Vpliv segregacij oligoelementov po mejah na lastnosti železovih zlitin

Influence of interfacial segregation of residuals on the properties of iron base alloys

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A. UVOD

Segregacije na kristalnih mejah so pojav, ki je pogosto vzrok poslabšanju lastnosti na kristalnih mejah različnih gradiv in v raznolikih delovnih pogojih. Vpliv tega pojava na poškodbe strojnih delov ni toliko znan, kot bi zaradi razširjenosti zaslužil. Namen prispevka je pokazati različne oblike tega pojava. Raziskovalni in tehnološki pomen ter zanimanje za segregacije so zasnovani na dejstvu, da je veliko število nečistoč ali namerno dodanih legirnih elementov nagnjeno k segregiranju in da so mnoge lastnosti medfaznih površin (kemične, mehanske, fizikalne) zelo odvisne od njihove kemične sestave.

Obravnavani so samo primeri, v katerih so bile segregacije zanesljivo identificirane in/ali izmerjene, ali primeri, v katerih ni bilo nobenega dvoma o vrsti segregacije, ki je povzročila spremembo določene lastnosti.

Reverzibilna popustna krhkost (RTE), ki se kaže v mnogih v tem članku obravnavanih pojavih, je le omenjena, saj je predmet drugih prispevkov te konference.

B. VISOKOTEMPERATURNA KRHKOST PRI LEZENJU

Kaže, da velja splošno pravilo, da se duktilnost pri porušitvi zaradi lezenja zmanjšuje z daljšanjem časa do porušitve. Zmanjšanje duktilnosti spremlja povečanje deleža interkristalnega preloma. Ta oblika poškodb je zelo pogosta pri lezenju. Vpliva segregacij v tem procesu pa ni bilo vedno mogoče ugotoviti.

V številnih novejših študijah so z različnim uspehom poskušali prikazati zvezo med nečistočami, ki segregirajo po kristalnih mejah, in zmanjšanjem duktilnosti. Problem je veliko bolj zamotan, kot je zapleteno razumevanje krhkosti pri nizkih temperaturah, zavoljo tega, ker se lahko sproži več mehanizmov delovanja zaradi segregacij teh elementov.

a) Do nukleacije por in razpok lahko pride na tri načine:

— segregacije na mejah kristalnih zrn ali mejah med delci sekundarne faze in matice povzroče

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A. INTRODUCTION

Intergranular segregation has recently emerged as a major cause of impairment of grain boundary properties in various materials and service conditions. However, the importance of such processes occuring at the atomic scale in the macroscopic failure of engineering components has not been as widely recognized as its ubiquity deserves, and it is the aim of the present paper to illustrate this variety.

The scientific and technological importance of intergranual segregations is based on the fact that a large number of elements present in materials as unwanted impurities or as intentionally added alloying species are susceptible to segregation, but also that many properties (mechanical, physical, chemical, etc.) of interfaces are critically sensitive to their chemical composition.

As a rule, only cases where segregations have effectively been identified and/or measured or cases where it is known for sure which segregation is involved, will be discussed. Reversible temper embrittlement (RTE), although it is actually involved in most of the phenomena discussed in this paper, will be omitted because it is the subject of another article in this Conference.

B. HIGH TEMPERATURE BRITTLENESS IN CREEP CONDITIONS

It appears to be generally true that the creep-rupture ductility of metals decreases with increasing time to rupture, and this decrease tends to be accompanied by increasing amounts of intergranular fractures. Since this fialure mode is so frequent in creep conditions, it has not always been realized that impurity segregations could take a part in this process. Recently, a number of studies have attempted, with varying degrees of succes, to correlate the effect of impurities which segregate to the grain boundaries with this trend towards ductility loss. However, the problem is much more complicated than that of low temperature brittleness since much large number of mechanisms can produce an effect of segregated or segregating elements:

a) Nucleation of cavities and cracks can be affected in three ways:

— By altering the cohesion of particle/matrix interfaces and of grain boundaries, segregation at nukleacijo por in razpok; ta proces poteka verjetno z lokalnimi krhkimi porušitvami mej[1,5], povečini tako kot pri nizkotemperaturni krhkosti;

— zdrs po kristalnih mejah (interkristalni zdrs) je eden od procesov, ki poveča deformacijo, potrebno za to dekohezijo (sl. 22); njegova hitrost pa je zanesljivo odvisna od kemične sestave kristalnih mej;

— segregacije na površinah novo nastalih por zmanjšujejo površinsko napetost por (γ_s) in s tem njihovo kritično velikost ($r_c = 2\gamma_s/\sigma$), nad katero lahko rastejo pri lokalni natezni napetosti (σ); segregacije tako povečujejo število rasti sposobnih por, oziroma navidezno hitrost nukleacije por.

b) Rasti por in razpok sta odvisni tudi od segregacij na mejah in prostih površinah, zato ker vplivajo na zdrs po kristalnih mejah in transportne pojave. Hitrost rasti je namreč odvisna od difuzije vzdolž kristalnih mej in po površinah novo nastalih por in razpok[3,4,5]. Ta pojav pa je prav tako tesno povezan s sestavo teh površin[6,7].

1. Porušitev pri lezenju

Pri iskanju povezave med segregacijami nečistoč in porušitvijo pri lezenju smo se močno opirali na izkušnje s popustno krhkostjo. Večina raziskav obravnava vpliv elementov IVa, Va in VIa skupin iz periodnega sistema elementov[8]. Rezultati so protislovni, ker vpliv mikrostrukture pri tem pojavu lahko presega vpliv segregacij. To je često primer pri bainitnem jeklu z 2,25 % Cr in 1 % Mo, ki je mnogo manj občutljivo na popustno krhkost od večine malolegiranih jekel.

Slika 1

Vpliv različnih kombinacij dodatkov Mn, Si in P v jeklu z 2,25 % Cr in 1 % Mo po stopenjskem ohlajanju na porušno trdnost (σ_r) in kontrakcijo (RA) po različnem času lezenja. (HP — zelo čista jekla, COM — tehniška jekla).

Fig. 1

Influence of Mn, Si, P additions in various combinations and of a step-cooling treatment prior to the creep tests, on the rupture stress (σ_r), ductility (RA), and creep life (t_r) of 2 1/4 Cr-1Mo steels (after ref. 8).

these interfaces can affect the nucleation of cavities and wedge-cracks respectively, since this proces is now believed to occur through localized brittle failure of these interfaces[1,5] in very much the same way as low temperature brittleness.

— Intergranular sliding is one of the proceses giving rise to the strain concentration necessary to produce these decohesions, fig. 22, and its rate is certainly dependent on grain boundarly composition.

— Segregation at the surface of a newly formed cavity decreases its surface tension γ_s and therefore the critical size $r_c = 2\gamma_s/\sigma$ above which it can grow under a local tensile stress σ: segregation will thus increase the number of cavities able to grow, i.e. the apparent nucleation rate.

b) Cavity and crack growth also depend on segregations at internal interfaces and at free surfaces, through their effect on:

— grain boundary sliding;

— transport phenomena, since the growth rate is also controlled by the diffusivities along grain boundaries and on the surfaces of the newly formed cavities or cracks[3,4,5] which are obviously dependent on the composition of these interfaces[6,7].

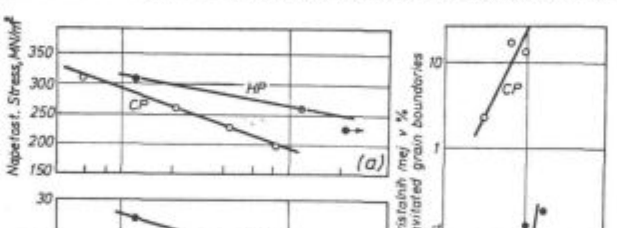
1. Creep rupture

In the attempts to correlate the effect of segregation impurities with creep, rupture properties the experiences with temper embrittlement have been heavily relied upon and most of the investigations have dealt with the effects of Group IV A, V A and VI A of the periodic table[8]. The evidence is conflicting because, in addition to the above mentioned reasons, the creep rupture properties are extremely sensitive to microstructure whose effects can largely over ride those of the segregations. This is often the case, for instance of the bainitic 21/4 Cr-1 Mo steels (which are, incidentall much less sensitive to temper embrittlement than the majority of low alloy steels). Lonsdale and Flewitt[2] showed that, in these steels, impurities can induce a definite decrease in creep life, which they attributed to the enhancing effect of impurities on both the nucleation and growth rate of cavities. However, Viswanathan[9] was unable to find any evidence of an impurity effect on their strength and ductility. Pope et al.[8] even found a beneficial effect of Mn, P and Si additions, and especially of their association, on the ductility of such steels, fig. 1. They suggest that this improvement can take place essentially because the segregations decrease the growth rate of cavities, probably by hindering intergranular diffusivity and in spite of their enhancing influence on cavity nucleation due to the embrittlement of particle/ /matrix interfaces. Conversely, when the steel is step-cooled prior to creep testing, the ductility is

Lonsdale in Flewitt[2] sta ugotovila, da lahko nečistoče v teh jeklih skrajšajo trajanje lezenja. To pripisujeta segregacijam zaradi vpliva na hitrost nukleacije, pa tudi na hitrost rasti por.

Viswanathanu[9] ni uspelo ugotoviti vpliva nečistoč na trdnost in duktilnost teh jekel. Pope in sodelavci[8] pa navajajo celo primere ugodnega vpliva Mn, P in Si na duktilnost tovrstnih jekel; posebej ugodna so bila jekla, ki so imela legirane kombinacije teh treh elementov (sl. 1). Po njihovem mnenju je bistvo izboljšanja duktilnosti v tem, ker naj bi te segregacije zmanjšale hitrost rasti por zaradi oviranja difuzije po mejah, kljub dejstvu, da segregacije sicer povečujejo nukleacijo por zaradi pojava krhkosti na medfazni površini segregacija/matica. Če je jeklo postopno ohlajeno pred lezenjem, pa je nasprotno njegova duktilnost obratno sorazmerna deležu nečistoč (sl. 1). Zato velike segregacije, ki so bile prisotne že na začetku lezenja, stimulirajo porušitev po mejah in večajo hitrost nukleacije por do takega obsega, da se duktilnost poslabša. Ta mehanizem je lahko primerna razlaga tudi za opazovano naraščanje hitrosti drsenja po kristalnih mejah.

Ponašanje Cr-Mo-V jekel je popolnoma drugačno, vplivi nečistoč na njihove lastnosti so različni. Vzrok tem razlikam naj bi bili vanadijevi karbidi, ki bolj utrjujejo matico kot kristalne meje. Tipler in Hopkins[10, 11] sta dognala, da so vse značilne karakteristike porušitve pri lezenju: trdnost, čas lezenja in duktilnost pri 550° C, v industrijskih talinah (CP) jekel z 0,5 % Cr, 0,5 % Mo in 0,25 % V in jeklih z 1 % Cr, 1 % Mo in 0,25 % V znatno manjše kot v ustreznih zelo čistih laboratorijskih talinah (HP), v katerih so bile koncentracije P, Sn, Sb, As in Cu na nižjem nivoju (sl. 2). Pogostost por na kristalnih mejah pri porušitvi se je v tali-

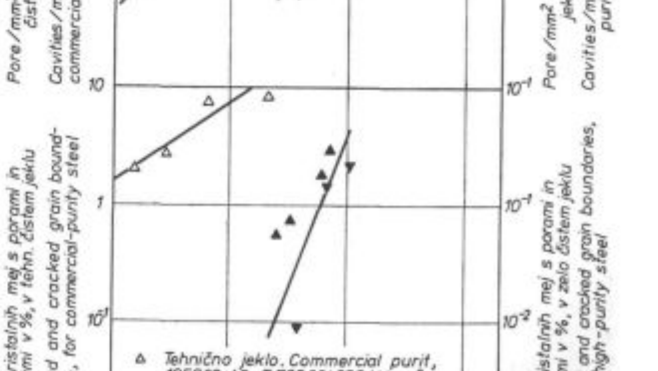


Slika 2
Primerjava »časa lezenja«, trdnosti (a), raztezka (b) in deleža por na mejah kristalnih zrn (c) pri porušitvi v tehniških (CP) in zelo čistih talinah (HP) jekla z 0,5 % Cr, 0,5 % Mo, in 0,5 % V, preizkušenih na lezenje pri 550 °C (po ref. 10).

