flaw, increasing with temperature. If the stress exceeds the strength of the flaw below the temperature of the transition from the elastic into plastic state (T_p^+ — under tensile load), the flaw breaks. The newly occurred crack continues the crack in the primary surface layer of the oxide. In this way, the oxidant has again a fast access to the metal reopened, stimulating the growth of the flaw in the direction of the crack. After several repetitions of the temperature cycle ($T_{\max} - T_{\min} - T_{\max}$), the flaw grows into a wedge of microscopic dimensions.

3. **STRESSES INDUCED BY OXIDE WEDGES**

The growth of the oxide wedge into the metal depends especially on how rapid is the access of the oxidant to the metal along the crack, and in the direction normally to the wedge face, on how strong is the diffusion through the oxide. In this way the wedge grows in the form of a triangle and keeps this form. Any crack through the primary oxide layer can mean the onset of an oxide flaw or wedge. As a result, on metal parts which are exposed to changing temperature conditions, a great number of microscopic defects in the form of oxide wedges can be found.

The stress state occurring in the system during the process of oxide wedge development, is investigated on a simplified model by choosing a thin layer of semi-space, representing the semi-plane with several oxide wedges. The stress state as function of thermal loads will be analysed only for three extreme temperatures.

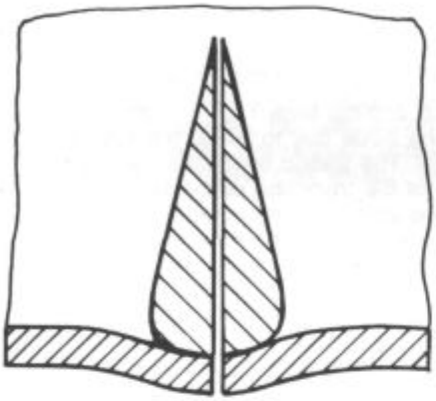
3.1. **Stress State at the Highest Temperture ($T_{\max}$)**

At this temperature the oxide wedge grows the most rapidly. Compressive stresses appear in it, attaining the

$$\varphi\,(C) = \frac{C\,(1-\nu)}{4\pi\,\mu\,\sigma_{zr}\,(T_{max})}\left[\frac{\mu}{1-\nu}\tan\Theta + \pi\,\sigma_{Tmin}\,(T_{max})\right],$$

kjer je Θ kot klina razpoke v kovini, ν Poissonovo število in μ strižni modul.

Kritična širina korena razpoke pri nestabilni razpoki pa je: $\varphi_C = 2\gamma/\sigma_{zr}\,(T_{max})$, kjer je γ površinska napetost. Razpoka je stabilna, če je $\varphi_C > \varphi\,(C)$. Če pa je $\varphi_C < \varphi\,(C)$, je nestabilna in vodi k porušitvi.

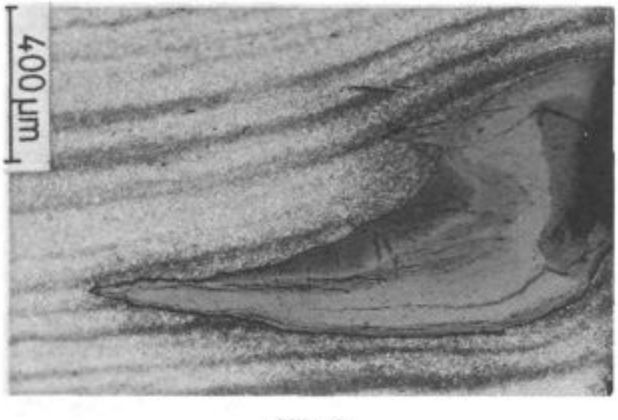


Slika 1

Razpoka skozi oksidno plast in klin do kovine na vrhu klina.

Fig. 1

A crack running through the oxide layer and the wedge right to the metal at the wedge tip



Slika 2

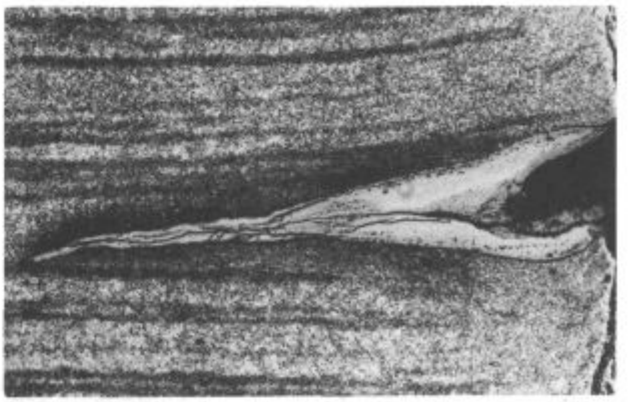
Deformacija kovine v okolici klina. Razpoke v smeri osi klina; 50 ×

Fig. 2

Deformation of the metal in the vicinity of the wedge. Cracks in the direction of the wedge axis; 50 ×

3.2 Napetostno stanje pri temperaturi prehoda iz plastičnega v elastično področje sistema, T_p

Tlačne napetosti v oksidnem klinu se povečajo, vendar ne čez mejo tečenja. V tem primeru lahko določimo največje napetostno stanje v kovini ob korenu oksidnega klina, prav tako pa faktor koncentracije napetosti[4]. Napetost v oksidnem klinu je enaka $\sigma_{T\,min}\,(T_p)$, faktor koncentracije napetosti pa: $K_I = 1{,}1209 \cdot \sigma_{T\,min}\,(T_p)\,\sqrt{c}$, kjer je c dolžina oksidnega klina. Če pa je na površini več klinov, je faktor koncentracije napetosti v kovini ob



Slika 3

Deformacija kovine in oksidnega klina zaradi odluščenja oksida na temenu klina; 40 ×

Fig. 3

Deformation of the metal in the oxide wedge due to oxide splitting on the wedge back face; 40 ×

minimum yield point of one of the system's components $\sigma_{T\,min}$. But since the oxide and the metal differ also in other properties, additional thermal stresses appear too. On the back face of the oxide wedge, i. e. on the semi-plane boundary, these stresses are compressive, and relatively high, acting in the direction parallel to the semi-plane. Under the semi-plane boundary considerable shear and normal stresses act on the wedge in the direction rectangular to the semi-plane (5). The comparative stress in the metal-oxide system is considerably higher than the yield point, therefore, the rate of plastic deformation is high, and the stress state does not exceed the $\sigma_{y\,min}$. The resultant of the forces arising from compressive stress on the wedge faces ($\sigma_{y\,min}$), acts in the direction towards the semi-plane boundary. Because of this and due to temperature stresses, the system undergoes a typical deformation.

The back face of the oxide wedge narrows, its place being taken by the plastically flowing metal. The consequence of the stresses resulting from this is the buckling of the semi-plane boundary around the oxide wedge, **(Fig. 1)**. Very distinct cases of plastic deformation of the system can be observed if on the back face of the wedge a tiny piece of the oxide splits off and destroys the equilibrium stress-state in this part of the semi-plane **(Fig. 2, 3)**.

The oxide wedge has an influence on the stable or unstable crack growth in the metal owing to compressive stresses being equal to the yield point $\sigma_{y\,min}\,(T_{max})$.

The actual width of the crack tip is (2)

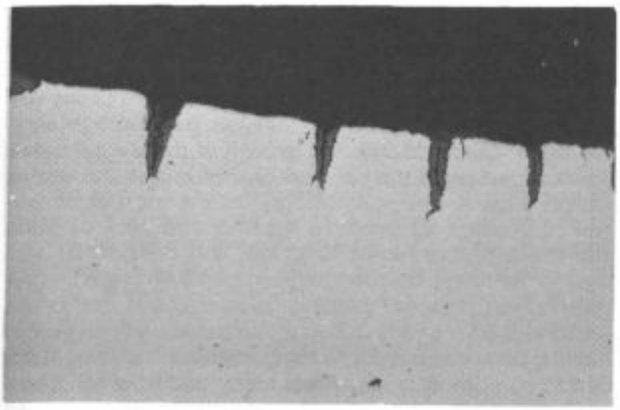
$$\vartheta\,(c) = \frac{c\,(1-\nu)}{4\,\pi\,\mu\,\sigma_u\,(T_{max})}\left[\frac{\mu}{1-\nu}\tan\Theta + \pi\,\sigma_{y\,min}\,(T_{max})\right] \quad (3)$$

where Θ is the wedge angle of the crack in the metal, ν Poisson's number and μ shear module.