Fig. 2
Comparison of creep lives, rupture stresses (a), ductilities (b) and densities of integranular cavities at rupture (c) in a commercial purity CP and high purity HP heat of 1/2 Cr — 1/2 Mo — 1/2 V steel, creep tested at 550 °C (after ref. 10).

adversely affected by the impurities, fig. 1. In this case, the large segregations which already exist at the onset of primary creep, during which highly localized strains are produced, favors interfacial fracture and therefore increase the nucleation rate to such an extent that ductility is impaired. This mechanism might also be responsible for the observed increase in grain boundary sliding rate.

The behavior of Cr-Mo-V steels is quite different: they are much more adversely affected by impurities. This difference may be due to the presence of vanadium carbides which preferentially harden the matrix with respect to the grain boundaries. Tipler and Hopkins[10, 11] have clearly established that all the creep-rupture characteristics, strength life and ductility at 550 °C are considerably lower in commercial purity heats (CP) of 1/2 Cr - 1/2 Mo — 1/4 V and 1 Cr — 1 Mo — 1/4 V steels than in the corresponding laboratory heats of higher purity (HP), i.e. in which the P, Sn, Sb, As and Cu content had been kept at a lower level, fig. 2. The cavity density on the grain boundaries at rupture is increased by up to three orders of magnitude by the presence of impurities[10], fig. 2, and this is already true throughout the creep test[11], fig. 3. The authors found that cavity density correlates better with the product ε . t of creep deformation ε and time t than with either of them separately[11], which indicates that cavitation is not controlled solely by plastic deformation but also by a diffus-



Slika 3
Vpliv čistosti jekla na nastajanje poškodb med lezenjem v odvisnosti od produkta trajanja lezenja (t) in raztezka (deformacije) (ε) (po ref. 11) (AC-hlajeno na zraku, T-popuščeno)

Fig. 3
Influence of purity on creep damage evolution throughout creep life plotted versus the product of creep duration t times elongation ε (after ref. 11).

nah s primesmi povečala za tri rede velikosti[10] (sl. 2), kar so potrdili tudi poskusi z lezenjem[11] (sl. 3). Ugotovili so, da je povezava med pogostostjo por in produktom deformacije in časa lezenja mnogo bolj izrazita od povezave s samo deformacijo ali časom lezenja[11]. To kaže, da pojav por ni odvisen zgolj od plastične deformacije, temveč tudi od difuzijskih procesov. Ločenega vpliva vsake nečistoče v tej študiji niso ugotovljali. Znano pa je da vse te nečistoče pri temperaturah poskusov lezenja segregirajo na kristalnih mejah ali prostih površinah[12]. Rezultati (sl. 3) jasno povedo, da je povečana nukleacija por zaradi segregiranih nečistoč osnovni vzrok znižanju lastnosti pri porušitvi zaradi lezenja.

Razen porušitve pri lezenju bomo analizirali še dve drugi lastnosti jekel, ki imata elemente mehanizma lezenja.

2. Pojav razpok pri žarjenju za odpravo napetosti (SRC)

Interkristalne razpoke, ki nastanejo pri žarjenju za odpravo napetosti v coni toplotnega vpliva ali v samih varih, so povezane z mehanizmom lezenja. Razpoke nastanejo pod vplivom lokalnih napetosti, oz. pod vplivom gradienta napetosti, ki ga povzroči naglo ogrevanje in ohlajanje med varjenjem. Razpokanje je torej v neposredni zvezi z lokalno duktilnostjo gradiva. V znanju o škodljivem vplivu nečistoč je še mnogo nejasnega. To znanje obsega le del spektra zlitin in možnih eksperimentalnih pogojev. Večina strokovne literature skuša povezati razpoke z nominalno koncentracijo nečistoč v jeklih, katerih sestava, mikrostruktura in mehanske lastnosti se spreminjajo v standardno predpisanih mejah in v pogojih preizkušanja, katerih ponovljivost ni bila ravno velika zavoljo različic, ki se pojavljajo pri varjenju ali varilnih poskusih[8]. Tovrsten vpliv nečistoč, posebej še v povezavi s popustno krhkostjo, sta jasno pokazala Brear in King[13] pri posodah z notranjim tlakom, izdelanih iz Mn-Mo-V jekel. Ugotovila sta, da zelo čista jekla niso občutljiva na pojav razpok, medtem ko je občutljivost jekel, ki so jim bile namenoma dodane nečistoče, rasla s koncentracijo le-teh. Nasprotno kot pri pojavu popustne krhkosti pri žarjenju za odpravo napetosti Sb, Sn in As bolj škodljivo vplivajo kot P. Prav tako je bil ugotovljen tudi škodljiv vpliv bakra[14].

Z Augerjevo spektroskopijo so na intergranularnem prelomu jekla z 0,5 % Cr, 0,5 % Mo in 0,25 % V po žarjenju za odpravo napetosti pri temperaturi 700 °C ugotovili precejšnje segregacije Sn, Sb, B, N in Cu, segregacij P pa zanemarljivo malo[15]. Izmerjene segregacije Sn in Sb se skladajo z opazovanji segregacij teh dveh kovin na prostih površinah v čistem železu[17, 18]. Novejša raziskava Popa in sodelavcev[8] je nadaljni prispevek k poznavanju pojava razpok pri žarjenju za odpravo napetosti pri jeklih za posode z notranjim

ion process. Although the specific influence of each impurity was not isolated in this study, it is known that all of them segregate to the boundaries and to the free surfaces[12] at the temperature of the creep tests, and the results in fig. 3 strongly suggest that the enhancement of cavity nucleation by segregating impurities is a major factor responsible for the loss of creep rupture characteristics.

Besides creep rupture itself two other properties of steels which involve creep mechanisms should be quoted.

2. Stress relief-cracking (SRC) (or »Reheat cracking«)

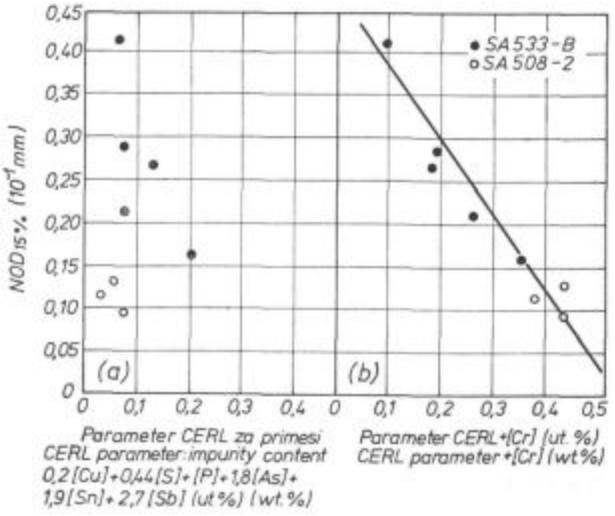
The formation of intergranular cracks in the heat affected zone or occasionally the weld metal in a welded assembly when it is reheated to relieve residual stresses is now recognized to be associated with a creep (or relaxation) mechanism under the local stress, more precisely the stress gradient, induced by the rapid heating and cooling of the welding cycle. The cracking is therefore directly related to the local creep ductility of the material.

Here again, the deleterious effect of impurity elements is far from being widely recognized. This is partly due to the variety of alloys and experimental conditions. In the majority of the published studies, it has been attempted to correlate the cracking behavior with the nominal impurity content in commercial steels whose compositions, microstructures and mechanical properties varied within the range of accepted standards and under test conditions whose reproducibility may not have been accurate enough, considering the severity of the welding or welding simulation test[8]. However such an effect of some impurities, in particular those associated with temper embrittlement, has unambiguously been demonstrated by Brear and King[13] for Mn-Mo-Ni pressure vessel steels (A 533-B).

They found that a high purity heat was not susceptible while the sensitivity of impurity-doped heats increased with addition of various impurities. In opposition to temper embrittlement, SRC appears rather more sensitive to Sb, Sn, As than to P; also- some sensitivity to Cu was observed which was not the the case with RTE[14].

Auger electron spectroscopy performed on the intergranular fracture urface of a 1/2 Cr—1/2 Mo — 1/4 V steel which had endured extensive cavitation during a stress relaxation test at 700 °C demonstrated that considerable segregation of Sn, Sb, B, N and Cu occured at the free surface of the cavities while that of P was negligible[15]. The observed segregations of Sn and Sb were in agreement with the free surface segregation measurements on pure iron[12, 16].

Recent work by Pope et al.[8] has provided further insight into the SRC behaviour of pressure



Slika 4

Zveza med krhkostjo zaradi žarenja za odpravo napetosti, merjeno pri 15 %-nem širjenju zareze (NOD) in nominalno sestavo jekla A533-B/A 508-2, (a). Če se spreminja količina Cr parameter nečistoč CERL ni zadosten za oceno krhkosti zaradi (SRC) (b). Če se v parameter vključi še količina Cr se dobi zelo dobra povezava (po ref. 8).

Fig. 4

Correlation between stress relief embrittlement (as measured in terms of notch opening displacement NOD for 15 % cracking) and nominal composition of A533-B/A508-2 steels (a). When the Cr content is varied, the CERL impurity parameter is insufficient to account for SRC behavior (b). When the Cr content is uncluded in the parameter an excellent correlation is obtained (after ref. 8).

tlakom. Potrdili so, da se občutljivost jekel A 508—C 1.3 in A 533—gr. B na pojav razpok pri žarjenju za odpravo napetosti (SRC) spreminja z vsebnostjo nečistoč skladno s parametrom sestave, ki so ga že poprej definirali drugi avtorji[13] ob upoštevanju vpliva legirnih elementov. V simuliranem ciklu varjenja je bil krom bolj škodljiv dodatek (sl. 4). To razloži, zakaj je jeklo A 508 — 3 (0,6 % Mn in 0,35 % Cr) bolj občutljivo na pojav razpok kot jeklo A 533 — B (1,4 % Mn in 0,11 % Cr). Škodljiv vpliv kroma pri žarjenju za odpravo napetosti je posledica utrjevanja trdne raztopine in zadrževanja poprave[8] zaradi ogljika, ki zavira gibanje dislokacij. Vpliv legirnih elementov, npr. kroma moramo skrbno ločiti od vpliva oligoelementov na pojav razpok pri žarjenju za odpravo napetosti, saj krom vpliva preko masnega efekta, oligoelementi pa s segregacijami na novo nastalih površinah por. Pospešeno segregiranje je pogojeno z difuzijo po mejah. Segregacije na mejah ferita s karbidi in na kristalnih mejah so prav tako pomembne za nukleacijo por.

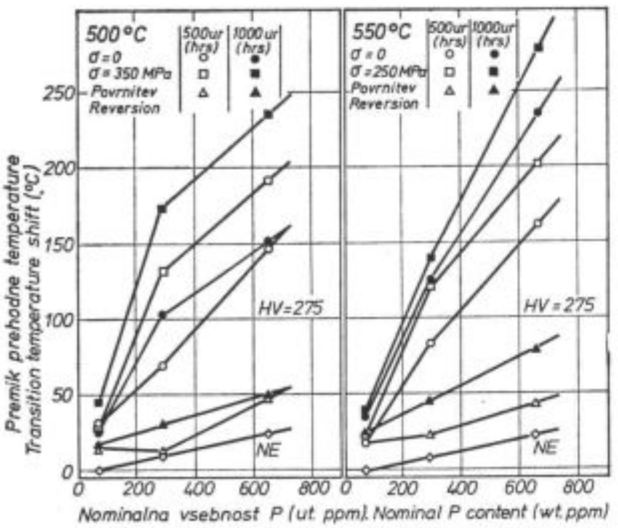
3. Popustna krhkost v pogojih lezenja in poprave

Vijaki parnih turbin so iz jekla odpornega proti lezenju (npr. 28 CDV 5—0,8, z 0,28 % C, 1,25 % Cr, 0,1 % Mo in 0,04 % V), ki je komaj podvrženo re-

vessel steels. They confirmed that the susceptibility of A 508-Cl. 3 and A 533-gr. B steels to SRC varies with impurity content according to the composition parameter defined by the previous authors,[13] provided that the effect of alloying elements is also taken into account. For the weld simulation cycle chosen, Cr was the more deleterious addition, fig. 4, which explains that A 508-3 (0.6 % Mn, 0.35 % Cr) is in general more susceptible than A 533-B (1.4 % Mn, 0.11 % Cr). This deleterious influence of Cr on SRC is essentially due to its strenghtening effect in solid solution which retards relaxation by interaction with carbon to impede dislocation motion[8]. The influence of alloying elements such as Cr and residual impurities on SRC must therefore be carefully distinguished, the former acting essentially via a bulk effect while the latter segregate to the surface of newly formed cavities. This very rapid segregation is certainly controlled by intergranular diffusion and is therefore accelerated when these impurities are segregated in the grain boundaries. Segregation at ferrite/carbide interfaces and grain boundaries is also important in that it controls cavity nucleation as already discussed above.

3. Temper embrittlement under creep or relaxation conditions

Steam turbine bolts are made of creep resistant steels (e. g. 28 CDV 5-08, i. e. 0.28 C — 1.25 Cr — 0.8 Mo — 0.4 V) which are hardly susceptible to reversible temper embrittlement[17]. However, these bolts may fracture intergranularly when cooling down after being refastened following a service period of several thousand hours. This phenomenon has been shown[17] to be a form of stress-enhanced temper brittleness: the embrittlement increases with applied stress and can become partly or totally irreversible, fig. 5, especially after ageing under stress at higher temperatures (e. g. 550 °C), the degree of irreversibility increasing with creep strain[17, 18], fig. 6. Intergranular failure results from the cumulative embrittling action of both the segregated impurities (P, Sn Sb) and creep cavities at the grain boundaries[18]. Irreversibility of embrittlement takes place when the latter is sufficient to promote intergranular decohesion at a smaller segregation level obtained after a given »de-embrittling« treatment (e. g. 650 °C, 1 h). This explains[18] that a threshold strain ε_t exists for the appearance of irreversibility, fig. 6. Below this value, the grain boundaries are not a preferred fracture path compared to cleavage in the »de-embrittled« condition (i. e. no irreversibility is observed), but in the embrittled condition where grain boundaries are already weakened by a larger segregation the embrittling effect of the same density cavities can take place because it only needs to add itself up to that of the impurities. This explains[18] that the enhancement of temper embrittlement by stress-induced cavitation is not necesverzibilni popustni krhkosti[17]. Ti deli se lahko porušijo z intergranularnim prelomom potem, ko se po nekaj tisoč urah dela ohlade. Ta pojav je oblika napetostne inducirane popustne krhkosti[17]. Krhkost narašča s prisotnimi napetostmi, postane pa lahko delno ali popolnoma ireverzibilna (sl. 5). V pogojih staranja pod obremenitvijo pri višjih temperaturah (npr. 550 °C) raste stopnja nepovračljivosti z deformacijo pri lezenju[17, 18] (sl. 6). Intergranularna porušitev je posledica skupnega vpliva na krhkost segregacij nečistoč (P, Sn, Sb) in tudi por, nastalih pri lezenju po kristalnih mejah[18]. Če število por preseže določeno množino, pride do ireverzibilne krhkosti tudi po ustreznih toplotnih obdelavah za odpravo krhkosti (npr. žarjenja 1h na 650 °C). To govori za to, da ireverzibilnost krhkosti nastopi potem, ko presežemo mejno deformacijo ε_t (sl. 6)[18]. Pod to deformacijo kristalne meje niso prednostna področja porušitve v primerjavi s cepljenjem v pogojih »nekrhkosti«. V pogojih krhkosti, kjer so meje zrn že oslabljene zaradi večjih segregacij, se lahko pojavi vpliv enake pogostosti por, saj se oba efekta seštevata. To kaže[18], da pospeševanje popustne krhkosti z napetostno inducirano poroznostjo ni nujno povezano z ireverzibilno krhkostjo, kot je to npr. po staranju

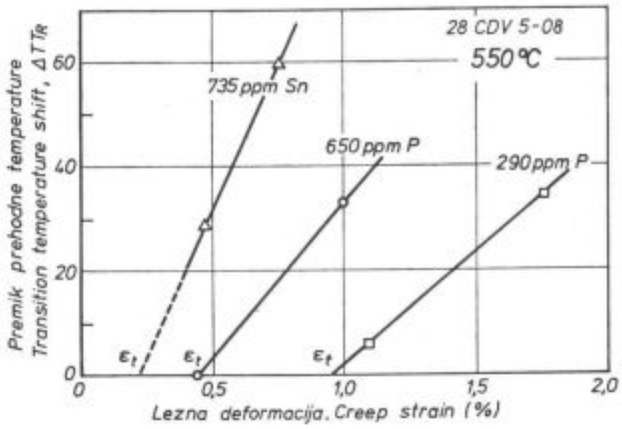


Slika 5

Vpliv napetosti na popustno krhkost. Razlike v prehodni temperaturi (ΔTT_X) po staranju brez (○●) ali pod vplivom napetosti (□■). Vidi se tudi preostala krhkost v »obrnjenih« pogojih (Δ) tj. potem, ko je bilo jeklo starano 1 h pri 650 °C in pod vplivom obremenitve. ΔTT_x je razlika v prehodni temperaturi jekla po določenem tretmanu (X) in »nekrhkim« zelo čistim jeklom, pri čemer so bile vse epruvete obdelane tako, da so imele enako trdoto (po ref. 18).

Fig. 5

Temper embrittlement under stress. Comparison of embrittlement ΔTT_X after ageing without (○●) and with (□■) an applied stress. The residual embrittlement in the »reverted« condition (Δ), i. e. tempered 1 h at 650 °C after embrittlement under stress, is also shown. ΔTT_X is the transition temperature shift between each condition X and the non-embrittled (NE) condition of the purest heat after correcting for constant hardness (after ref. 18).



Slika 6

Nepovračljivost popustne krhkosti zaradi staranja pod vplivom napetosti; ΔTT_R kot funkcija deformacije pri lezenju (ε); ΔTT_R je razlika med prehodno temperaturo v, obrnjenih pogojih in tisto za nekrhko najčistejše jeklo (po ref. 18).

Fig. 6

Irreversibility of temper embrittlement induced by ageing under stress. ΔTT_R, as a function of the creep strain ε. ΔTT_R is the difference between the transition temperature of the reverted condition and that of the NE condition of the purest heat (after ref. 18).

sarily accompanied by an irreversibilty of this embrittlement, as is the case e. g. after ageing under stress at 500 °C, fig. 5.

Temper embrittlement and cavitation-induced embrittlement are therefore not simply additive, especially if it is remembered that cavitation itself is strongly influenced by the segregating impurities. This phenomenon therefore provides us with a striking example of the co-operative and synergistic action of two different phenomena, involving interfacial segregation effects, on the impairment of mechanicial properties in service condition.

C. BEHAVIOR OF GRAIN BOUNDARIES IN AGGRESSIVE ENVIRONMENTS

1. Hydrogen-assisted cracking in temper brittle steels

It has been suspected for a long time that RTE and hydrogen-assisted cracking (HAC) must be connected or interact with each other. Cabral, and Constant[19] gave the first evidence for such an interrelation by showing that a temper embrittling treatment at 500 °C reduced the resistance of smooth specimens of a 0.3 C — 2.75 Ni — 0.7 Cr (30 NC 11) steel to HAC in H_2SO_4 solution and changed the fracture mode from transgranular to intergranular.

More recent work has taken advantage of the development of Auger Electron Spectroscopy and of fracture mechanics techniques. Systematic investigations on the behavior of several high pod obremenitvijo pri temperaturi 500 °C (sl. 5). Popustna krhkost in s porami inducirana krhkost zato nista enostavno aditivni, posebej če vemo, da na nastanek por močno vplivajo segregacije nečistoč. Ta fenomen je tipičen primer kooperativnega in poudarjenega delovanja dveh različnih pojavov na poslabšanje mehanskih lastnosti v delovnih pogojih.

C. OBNAŠANJE KRISTALNIH MEJ V AGRESIVNIH OKOLJIH

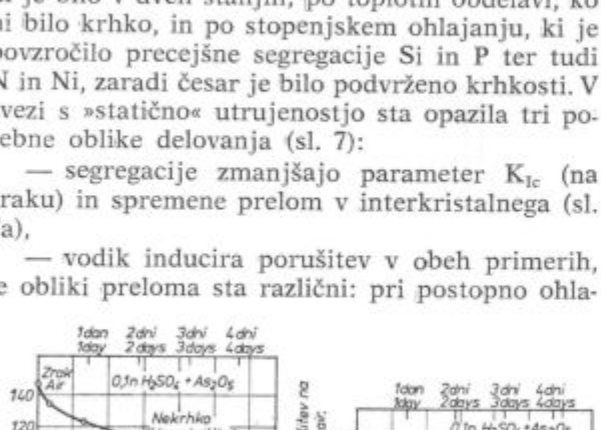
1. Vodikova krhkost

Že dlje časa je veljal sum, da sta reverzibilna popustna krhkost (RTE) in vodikova krhkost (HAC) povezani, ali pa da vplivata druga na drugo. Cabral, Hacke in Constant[19] so prvi dokazali to povezavo s poskusi na poliranih epruvetah jekla z 0,3 % C, 2,75 % Ni in 0,7 % Cr (30 NC11). Zaradi popustne krhkosti, nastale z žarjenjem pri 500 °C, se je zmanjšala tudi odpornost proti HAC (v raztopini H_2SO_4) in se je spremenil tudi mehanizem porušitve iz transkristalnega v interkristalnega.

Novejše raziskave izkoriščajo možnosti Augerjeve spektroskopije in lomne mehanike za sistematične raziskave visokotrdnih jekel v različnih medijih (npr. H_2SO_4, H_2S, vodiku ipd.). Joshino in Mc Mahon[20] sta primerjala poškodbe jekla HY 130, ki je bilo v dveh stanjih; po toplotni obdelavi, ko ni bilo krhko, in po stopenjskem ohlajanju, ki je povzročilo precejšne segregacije Si in P ter tudi N in Ni, zaradi česar je bilo podvrženo krhkosti. V zvezi s »statično« utrujenostjo sta opazila tri posebne oblike delovanja (sl. 7):

— segregacije zmanjšajo parameter K_{Ic} (na zraku) in spremene prelom v interkristalnega (sl. 7a),

— vodik inducira porušitev v obeh primerih, le obliki preloma sta različni: pri postopno ohla-



Slika 7

Vpliv predhodne toplotne obdelave na nastanek krhkosti jekla. Čas do porušitve v odvisnosti od razmerja začetnih faktorjev intenzivnosti napetosti K_{Ii}. Jeklo HY 130 je preizkušano v 0,1 n H_2SO_4 (po ref. 20) in na zraku.