And the critical width of the crack tip at unstable growth is: $\varphi_c = 2\,\gamma/\sigma_{zr}\,(T_{max})$ where γ is the surface stress. Crack growth is stable if $\varphi_c > \vartheta\,(c)$ and unstable and leading to failure if $\vartheta_c < \vartheta\,(c)$.

3.2. Stress State at the Transition Temperature from the Plastic into Elastic State (T_p)

In this case the compressive stresses in the oxide wedge are increased, however not beyond the yield



Slika 4
Skupine oksidnih klinov; 50 ×
Fig. 4
Groups of oxide wedges; 50 ×

korenih klinov manjši **(sl. 4, 5)**. Če je v polravnini več klinov dolžine c, ki so med sabo oddaljeni z d, je faktor koncentracije napetosti $K_I = \beta_I \cdot \sigma_{T\,min}\,(T_p)\,\sqrt{c}$.

λ	0	0,2	0,4	0,6
β_I	1,1209	0,87186	0,62536	0,51046
	0,8	1,0	2,0	3,0
	0,4446	0,39866	0,282206	0,2303

kjer je $\lambda = c/d$.

Sistem z več enako velikimi oksidnimi klini v polravnini je odpornejši proti porušitvi v primerjavi s sistemom, ki ima le enega samega iste dolžine.

3.3 Napetostno stanje pri najnižji temperaturi, T_{min}

Tlačne napetosti v oksidnem klinu se povečujejo in dosežejo pri neki T_{min} vrednost, ki presega napetostno stanje pri vseh višjih temperaturah. Faktor koncentracije napetosti se zato poveča in je določen na enak način kot zgoraj.

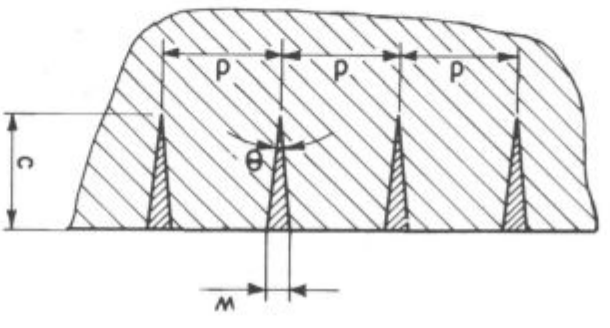
Tako kot pri najvišji, je tudi pri najnižji temperaturi zanimiv odgovor na vprašanje o stabilnosti razpoke v kovini. Hitrost širjenja razpoke $\dot{c}\,(t)$ je:

$$\dot{c}\,(t) = \frac{\mu\,\omega\,(t)}{\pi\,(1-\nu)} \left\{ \left[1 - \frac{\omega\,(t)\,\sigma}{2\,\gamma} \right]^{-0,5} - 1 \right\}$$

Odtod sledi pogoj za nestabilno rast razpoke: $\omega = 2\,\gamma/\sigma$, kjer je ω širina temena oksidnega klina. V tem primeru je hitrost širjenja razpoke neskončno velika.

4. MOTNJE V RASTI OKSIDNEGA KLINA

Motnje v rasti oksidnega klina se pojavijo takrat, ko se v določenih razmakih ne obnavlja razpoka v oksidni plasti ali klinu kot hitra pot za prenos kisika do kovine na vrhu klina. V nekaterih primerih se lahko zgodi, da oksid zapre zunanjo stran razpoke, tako da se tudi pri nihanju temperature zapreka ne poškoduje oz. ne poči. Takrat je oksidacija vezana zgolj na transport skozi oksid. Rast klina se tedaj upočasni, posebej še na korenu, zato se mu spremeni tudi oblika. Zelo trdno zaporo



Slika 5
Shema sistema kovina-oksidni klini.
Fig. 5
Scheme of the metal/oxide wedge system

point. We can define the maximum stress state as well as the stress concentration factor in the metal around the oxide wedge tip[4]. The stress in the oxide wedge is equal to $\sigma_{T\,min}\,(T_p)$ and the stress concentration factor is $K_I = 1,1209 \cdot \sigma_{T\,min}\,(T_p)\,\sqrt{c}$, where c represents the length of the oxide wedge. In case of several wedges on the surface, the stress concentration factor in the metal around the wedge tips is smaller **(Fig. 4, 5)**. If there are several wedges in the semi-plane of various lengths (c) and distances (d), then the stress concentration factor is $K_I = \beta_I \cdot \sigma_{T\,min}\,(T_p)\,\sqrt{c}$.

λ	0	0,2	0,4	0,6
β_I	1,209	0,87186	0,62535	0,51046
	0,8	1,0	2,0	3,0
	0,4446	0,39866	0,28206	0,2303

where $\lambda = c/d$

A system with several equally sized oxide wedges in the semi-plane is more resistant to rupture than a system with only one wedge of the same length.

3.3. **Stress State at the Lowest Temperature (T_{min})**

The compressive stresses in the wedge increase, and at a certain minimum temperature (T_{min}), attain the value which exceeds the stress state at all higher temperatures. The stress concentration factor is therefore increased, and can be defined in the same way as above.

Similarly as for T_{max}, we are also for T_{min} interesed in the answer to the question of stable or unstable crack growth.

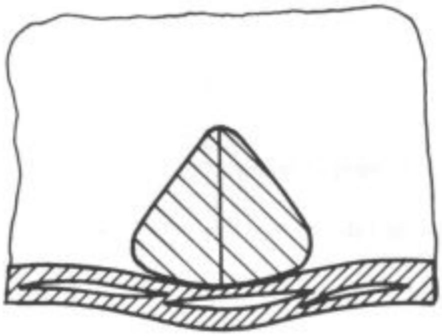
The rate of crack propagation c (t) (2) is:

$$c\,(t) = \frac{\mu\,w\,(t)}{\pi\,(1-\nu)\,\sigma} \left\{ \left[1 - \frac{w\,(t)\,\sigma}{2\,\gamma} \right]^{-0,5} - 1 \right\} \qquad (4)$$

Therefrom the condition for the unstable crack growth is obtained: $w = 2\,\gamma/\sigma$ where w is the width of the oxide wedge back face. In this case the rate of crack propagation is infinite.

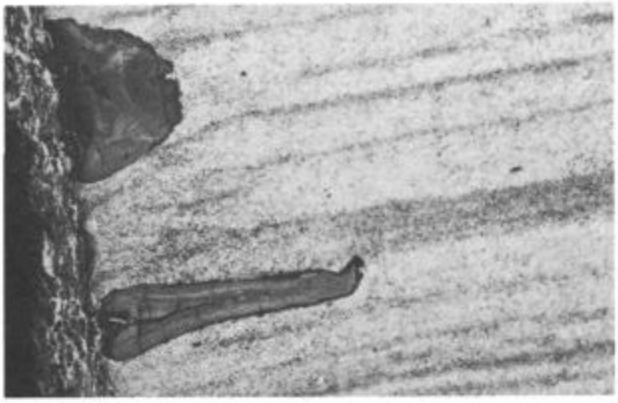
4. **RETARDATION IN GROWTH OF AN OXIDE WEDGE**

Retardation in the growth of an oxide wedge takes place when from time to time a crack enabling a fast za dostop kisika predstavlja npr. kompozitna plast oksida in kovine, ki lahko nastane v določenih delovnih okoljih oz. pogojih. Ta je odporna na menjajoče se temperaturne obremenitve, posebej v fazi ogrevanja (nateg) in je vzrok dolgotrajni motnji v rasti oksidnega klina. Taka kompozitna zapora je manj odporna na tlačne oz. strižne obremenitve, zaradi katerih se lahko odlušči s površine in motnja preneha **(sl. 6, 7, 8)**.



Slika 6
Mehanske stabilne pregrade (komposit oksid-kovina) nad oksidnim klinom.