Fig. 7

Influence of a prior temper embrittling treatment on time to failure plotten as a function of the initial stress intensity factor K_{Ii} for a HY 130 steel tested in 0,1 n H_2SO_4 (after ref. 20).

strength steels in various environments (H_2SO_4, H_2S, gaseous H_2 etc.) were undertaken. Yoshino and Mc Mahon[20] compared the delayed failure behaviors in a H_2SO_4 solution of a 5 Ni-Cr-Mo-V steel (HY 130) in unembrittled condition and after a step-cooling treatment which induces considerable segregations of Si and P but also of N and Ni. Three essential features can be seen on the static fatigue plots, fig. 7:

— segregation causes the toughness in air K_{Ic} to decrease and the fracture mode to become intergranular, as already mentioned, fig. 7-a;

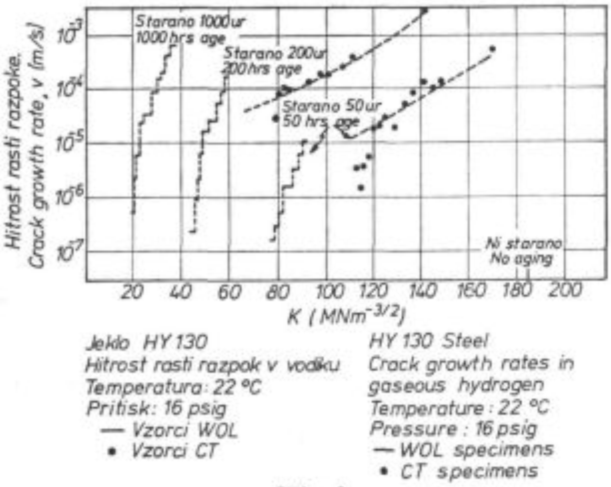
— hydrogen induces delayed fracture in both conditions but the failure modes are different: it is always intergranular decohesion in the step-cooled samples while it remains transgranular cleavage in the unembrittled condition at all failure times;

— the segregated (step-cooled) condition is much more sensitive to hydrogen than the unembrittled condition as shown by fig. 7-b where the initial K_{Ii} for failure at time t in H_2SO_4 have been normalized with respect to their value in air for each heat treatment. In unembrittled state, this ratio decreases slowly by 30 % in 100 h, while in the presence of segregation, it rapidly decreases by 60 % within the first hour of the test.

Briant, Mc Mahon and Feng[21] have measured the crack propagation velocities of the same steel in gaseous H_2 after varying the time of the segregation ageing at 480 °C. Fig. 8 shows that this rate increases drastically with ageing time at all values of the applied stress intensity K. Moreover, the threshold value of K, K_{TH}, i. e. that corresponding to the detectable crack growth rate of 10^{-7} m/s, was very high in non-embrittled condition ($\sim$ 185 MN m^{-2}) while HAC remained essentially transgranular. However, K_{TH} decreases catastrophically and intergranular decohesion appeared when the ageing time was increased. This behavior is illustrated in fig. 9, where it appears that very rapid initial decrease in K_{TH} is apparently associated with rapid although limited segregation of P while the later steady decrease is apparently associated with a larger but more steady increase in Si segregation. If the effect of both elements is additive, P is apparently much more harmful than Si with regard to the resistance to HAC, but the effect of each individual segregant is still far from bein accurately characterized.

Hydrogen is much more deleterious in high strength steels sensitive to one-step temper embrittlement (OSTE, cf Dumoulin, this Conference). This is in particular the case of 0.4 C — 1.75 Ni-Cr-Mo steels (4340) and of silicon-modified 4340 steels (300 M i. e. 4340 + 1.6 % Si) tempered at low temperatures[22]. In these steels, fracture is always intergranular in the presence of hydrogen, as it already is in a non-agressive medium, and the jenih epruvetah je prelom vedno interkristalen; v nasprotnem primeru pa ostaja značilna oblika transkristalnega cepljenja,

— jeklo s segregacijami nečistoč po kristalnih mejah (stopenjsko ohlajeno) je mnogo bolj občutljivo na porušitev ob prisotnosti vodika, kot jeklo brez segregacij. To ugotovitev ilustrira sl. 7b, kjer je prikazana odvisnost med razmerjem faktorjev koncentracije napetosti K_{Ii} za preizkušance v H_2SO_4 ter na zraku in časom do porušitve, in sicer za »krhko«, t.j. postopno ohlajeno in »nekrhko« jeklo.



Slika 8

Vpliv staranja pri 480 °C na hitrost razpokanja jekla HY 130 v vodiku (po ref. 21).

Fig. 8

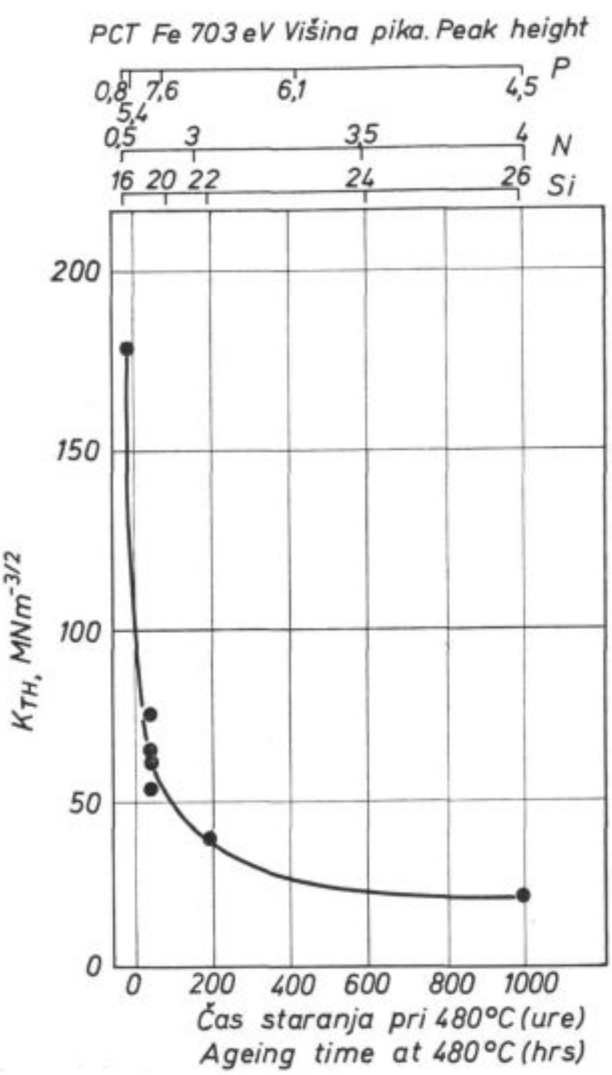
Influence of ageing at 480 °C on crack velocity of HY 130 steel in gaseous hydrogen (after ref. 21).

Briaut, Mc Mahon in Feng[21] so na vzorcih istega jekla, staranih pri temperaturi 480 °C, merili hitrosti napredovanja razpok v vodiku v odvisnosti od časa staranja. Sl. 8 kaže, da se hitrost rasti razpok povečuje zelo hitro s časom staranja, ne glede na vrednosti faktorja intenzivnosti napetosti K. Mejna vrednost faktorja K, K_{TH}, ki ustreza merljivi hitrosti napredovanja razpoke (10^{-7} m/s), je pri »nekrhkem« jeklu zelo velika (pribl. 185 MN m^{-2}). Porušitev zaradi vodika (HAC) je ostala v bistvu transkristalnega tipa, vendar se je K_{TH} s časom staranja izredno hitro zmanjševala ter se je pojavil interkristalni prelom. Ta pojav ilustrira sl. 9. Skokovitemu padcu faktorja intenzivnosti napetosti na začetku je kriv fosfor; nadaljnje, sicer počasnejše zmanjševanje pa je povezano z večjim, a stalnim porastom segregacij silicija. Če se vpliva obeh elementov glede HAC seštevata, je fosforjev očitno mnogo bolj škodljiv kot vpliv silicija.

Vodik je veliko bolj škodljiv v visokotrdnih jeklih, občutljivih na enostopenjsko popustno krhkost. To je posebno izrazito pri jeklih z 0,4 % C, 1,75 % Ni, Cr in Mo (4340) in v istih jeklih z dodatkom silicija (300 M tj. 4340 z 1,6 % Si), ki so bila popuščana pri nizkih temperaturah[22]. V teh effect of a temper embrittling treatment is much less conspicious. However in a high purity laboratory heat of 4340 steel, intergranular failure in H_2 disappears and the threshold K_{TH} value is five-fold that of a commercial heat of similar base composition[22], compare B 7 and B 2 in fig. 10. The threshold is again lowered by an addition of Mn + Si, as shown for heat B 6 in fig. 10.

As in the case of one-step temper embrittlement of the same steels, the effect of impurities (here Si) is evident even at the very low segregation levels produced by austenitizing treatment owing to very high strength levels and probably the presence of plate-like carbides in grain boundaries.

The behaviour of steels in the presence of hydrogen therefore reflects the characteristics of

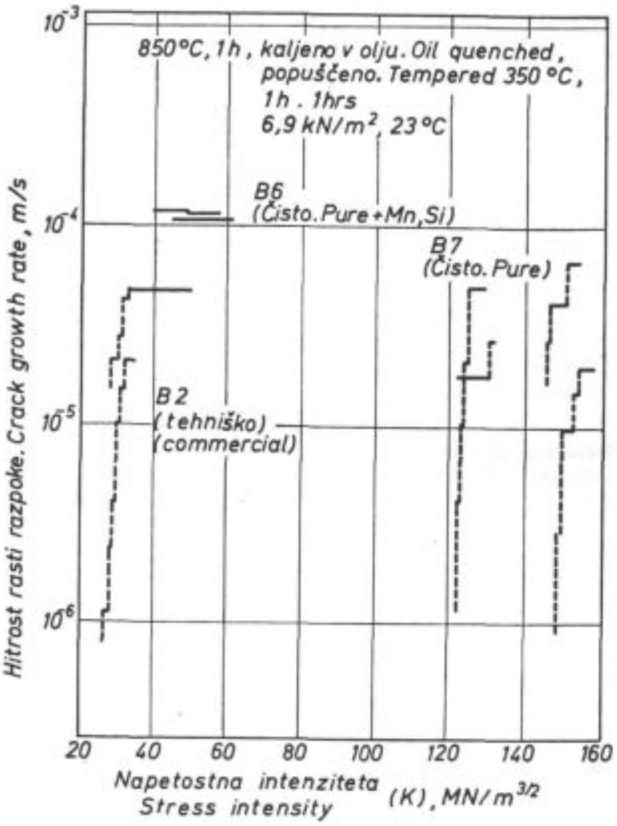


Slika 9

Vpliv časa staranja pri 480 °C in pridruženih segregacij na mejah zrn na prag koncentracije napetosti za širjenje razpok v vodiku (po ref. 21).

Fig. 9

Influence of ageing time at 480 °C and associated grain boundary segregations on the threshold stress intensity for crack propagation in gaseous hydrogen (after ref. 21).



Slika 10

Vpliv čistosti na hitrost širjenja razpok za jeklo 4340 v vodiku (po ref. 22).

Fig. 10

Influence of purity on crack velocity in 4340 steels tested in gaseous hydrogen (after ref. 22).

jeklih je ob prisotnosti vodika prelom vedno interkristalen, kot v neagresivnem okolju. V zelo čistih laboratorijskih talinah jekla 4340 v vodiku ni bilo več interkristalnega preloma, prag za faktor intenzivnosti napetosti pa je v primerjavi s tehničnimi talinami podobne osnovne sestave zrastel petkrat[22]. To kaže primerjava talin B7 in B2 na sl. 10. Prag se znova znižuje z dodatkom Mn in Si, kar pove primer taline B6 na sl. 10. Tako kot pri enostopenjski popustni krhkosti (OSTE) istega jekla se vpliv nečistoč (Si) kaže celo pri zelo nizkem nivoju segregacij, nastalih pri avstenitizaciji zaradi visoke trdnosti jekla ali različnih precipitatov na kristalnih mejah. Obnašanje jekel v prisotnosti vodika odraža najvažnejše značilnosti mehanizma povezave med krhkostjo in segregacijami. Pri visokotrdnih jeklih, popuščanih pri nizkih temperaturah, se to zelo dobro sklada z OSTE, saj se podedujejo manjše segregacije še od avstenitizacije. Enako velja za reverzibilno popustno krhkost (RTE) pri jeklih manjše trdnosti, ki so bila popuščana pri višjih temperaturah v področju α, kjer so nastale večje segregacije nečistoč.

Mehanizem tega povezanega delovanja vodika in nečistoč še ni povsem pojasnjen. O tem je znanih več različnih hipotez[20, 21, 23]:

their major embrittlement/segregation mechanisms: it is closely related to OSTE in very high strength steels tempered at low temperature and exhibiting only small segregations inherited from the austenitizing treatment, and to RTE in lower strength steels tempered at higher temperatures of the α-range where large segregation takes place. Several hypotheses can be proposed :

The mechanisms of these conjugate actions of hydrogen and impurities is not understood yet. Several hypotheses can be proposed:[20, 21, 23]

(i) Both effects could be purely additive. Hydrogen would equally embrittle all parts of the material, grain interior as well as grain boundaries, and the segregation would merely decrease the resistance of the boundary relative to that of the crystal.

(ii) Synergistic effects can also be involved. The segregated impurities could preferentially attract hydrogen to the grain boundaries and both segregants would impair boundary cohesion.

(iii) Another type synergistic effect could be that the presence of segregated elements acting as recombination poison for hydrogen would favor the hydrogen-assisted propagation of cracks along the boundaries which are moreover, already weakened by the segregations. However, this mechanism can be effective only in conditions of slow crack propagation which were not fulfilled in the above-quoted examples where propagation occurred in bursts as shown by the broken lines in figs. 8 and 10. However, it can be the case for example in long time delayed failure at low stresses or in fatique conditions under small ΔK as discussed below in chapter D.

It should be mentioned that in austenitic stainless steels phosphorus also segregates to the grain boundaries but it plays a secondary role in the hydrogen-assisted cracking of these materials[24]. It can only amplify the effect when other embrittling phenomena, such as the formation of martensite also occur at the grain boundaries.

2. Intergranular corrosion

It has been known for a long time that the electrochemical properties of grain boundaries are extremely sensitive to their composition.[25, 26]

a — The selective etching of grain boundaries by specific metallographic

reagents is the most classical example. In particular, picric-acid alcoholic, ethereal or aqueous solutions have long been known as able to differentiate between embrittled and non-embrittled (i. e. segregated and non-segregated) conditions of temper brittle steels[27], fig. 11. Incidentally, the improved selectivity of these etchants in the presence of specific additives (like »Zephiran chloride«) has repeatedly been attributed to the surfa-

a) Po prvi naj bi se oba vpliva seštevala. Zaradi vodika naj bi bila vsa kovina, tako na kristalnih mejah kot v notranjosti zrn enako krhka. Segregacije nečistoč samo zmanjšujejo odpornost mej v primerjavi s kristalnim zrnom.

b) Prav tako je lahko sprejemljiv efekt poudarjenega skupnega delovanja obeh pojavov. Zaradi segregacij nečistoč naj bi se tudi vodik koncentriral predvsem na kristalnih mejah in skupaj z nečistočami zmanjšal kohezijo na teh delih kovine.

c) Drug način poudarjenega skupnega delovanja naj bi povzročile segregacije nečistoč, ki neugodno vplivajo na pojav rekombinacije vodika iz atomarnega v molekularno obliko ter pospešujejo nastanek z vodikom induciranih razpok (HAC) vzdolž kristalnih mej, ki so že oslabljene zaradi segregacij.

Vendar ta mehanizem lahko deluje le pri počasni rasti razpok; razpoke pa so se v tem primeru širile skokovito, kot kažeta sl. 8 in 10. Lahko pa je ta pogoj izpolnjen pri dolgo trajajoči porušitvi pri nizkih napetostih ali pa pri pojavu utrujenosti, če je ΔK majhen (glej poglavje D).

V literaturi obstaja mnenje, da v nerjavnih avstenitnih jeklih fosfor, ki prav tako segregira na mejah kristalnih zrn, igra le drugotno vlogo v pojavu HAC[24]. Fosfor naj bi podkrepil ta pojav le, če so na kristalnih mejah prisotni mikrostrukturni elementi krhkosti, npr. martenzit.

2. Interkristalna korozija

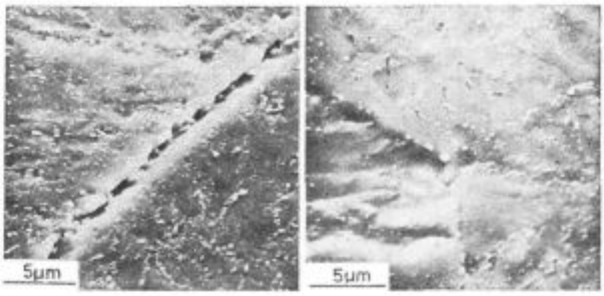
Že dolgo je znano, da so elektrokemične lastnosti kristalnih mej zelo odvisne od njihove kemične sestave[25, 26]:

a) *selektivno jedkanje kristalnih mej s posebnimi jedkali* je najbolj klasičen primer.

Raztopine pikrinske kisline v alkoholu, etru ali vodi so že dlje znane kot primerne za odkrivanje segregacij v jeklih s popustno krhkostjo[27] (sl. 11). Izboljšano selektivnost teh jedkal pripisujejo posebnim, površinsko aktivnim dodatkom (npr. zephir klorid); bolj verjetno pa je to posledica prostih ionov halogenov v raztopini, ki pospešujejo jedkanje tako, da porušijo pasivacijski film[28]. V prid temu govori enak vpliv minimalnih dodatkov solne kisline, ki prav tako olajšujejo odkrivanje kristalnih mej[27].

Z jedkanjem v vodni raztopini oksalne kisline in vodikovega peroksida je na podoben način mogoče odkriti segregacije žvepla v zelo čistem železu[29] (sl. 2).

b) *Interkristalna korozija železovih in nikljevih avstenitnih zlitin* je bolj zamotan in polemičen problem. Interkristalne korozije, ki jo pripisujemo nekaterim vrstam segregiranih nečistoč po kristalnih mejah, ni mogoče povezovati z osiromašenji kroma po določeni toplotni obdelavi in prav tako osiromašenje s kromom ne more biti vzrok koroziji, katere obseg se ne more enostavno povezati v kislih medijih z visoko oksidacijsko stopnjo, katerih značilen primer je vroča solitrna kisli-

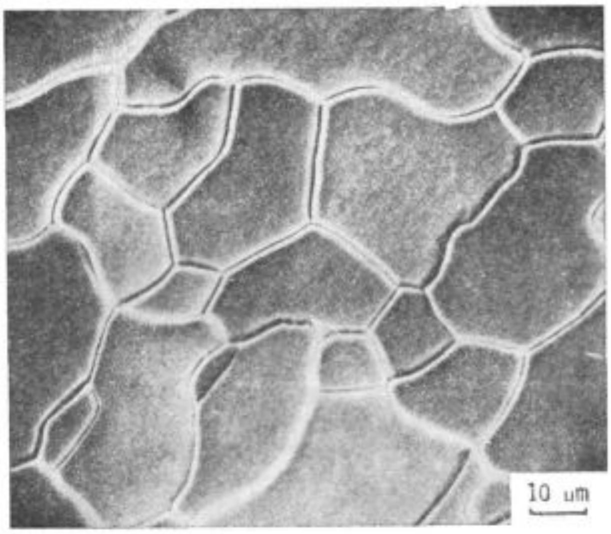


Slika 11

Vpliv popustne krhkosti 2 % Mn jekla z dodatki Sb na jedkanje v raztopini pikrinske kisline (po ref. 27).

Fig. 11

Influence of temper embrittlement on the etching behaviour of a 2 % Mn-Sb doped steel in picric acid solution (after ref. 27).



Slika 12

Jedkanje mej v zelo čistem železu v raztopini oksalne kisline in H_2O_2, povezano s segregacijami žvepla (po ref. 29).

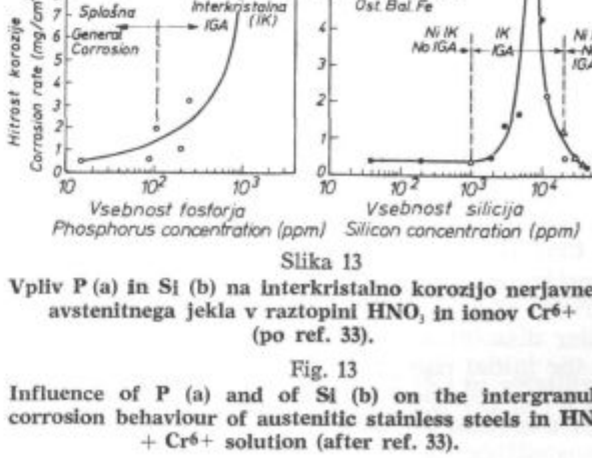
Fig. 12

Intergranular etching of high purity Fe in an oxalic acid + H_2O_2 solution, associated with sulfur segregation (after ref. 29).

ceactive (wetting) properties of the latter[27] but it is more likely due to the halogen ions they liberate into the solution which facilitate the onset of etching in beaking passive film by a pitting corrosion process[28]. This is substantiated by the fact that minute additions of HCl also amplify intergranular attack[28].

Similarly the segregation of sulfur in high purity iron can be revealed by chemical etching in oxalic acid-hydrogen peroxide aqueous solution[29], fig. 12.

b — The intergranular corrosion of austenitic iron-base (stainless steels) or nickel-base alloys is a much more complex and controversial problem. The intergranular corrosion phenomena



Slika 13

Vpliv P (a) in Si (b) na interkristalno korozijo nerjavnega avstenitnega jekla v raztopini HNO_3 in ionov Cr^{6+} (po ref. 33).

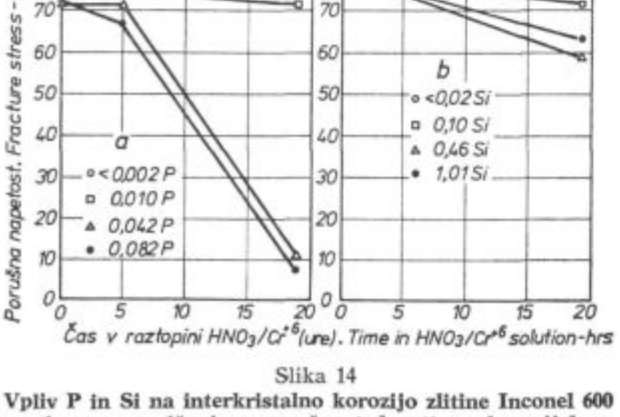
Fig. 13

Influence of P (a) and of Si (b) on the intergranular corrosion behaviour of austenitic stainless steels in HNO_3 + Cr^{6+} solution (after ref. 33).

na s kalijevim dikromatom (Cr^{6+}), je lahko izrazito omejena na kristalne meje celo pri zlitinah, ki so npr. gašene s temperature raztopnega žarjenja. Chaudron[32] je prvi dognal, da zelo čiste zlitine niso podvržene temu pojavu. Sistematične raziskave so pokazale, da je ta način korozije tesno povezan z vsebnostjo P in Si. Armijo[33] je ugotovil, da raste hitrost korozije avstenitnega jekla s koncentracijo fosforja, če le-ta preseže 100 ppm. Krivulja raste zaradi prednostnega raztapljanja jekla na kristalnih mejah (sl. 13a).