Fig. 6
Stable mechanical closure barrier (an oxide/metal composite) above the oxide wedge



Slika 7
Mehanske stabilne pregrade (komposit kovina-oksid) nad dvema degeneriranima oksidnima klinoma; 50 ×

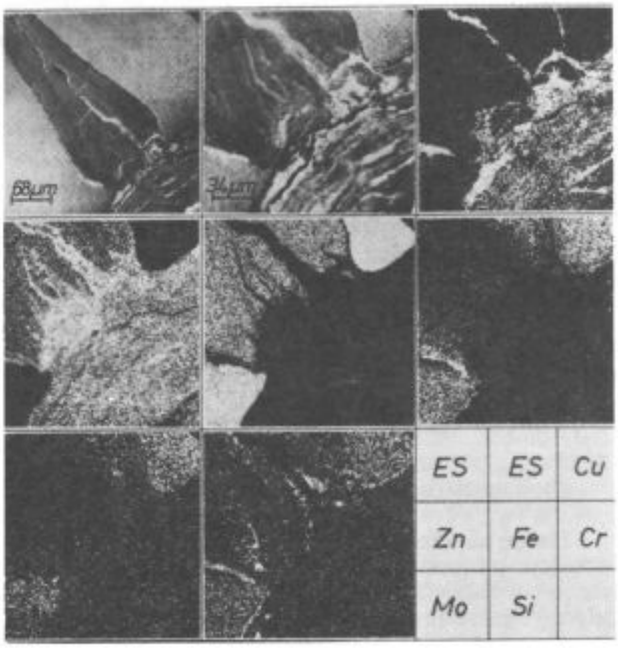
Fig. 7
Stable mechanical barrier (an oxide/metal composite) above two degenerated oxide wedges; 50 ×

5. PRIMERI NASTAJANJA OKSIDNIH KLINOV

5.1

Bat stroja za tlačno litje medi je izdelan iz orodnega jekla za delo v vročem (0,4 % C, 5 % Cr, 1,3 % Mo in 0,4 % V)[5]. V stacionarnih pogojih dela je nihala temperatura na površini bata v približno 11 sekundah od 780 °C (T_{max}) do 600 °C (T_{min}), ob prekinitvah pa se površina bata ohladi pod 200 °C ali celo na temperaturo okolice. Po določenem času dela se je bat poškodoval zaradi t. i. toplotnega razpokanja na delovni površini. Te poškodbe se kažejo v mreži bolj ali manj globokih razpok-kanalov, ki se širijo v kovino v obliki oksidnih klinov. Na osnih presekih bata je tako moč opaziti

transfer of oxygen to the metal does not reopen. In some cases it can happen that corrosion products close the crack from the outside so that even at varying temperature this closure does not break. In these cases oxidation depends only on the oxygen transport through the oxide. Owing to this, the growth of the wedge slows down especially at the tip, thus changing also the wedge morphology. A very solid closure for the transfer of oxygen represents for example a composite layer of oxide and metal created in specific working conditions. This layer is resistant to changing temperature loads, especially in the phase of heating (tension), and this is the reason for a long retardation in the oxide wedge growth. Such a composite closure can, however, be less resistant to compressive and shear loads due to which it can peel off the surface, and the wedge starts growing again **(Fig. 6, 7, 8)**.



Slika 8
Kemična sestava oksidnega klina in stabilne pregrade.

Fig. 8
Chemical composition of the oxide wedge and the stable barrier

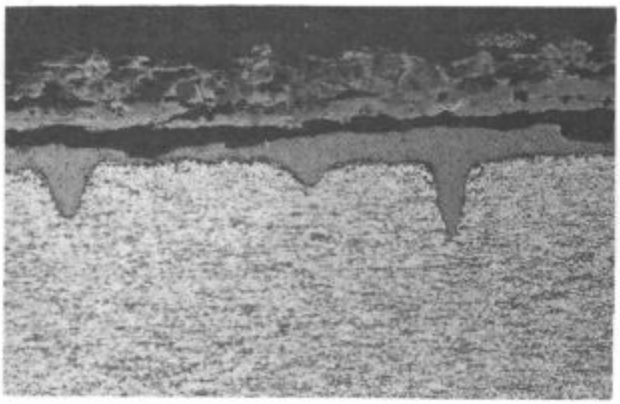
5. SOME EXAMPLES OF OXIDE WEDGE OCCURRENCE

5.1.