Podoben jasen maksimum je povezan s koncentracijo silicija (pribl. 1 %), pri čemer je maksimum posledica interkristalne korozije jekla[33] (sl. 13b).

Vermilyea in sodelavci[34] so ugotovili, da z nominalno koncentracijo fosforja raste hitrost interkristalne korozije v zlitini Inconel 600 (sl. 14a). Vpliv silicija na pojav interkristalne korozije je v tej zlitini mnogo manj pomemben. Stopnjo korozije



Slika 14

Vpliv P in Si na interkristalno korozijo zlitine Inconel 600 merjen z zmanjšanjem porušne trdnosti po korozijskem testu (po ref. 34).

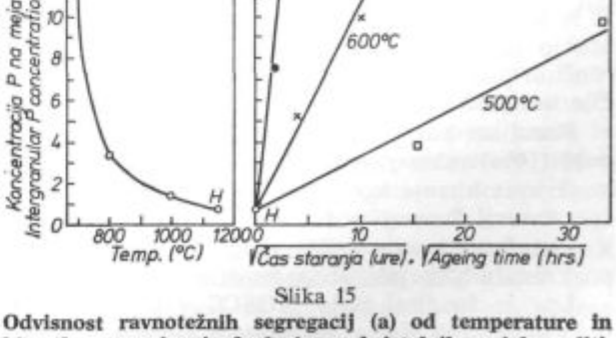
Fig. 14

Influence of P and Si on the intergranular corrosion of Inconel 600 as measured by the decrease in fracture strength after corrosion tests (after ref. 34).

which have been tentatively attributed to some kind of intergranular segregation are those which could not be associated with a Cr-depleted zone such as that induced by the so-called sensitization treatment or those whose magnitude did not correlate in a simple way with that of Cr-depletion.[31]

In particular, corrosion in highly oxidizing acid media such as boiling nitric acid containing potassium dichromate (Cr^{+6} ions) can be drastically localized at the grain boundaries even in unsensitized alloys (i. e. quenched from the solution temperature). Chaudron[32] first showed that a high purity alloy was not susceptible. Systematic research showed that this type of intergranular corrosion was very sensitive to the P an Si content. Armijo[33] demonstrated that the corrosion rate of an austenitic stainless steel increases steeply with phosphorus content above 100 wt. ppm this increase being associated with the onset of preferential intergranural dissolution, fig. 13-a. A marked maximum is also observed with respect to Si content around 1wt%, the peak region corresponding to intergranular corrosion[33], fig. 13-b. In the nickelbase alloy 600 Vermilyea et al[34]. showed that intergranular penetration measured as the decrease in fracture strength of a smooth specimen after the corrosion test also increases with nominal P content, fig. 14-a, but that the effect of Si is much less critical in this alloy, fig. 14-b.

Several studies have demonstrated that phosphorus actually segregates at the grain boundaries of austenitic stainless steels[24] and alloy 600[35, 36, 37]. In particular it has been shown that segregation in alloy 600 obeys the laws of equilibrium segregation,[37] fig. 15. It is therefore qualitatively similar in Ni-base alloys and in temper brittle steels, although it occurs at higher temperatures and with a higher enrichment ratio in the former alloy (~ 1000 at 700 °C), indicating that the segregation energy is larger. Another quantitative difference



Slika 15

Odvisnost ravnotežnih segregacij (a) od temperature in kinetike segregiranja fosforja na kristalnih mejah v zlitini Inconel 600 (po ref. 37).

Fig. 15

(a) Temperature dependence of equilibrium segregation and (b) segregation kinetics of P in the grain boundaries of alloy 600 (after ref. 37).

so ocenjevali iz zmanjšanja porušnih trdnosti poliranih epruvet po korozijskem preizkusu (sl. 14b). V različnih študijah je pokazano, da se kristalne meje avstenitnih jekel[24] in v Inconelu 600[35, 36, 37] obogate s fosforjem. Za zlitino Inconel 600 je ugotovljeno, da količina segregacij sledi zakonu o ravnotežnih segregacijah[37] (sl. 15). Podobno velja za druge nikljeve zlitine in popustno krhka jekla. Dejstvo, da se v Inconelu 600 to pojavlja pri višjih temperaturah in pri večjih obogatitvah (npr. obogatitev 1000× pri 700 °C), kaže da je energija segregiranja večja. Druge kvantitativne razlike pa so zato, ker je kinetika difuzije v ploskovno centrirani rešetki počasnejša kot v matici s prostorsko centrirano rešetko.

Analize s pomočjo Augerjeve spektroskopije dokazujejo torej interkristalen mehanizem korozije, kar je ilustrirano s sl. 14a.

c) *Elektrokemična korozija na kristalnih mejah.*

Pojav interkristalne korozije je lahko razložiti tudi s pomočjo elektrokemičnih poskusov. Korozijski potencial raztopine kromovih (Cr^{6+}) ionov v solitrni kislini ustreza t.i. transpasivacijskemu področju, in kot je opisano v referenci[38], je precejšnje število zlitin, pri katerih pride do prednostnega interkristalnega korozijskega napada, brž ko potencial raztopine seže do začetka transpasivacijskega vrha. Raztopina solitrne kisline in kromovih (Cr^{6+}) ionov ni specifična za s kromom osiromašena področja, saj v transpasivacijskem področju pada kar je popolnoma nasprotno obnašanju v aktivacijskem in pasivacijskem področju. Mnogo avtorjev meni, da je prednostna korozija po kristalnih mejah v tej raztopini jasen znak segregacij po kristalnih mejah[30, 39].

3. Interkristalna napetostna korozija (IGSCC)

V nekaterih posebnih primerih je lahko nedvoumno pokazati škodljiv vpliv segregacij nečistoč na odpornost proti interkristalni napetostni koroziji (IGSCC). Tak primer je zlitina železa s 3 % niklja in z dodatki P in Sn[40], ki je bila preizkušana v 5-molarni raztopini NaOH in obremenjena do 90 % meje tečenja. Za primerjavo s popustno krhkostjo je bila dolžina razpok primerjana v referenčnih pogojih in pogojih, ko so nastale segregacije nečistoč zaradi staranja po 11^h pri 550 °C.

Rezultati kažejo, da po določeni inkubacijski dobi (10^5 s) raste razpoka v starani zlitini približno 3 krat hitreje kot v primerjalnih vzorcih (sl. 16). Avtorji [40] menijo, da ima ta pojav svoj vzrok v pospeševanju anodnega raztapljanja materiala po kristalnih mejah, obogatenih z nečistočami.

Lea je študiral pojav IGSCC v Cr-Mo jeklih (2,25 % Cr, 1 % Mo) v raztopinah amonijevega nitrata[41]. Primerjali so razmerje R ($R = K_{min}/K_{max}$) med povprečnim časom do porušitve v korozijskem mediju in inertni sredini (vroč parafin) za jekla z različno koncentracijo P. Primerjali so rezultate talin, v katerih so bile segregacije fosforja

is that the diffusion kinetics is slower in the f.c.c. than in the b.c.c. matrix.

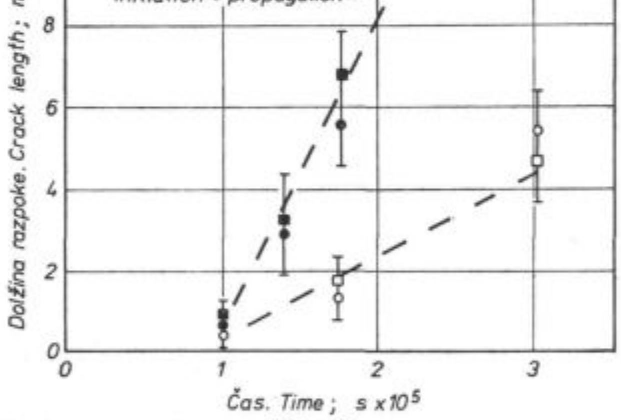
The Auger results therefore substantiate the intergranular corrosion behaviour illustrated by fig. 14-a.

c — Electrochemical corrosion of grain boundaries

The intergranular corrosion results can be interpreted in the light of electrochemical experiments. The corrosion potential of nitric acid $+ Cr^{6+}$ solution is actually situated in the transpassive region, and it has been shown[38] that a variety of alloys exhibited preferential intergranular dissolution when the potential was chosen in the initial rise of the transpassive peak. It can be understood now that the $HNO_3 + Cr^{6+}$ solution is not specific to Cr-depleted zones because in the transpassive region the corrosion rate **decreases** with decreasing Cr content, in opposition to the well known behaviour in the active and passive regions. Many authors now agree that preferential attack of the grain boundaries in this solution is essentially indicative of intergranular segregation[30, 39].

3. Intergranular stress corrosion cracking (IGSCC)

In some cases deleterious effect of a segregated impurity on resistance to IGSCC can be unambiguously demonstrated. This is the case[40] of a Fe-3 % Ni alloy doped with P and Sn and tested in 5 m NaOH under a stress equal to 90 % of its yield strength. In reference to temper embrittlement, the crack lengths were compared in a reference condition and in a segregated condition

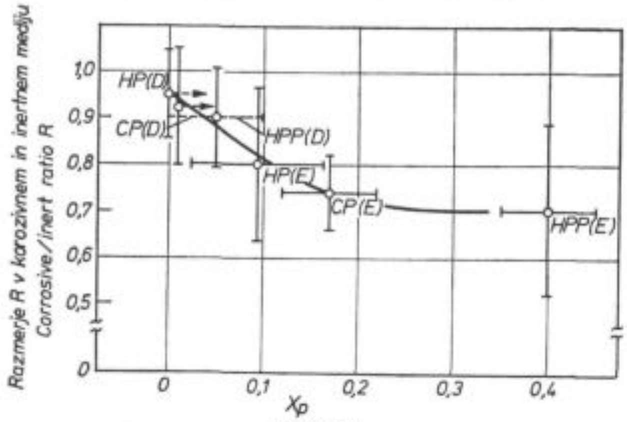


Slika 16

Vpliv popustne krhkosti na dolžino razpok vsled napetostne korozije v zlitini Fe — 3 % Ni v NaOH (po ref. 40).

Fig. 16

Influence of temper embrittlement on the length of stress corrosion cracks in Fe — 3 % Ni tested in 5 M NaOH (after ref. 40).



Slika 17

Vpliv količine P na kristalnih mejah (X_p) na občutljivost za napetostno korozijo (SCC) jekla z 2,25 % Cr in 1 % Mo. (CP) — tehniško jeklo, (HP) — zelo čisto jeklo, HPP = HP zelo čisto jeklo z dodatki P (po ref. 41).

Fig. 17

Influence of P content at the grain boundaries X_p on the SCC susceptibility of 2 1/4 Cr-1 Mo steel. CP: commercial purity heat; HP: high purity heat; HPP = HP doped with P (after ref. 41).

na kristalnih mejah, in tiste, kjer tega pojava ni bilo (sl. 17). Ta slika pove, da se nevarnost porušitve zaradi napetostne korozije povečuje s koncentracijo fosforja na kristalnih mejah do približno 20 % P in da je nevarnost napetostne korozije že pri segregacijah, ko je približno 5 % P v mejnem sloju.

Z dodatkom lantana, ki veže fosfor v matici, se lahko znatno izboljša odpornost proti napetostni koroziji.

4. Krhkost zaradi staljenih kovin (LME)

Podobno vodikovi krhkosti lahko povzroči LME transkristalen ali interkristalen prelom. Ta vrsta krhkosti je vendarle bolj poudarjena na kristalnih mejah, kar je tudi posledica kemične sestave tega dela kovine. Dinda in Warke[42] sta ugotovila, da kositer in antimon povečujeta LME jekel 3340 (3,5 % Ni, 1,7 % Cr) v talinah svinca in kositra. Nasproten vpliv ima fosfor, ki naj bi očitno povečal odpornost proti LME v talinah teh dveh kovin.

D. UTRUJENOST

V martenzitnih jeklih, ki so bila podvržena popustni krhkosti, je bil tudi ugotovljen vpliv segregacij nečistoč na pojav utrujenosti. Pri napredovanju utrujenostne razpoke so bile ugotovljene tri značilnosti[43] (sl. 18), ki jih lahko označimo kot parametre mikrostrukture. Pri majhnih hitrostih rasti razpoke (režim A) in ko sprememba faktorja koncentracije napetosti ΔK doseže svojo mejno vrednost ΔK_o, je zelo velik vpliv mikrostrukture in povprečne napetosti na hitrost rasti razpok. Na to vpliva tudi predhodno spreminjanje napetosti in okolica. Pri večjih hitrostih napredovanja razpok (režim C), ko vrednost K_{max} doseže K_{Ic}, sta vpliva mikrostrukture kovine in povprečnih napetosti

obtained by ageing 11 h at 550 °C. The results indicate, fig. 16, that after the same incubation period of 10^5 s, the crack growth rate in aged (segregated) specimens were increased by a factor of 3 with respect to that in reference samples. The authors suggested[40] that this effect was actually due to the acceleration of anodic reaction of dissolution of the grain boundary material by segregated impurities.

Lea has studied the IGSCC behaviour of 2 1/4 Cr-1 Mo steels in ammonium nitrate solution[41]. The ratios R of the average times to failure in the corrosive solution and in an inert medium (hot paraffin) were compared for heats of various P content in both the embrittled E (step-cooled) and de-embrittled D (quenched from 700 °C) conditions, fig. 17. This figure shows that SCC properties deteriorate with increasing phosphorus grain boundary level up to about 20 % and that SCC susceptibility is affected even at very low P segregation levels (5 % monolayer). An addition of La which ties up P in the matrix produces a marked improvement in SCC properties.

C 4. Liquid metal embrittlement (LME)

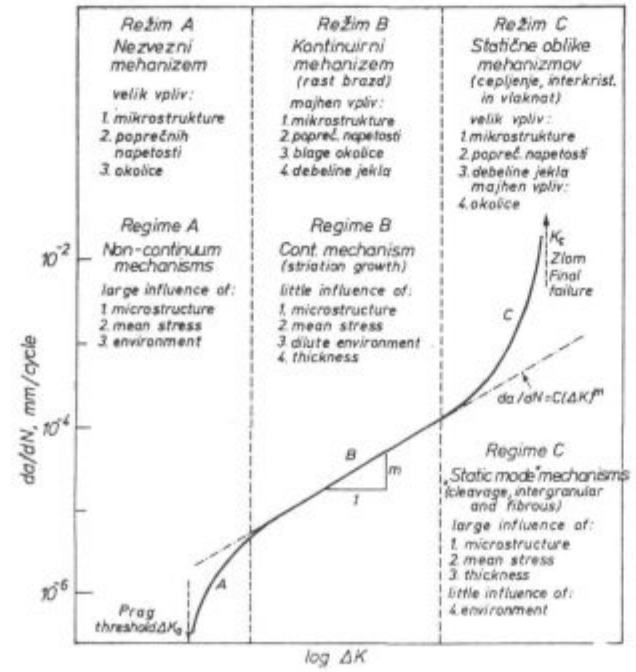
Like hydroden-induced cracking LME can be either intergranular or transgranular. However it is often more severe at grain boundaries and here again an influence of grain boundary composition can be expected.

Dinda and Warke[42] have observed that the segregation of Sn and Sb enhanced the susceptibility of temper embrittled 3.5 Ni — 1.7 Cr steels (3340) to LME by Pb or Sn. However, a reverse effect was noted for P which apparently improves the resistance to LME in these two environments.

D. FATIGUE

It is again in martensitic steels susceptible to reversible temper embrittlement that the effect of segregated impurities on fatigue properties has been clearly established.

In the fatigue crack propagation curve, three ranges of behaviours should be distinguished[43], fig. 18, in relation to the effects of what could be called the »microstructural« parameters which include intergranular segregation, on primary fracture mechanisms. At low growth rates (regime A) when the alternating stress intensity ΔK approaches its threshold value ΔK_o there is a strong influence of microstructure and mean stress (characterized by the load ratio $R = K_{min}/K_{max}$) on growth rates, together with an increased sensitivity to stress history and environmental effects. At higher growth rates, (regime C), when K_{max} approaches K_{Ic} the influence of microstructure and mean stress is also prominent. Only in the



Slika 18

Osnovni mehanizmi porušitve v povezavi s tremi področji na krivulji spreminjanja hitrosti rasti utrujenostne razpoke (da/dN) s koncentracijo napetosti (ΔK) (po ref. 43).

Fig. 18

Primary fracture mechanisms associated with the three regions in the sigmoidal variation of fatigue crack propagation rate (da/dN) with alternating stress intensity (ΔK) (after ref. 43).

prav tako odločilna. Le pri vmesnih hitrostih napredovanja razpoke (režim B), kjer v splošnem velja Parisov zakon, sta vpliva povprečnih napetosti in mikrostrukture manjša.

Ritchie[43] je primerjal širjenje razpoke v jeklu 4340 z dodatkom silicija (300 M). Za poskuse, ki jih je opravil na vlažnem zraku, je izbral v olju ohlajene (s 650 °C) in popustne (postopno ohlajene) preizkušance, ki so imeli bistveno večje segregacije P in Si na kristalnih mejah.

a) **Pri srednjih hitrostih rasti razpoke** (10^{-3} mm/nihaj > da/dN > 10^{-5} mm/nihaj) (sl. 19) so bile za prelom po obeh toplotnih obdelavah značilne brazde (»letnice«), ki so nastale s transkristalnim širjenjem razpoke.

Hitrost rasti razpoke ne kaže posebne odvisnosti od segregacij in sprememb obremenitvenega razmerja R.

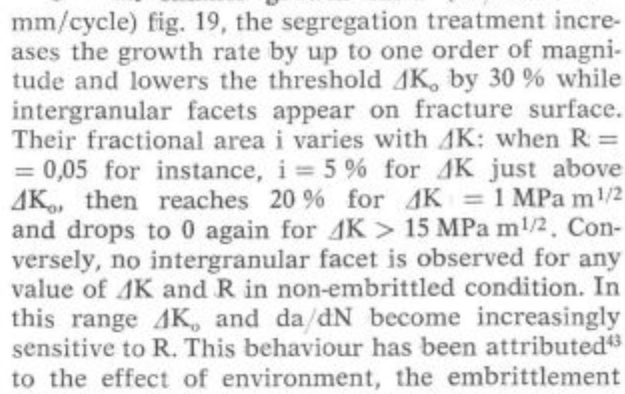
b) **Pri manjših hitrostih rasti razpoke** (da/dN < 10^{-5} mm/nihaj) (sl. 19) se s segregacijami nečistoč povečuje hitrost rasti razpoke celo za velikostni red. Sočasno pa se znižuje prag ΔK_o za približno 30 % in se na prelomu pojavijo interkristalna področja. Delež teh področij na prelomljeni površini i se spreminja z ΔK; npr pri R = 0.05 je i = 5 %, ko je ΔK tik nad ΔK_o; pri ΔK = 10 MPa $m^{1/2}$ doseže i = 20 % in izgine pri ΔK = 15 MPa $m^{1/2}$. Nasprotno pa pri jeklu, ohlajenem v olju, ni bilo interkristalnih prelomnih površin, ne glede na velikost ΔK in R.

midrange of growth rates (regime B), where Paris' law is in general obeyed is there a little influence of mean stress and microstructure.

Ritchie[43] has compared the crack propagation behavior in humid air of a Si-modified 4340 steel (300 M) in two quenched and tempered conditions the so-colled non-embrittled condition (oil quenched from 650 °C) and embrittled condition (step-cooled from 650 °C), which differ essentially by a high segregation level of P and Si in grain boundaries of the latter.

a — **In the intermediate range of growth rates** (10^{-3} mm/cycle > da/dN > 10^{-5} mm/cycle) fig. 19, the failure mode remains transgranular striation in both conditions and the growth rates are not very much affected by the segregation treatment and variations of the load ratio R.

b — **At smaller growth rates** (da/dN < 10^{-5} mm/cycle) fig. 19, the segregation treatment increases the growth rate by up to one order of magnitude and lowers the threshold ΔK_o by 30 % while intergranular facets appear on fracture surface. Their fractional area i varies with ΔK: when R = = 0,05 for instance, i = 5 % for ΔK just above ΔK_o, then reaches 20 % for ΔK = 1 MPa $m^{1/2}$ and drops to 0 again for ΔK > 15 MPa $m^{1/2}$. Conversely, no intergranular facet is observed for any value of ΔK and R in non-embrittled condition. In this range ΔK_o and da/dN become increasingly sensitive to R. This behaviour has been attributed[43] to the effect of environment, the embrittlement in fatigue conditions being attributed to the adsorption of hydrogen at the crack tip. Segregated impurities would play the role of recombination poison for H into gaseous H_2 there, favoring the propagation of crack along grain boundaries. At higher growth rates those processes would not have eno-



Slika 19

Vpliv popustne krhkosti na širjenje utrujenostne razpoke v jeklu 300 M na zraku, v okolici praga ΔK (po ref. 45).

Fig. 19

Influence of temper embrittlement on fatigue crack propagation for 300-M steel tested in air, in the vicinity of the threshold region (after ref. 45).

V tem področju postaneta ΔK_0 in da/dN zelo odvisna od razmerja R. To pripisujejo[43] vplivom okolice. Krhkost pri utrujanju je posledica adsorbcije vodika na čelu razpoke. Segregacija nečistoč naj bi vplivala na prehod vodika iz atomarnega v molekularno stanje in pospeševale širjenje razpok vzdolž kristalnih mej. Pri večjih hitrostih širjenja razpok ta proces ne more dovolj hitro slediti napredovanju razpoke. Zato prevladuje transkristalno širjenje razpoke v stopnjah.