The plunger of a die casting machine for brass is made from hot-working tool steel (0.4 % C, 5 % Cr, 1.3 % Mo and 0.4 % V) (5). At stable operating conditions the temperature on the plunger surface varies in approx. 11 seconds from 780° C (T_{max}) to 600° C, while at work stoppage, the plunger surface cools down below 200° C, or even down to the ambient temperature (T_{min}). After a certain time of operation, heat cracking occurs on the working surface of the plunger. These defects can be seen as a network of more or less deep cracks — channels — extending into the metal in the form of oxide wedges. On the axial cross section of the plunger it is thus possible to observe practically all the above depraktično vse prej opisane pojave: razpoke v klinih, deformacije klinov in okolišnje kovine, zaprtje razpok in motnje v rasti oksidnega klina **(sl. 2, 3, 6, 7, 8)**.

5.2

Na zunanji steni cevi pregrevalnika pare, ki dela pri nižjem temperaturnem nivoju kot bat, so se pod relativno tanko plastjo škaje pojavili oksidni klini. V nekaterih primerih se je iz teh klinov razvila poškodba do porušitve stene cevi. Poleg agresivnega delovanja okolice (dimni plini) je sistem cevi podvržen tudi obremenitvam zaradi nihanja temperature **(sl. 9)**.



Slika 9

Oksidni klini z zunanje stene cevi pregrevalnika pare; 100 ×

Fig. 9

Oxide wedges from the outer side of the steam superheater tube; 100 ×

5.3

Povsem enake poškodbe, v obliki klinov korozijskih produktov, so nastale na pozitivnih elektrodah akumulatorskih baterij in so pripeljale do lokalnih zlomov palic in uničenja baterije. Palice iz malolegirane svinčeve zlitine so obešene v bateriji in zato so ves čas zaradi lastne teže obremenjene na nateg. Pri polnjenju in praznjenju baterije poteka kemična reakcija, katere produkti se močno razlikujejo v gostoti. Trdnost sulfata $PbSO_4$ je manjša od napetosti zaradi teže palice in se poruši. Menjajoči se ciklusi praznjenja in polnjenja pri stalni natezni obremenitvi omogočajo rast korozijskega produkta v obliki klinov **(sl. 10)**. Ko seže poškodba zadosti globoko v kovino, se palica nenadno poruši (krhko).

6. ZAKLJUČEK

Kovinski deli orodij in naprav, ki delajo v agresivnih okoljih, se prekrijejo s plastmi korozijskih produktov. Zaradi mehanskih ali temperaturnih obremenitev so korozijski produkti pogosto mehansko nestabilni, kar pripelje do lokalnih porušitev. Skozi razpoke prihaja medij zelo hitro do kovine in na teh mestih začno rasti korozijski produkti v obliki klinov.

Če so izpolnjeni pogoji trajne mehanske nestabilnosti korozijskih produktov, klin raste in pripelje do porušitve istema. V sistemih s korozijskimi klini nastanejo značilna napetostno deformacijska stanja. Ta vplivajo na oblikovanje sistema in eventuelno porušitev. Mot-

scribed phenomena: cracks in the wedges, deformation of wedges and the surrounding metal, crack closure and retardation in the growth of the oxide wedge etc. **(Fig. 2, 3, 6, 7, 8)**.

5.2.

On the outer wall of a steam superheater, operating at a lower temperature level than the plunger, oxide wedges were observed under a relatively thin layer of oxide scale. In some cases the defects arising from these wedges developed into total failure of the pipe wall. Besides the agressive effect of the environment (flue gases), the piping system is subjected also to loads arising from temperature variation **(Fig. 9)**.

5.3.

The same kind of defects in the form of corrosion product wedges were found on positive electrodes of a car battery.

These defects resulted in local breaking of anode rods and total failure of the battery. The anode rods, which are made of a low-alloyed Pb-alloy, are hung onto the battery boxing and thus constantly under tension load. During battery charging and discharging a chemical reaction takes place. Its products differ very much in specific volume, so the $PbSO_4$ probably cannot bear the weight of the anode rod and breaks. The exchanging cycles of discharing and charging at constant tensile load enable the growth of corrosion products in the form of wedges **(Fig. 10)**. When the crack reaches a certain critical point deep enough in the metal, the rod undergoes a sudden brittle failure.

Slika 10

Klin v anodni palici akumulatorske baterije; 100 ×

Fig. 10

A wedge in the anode rod of a car battery; 100 ×

6. CONCLUSION

Metal parts of tools and machines, operating in agressive environment, get covered with corrosion product layers. Due to mechanical and thermal loads corrosion products are subject to mechanical instability, leading to local failures. Through cracks the oxidant rapidly reaches the metal and on these places corrosion products start growing in the form of wedges.

In the conditions of permanent mechanical instability of corrosion products, a wedge grows and causes a fainje, ki preprečujejo hiter dotok korozijskega medija do kovine na vrhu klinov, zavro njihovo rast in spremene njihovo obliko. Ugotovljeno je tudi, da je rast skupine oksidnih klinov v enakih pogojih počasnejša kot pa takrat, če je v sistemu en sam klin.

V prispevku smo obravnavali rast klinov v kemično in mikrostrukturno homogenem kovinskem materialu.

V kemično nehomogenih materialih so s potekom koncentracije legirnih elementov določena prednostna mesta nastanka in rasti klinov. Če je medsebojna orientacija nehomogenosti in komponent temperaturnih napetosti ugodna, potekajo razpoke oz. oksidni klini vzdolž negativnih izcej. Na teh mestih so razlike v razteznostnih koeficientih kovine in oksida največje; oksid nad negativno izcejo je med nihanjem temperature znatno bolj obremenjen kot nad pozitivno, zato večina razpok v oksidu nastane nad negativnimi izcejami. Analiza takega primera je zahtevnejša in bo vsebina samostojnega prispevka.

lure of the system. In corrosion wedge systems very typical stress-strain states occur, affecting the morphology of the system and inducing a possible failure. Closures preventing a rapid access of the oxidant to the metal at the wedge tip, retard the growth of the wedge and change its morphology. The authors also found out that the growth of a group of oxide wedges is slower than that of only one wedge in the system.

This contribution treats oxide wedge growth in a homogeneous metal material. In metal materials with nonhomogeneous chemical composition and microstructure the places likely for the occurrence and growth of wedges are defined from the concentration distribution of the alloying elements. If the interorientation of nonhomogeneities and thermal load components is favorable, cracks or wedges run along the negative segregations. On these places the differences in thermal expansion coefficients between the metal and the oxide are the greatest; the oxide above the negative segregation is during temperature variation under much greater load than above the positive segregation, therefore the major part of cracks in the oxide are to be found above the negative segregations. The analysis of such a case demands special attention and efforts, and will be the subject of a separate investigation.

LITERATURA/REFERENCES

1. Heald P. T.: The Oxide Wedging of Surface Cracks, Material Science and Engineering, 35, 1978, 165—169, Lausanne, Swiss.
2. Kosel F. In Kosec L.: Toplotno razpokanje orodij za delo v vročem, Strojniški vestnik, 1983, 7—9, , 151—159, Ljubljana, Yugoslavia
3. Vodopivec F., Ralić B. in Dobovišek B.: Poškodbe na ceveh visokotlačnega parnega kotla zaradi kombiniranega vpliva mehanske in kemijske obremenitve, Strojniški vestnik, 1985, 1—3, 6—12, Ljubljana, Yugoslavia
4. Berežnickij L T., Pansjuk V. V. in Staščuk N. G.: Vzaimodejstvie žestkih linejnih uključenij i treščin, Naukova Dumka, 1983, Kiev, USSR.
5. Kosel F. in Kosec L.: High Temperature Fatigue in Nonhomogeneous Continuum, Fatigue and Fatigue Thresholds, 1, 1984, 613—623, Birmingham, England.
6. Kosel F., Kosec L.: Occurrence and Growth of Fatigue Cracks in Corrosion Environment, Fatigue 87, 3, 1987, 1201—1210, Virginia, USA.