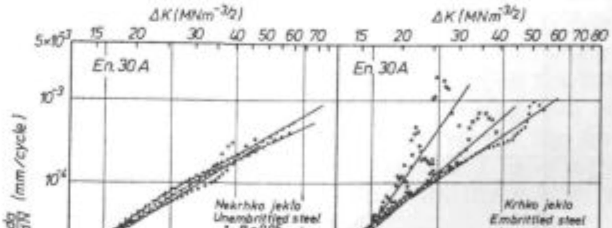
c) **Področje večjih hitrosti rasti razpok** sta na primeru jekla s 4 % niklja (En 30 A) raziskovala Ritchie in Knott[44]. To jeklo ima manjšo natezno trdnost od jekla 4340. Hitrost rasti razpoke 10^{-4} mm/nihaj lahko še štejemo v to skupino (sl. 20). V jeklu, ki je toplotno obdelano tako, da ni krhko zaradi segregacij, je hitrost napredovanja razpoke (da/dN) neodvisna od R; pa tudi Parisovemu zakonu je zadoščeno tako, da se eksponent m spreminja samo med 2 in 3,4, ko R raste od 0,05 do 0,60. Pri manjših hitrostih rasti razpoke je le malo interkristalnih prelomnih površin. Po toplotni obdelavi, ki naj bi povzročila krhkost jekla (8^h pri temp. 540 °C), se hitrost rasti razpoke poveča za velikostni razred, eksponent m pa podvoji od 2,7 na 5,8, ko R naraste od 0,05 do 0,6. Istočasno so se na prelomu med brazdami pojavila tudi področja interkristalnega preloma. Pri teh večjih vrednostih ΔK se K_{max} približuje K_{Ic}. Takrat lahko prevlada način širjenja razpoke, ki ga avtorja označujeta s t.i. statično obliko, oz. načinom: to so oblike zelo hitrega širjenja razpoke, kot cepljenje, interkristalni ali vlaknati prelom, ki obsegajo posamezna zrna ali skupine zrn med področji postopne (brazdaste) rasti razpoke. Segregacije po mejah izrazito favorizirajo interkristalno dekohezijo, posebej če ΔK in R naraščata, t.j. v pogojih, ko se K_{max} bliža K_{Ic}, ki se verjetno zaradi segregacij lokalno zmanjša. Deležu tako nastalega preloma med sicer značilno utrujenostno prelomno površino (brazde) je pripisati velik raztros rezultatov kinetike rasti razpok pri krhkih preizkušancih (sl. 20).

Pineau in Castagné[45] sta dobila podobne rezultate pri martenzitnem jeklu z 12 % kroma, v katerem so bile nedvoumno ugotovljene[46] segregacije nečistoč (posebej fosforja) in popustna krhkost. Študirala sta tudi zelo podrobno povezavo med interkristalno dekohezijo in utrujenostjo pri večjih hitrostih napredovanja razpoke. Razen porasta hitrosti širjenja razpoke (da/dN) z razmerjem R v pogojih krhkosti (po staranju 1^h pri 540 °C (sl. 21) sta opazila, da je pri 120 °C širjenje razpoke počasnejše kot pri temperaturi okolice (sobni temperaturi) in neodvisno od velikosti R. Istočasno izgine tudi pojav integranularne dekohezije, kar je tipičen primer prehodne temperature in analogen tistemu, ki ga srečujemo pri krhkem prelomu.

ugh time to take place at the advancing crack tip and a transgranular striation mechanism would be preferred.

c — **The range of higher growth rates** has been studied by Ritchie and Knott in a 4 Ni steel (En 30A)[44]. For this material exhibiting somewhat smaller tensile strength than the former a growth rate of 10^{-4} mm/cycle can already be considered as a large one, fig. 20. In non-embrittled condition da/dN is independent of R and Paris' law is obeyed with an exponent m varying only between 2 and 3.4 as R is varied between 0.05 and 0.60. A minority of intergranular facets are observed in the lower range of growth rates. In the embrittled condition (obtained by ageing the former during 8 hours at 540 °C) da/dN increases by an order of magnitude and m doubles, from 2.7 to 5.8, as R is increased from 0.05 to 0.60 while brittle intergranular facets appear on the fatigue fracture surface between areas of striation growth. At these larger values of ΔK, K_{max} approaches K_{Ic}, and what the authors have called the »static modes« of propagation can become predominant: these are in effect rapid propagation modes, such as cleavage, intergranular or fibrous fracture, involving at least a whole grain and more often a number of grains between areas of striation growth. Grain boundary segregation obviously favors the occurence of one of these modes, intergranular decohesion, as ΔK and R increase, i. e. in conditions where K_{max} approaches K_{Ic} most likely because locally K_{Ic} is decreased by these segregations. Due to its local character among the general striated fracture surface this static mode is responsible for the increasing dispersion observed on the growth curves of embrittled condition, fig. 20.

Pineau and Castagné[45] have obtained similar results with a 12 % Cr martensitic steel in which the segregation (essentially of phosphorus) and temper embrittlement behaviours had been thoroughly characterized[46].

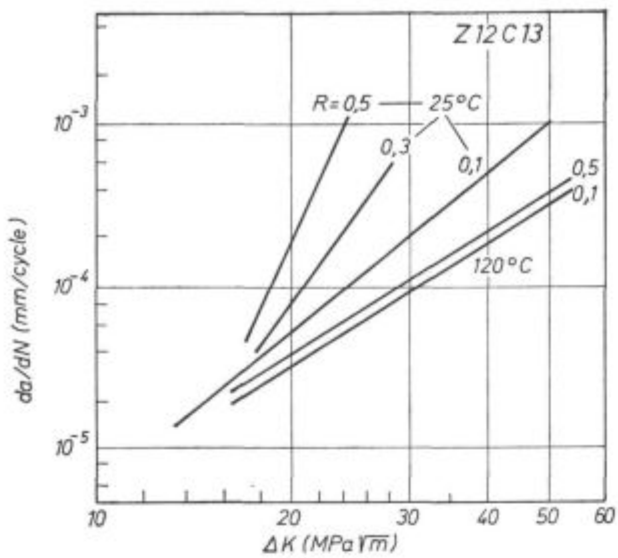


Slika 20

Vpliv popustne krhkosti na širjenje utrujenostne razpoke v jeklu En 30-A pri velikih vrednostih ΔK (po ref. 44).

Fig. 20

Influence of temper embrittlement on fatigue crack propagation of En 30-A steel at high values of ΔK (after ref. 44).



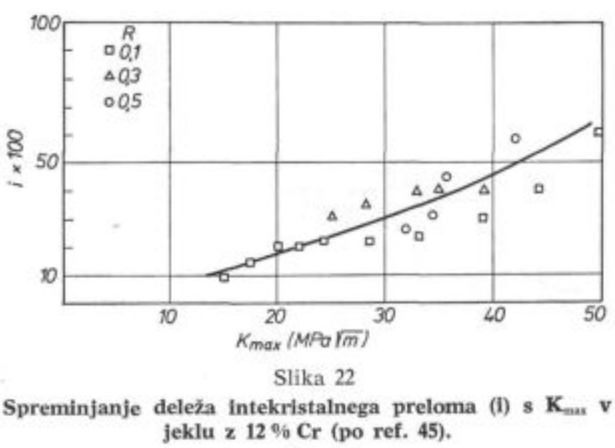
Slika 21

Vpliv temperature preizkušanja in razmerja $R = K_{min}/K_{max}$ na hitrost širjenja razpoke v krhkem martenzitnem jeklu z 12 % Cr (po ref. 45).

Fig. 21

Influence of test temperature and of $R = K_{min}/K_{max}$ on crack propagation rate of embrittled 12 % Cr martensitic steel (after ref. 45).

Delež interkristalno prelomljene površine (i) raste z ΔK in R; mnogo bolj zanimiva ugotovitev pa je, da je i približno funkcija K_{max}, torej neodvisen od R (sl. 22). To potrjuje, da je interkristalni prelom statičen, z natezno napetostjo kontrolirana oblika širjenja razpoke, ki se enostavno superponira k postopnemu transkristalnemu širjenju razpoke (z brazdami). Pri 25 °C velja zatorej enostavna povezava med deležem interkristalnega preloma (i) in hitrostjo širjenja razpoke (da/dN) (sl. 23). Na tej sliki je hitrost širjenja razpoke pri 25 °C, izražena v primeru s hitrostjo pri 120 °C, ki je privzeta za referenčno stanje za pogoje krhkosti in pri kateri se razpoka širi pretežno transkristalno in neodvisno od R.



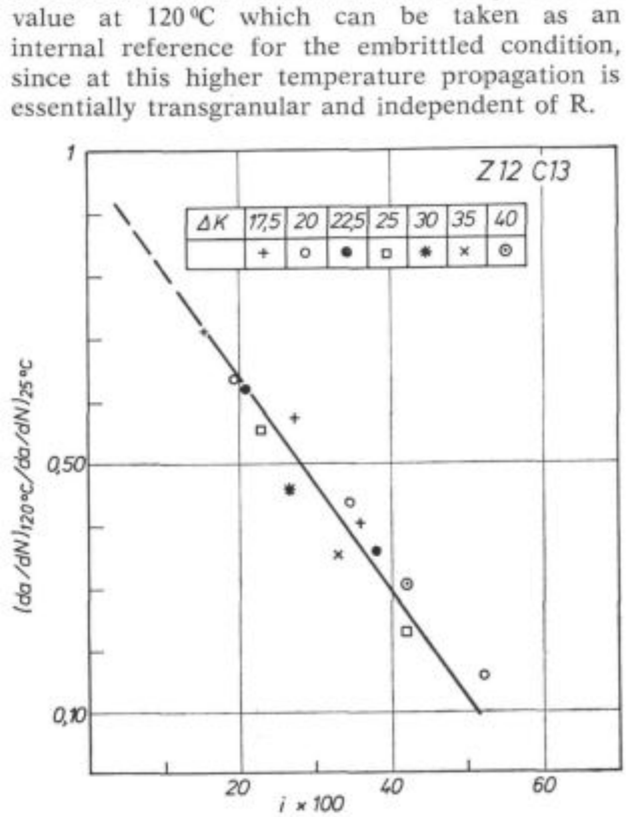
Slika 22

Spreminjanje deleža intekristalnega preloma (i) s K_{max} v jeklu z 12 % Cr (po ref. 45).

Fig. 22

Variation of the percentage of intergranular decohesion i with K_{max} in a 12 % Cr steel (after ref. 45).

They have studied in further details the relationships between intergranular decohesion and fatigue growth in this range of higher growth rates. Besides the increase of da/dN with R in embrittled (1 h at 540 °C) condition, fig. 21, they notice that at 120° C the crack growth rate is lower than at room temperature and insensitive to the value of R while intergranular decohesion disappears: this is typically a transition temperature effect analogous and akin to that encountered with brittle failure. The fractional area i of intergranular decohesion increases with ΔK and R, but the more interesting result is that it is approximately a unique function of K_{max} and independent of R values, fig. 22. This confirms that intergranular fracture here is a tensile stress-controlled static mode of propagation which is simply superposed to the transgranular striation mode. Therefore there exist a unique relationship between i and da/dN at 25 °C, fig. 23. On this figure, da/dN at 25 °C has been normalized with respect to its value at 120 °C which can be taken as an internal reference for the embrittled condition, since at this higher temperature propagation is essentially transgranular and independent of R.



Slika 23

Zveza med »normalizirano« hitrostjo rasti razpoke pri sobni temperaturi in deležem interkristalnega preloma v v jeklu z 12 % Cr (po ref. 45).

Fig. 23

Correlation between normalized crack propagation rate at room temperature and fraction of intergranular decohesion in a 12 % Cr steel (after ref. 45).

Summarizing, reversible temper embrittlement, i. e. the intergranular segregation of impurities in martensitic steels promotes preferential crack

Segregacije nečistoč na mejah kristalnih zrn martenzitnih jekel pospešujejo prednostno rast razpok vzdolž kristalnih mej pri zelo majhnih, kot tudi pri velikih hitrostih širjenja razpoke, toda iz povsem različnih vzrokov:

— pri večjih vrednostih ΔK, t.j. pri večjih K_{max} je statični tip krhkosti zelo soroden navadni popustni krhkosti,

— v okolici praga za ΔK_o je vpliv okolice soroden krhkosti, ki je posledica interakcije vodika in segregacij (HAC).

Primeri utrujenosti zgovorno ilustrirajo različne kombinacije škodljivih vplivov s segregacijo nečistoč na uporabne lastnosti gradiv.

F. ZAKLJUČKI

V tem preglednem članku je pokazano, da lahko v tehnološko pomembnih železovih zlitinah segregira na kristalnih mejah precejšnje število nečistoč, kar močno vpliva na njihove lastnosti. Le v malo primerih je bil ugotovljen ugoden vpliv teh nečistoč.

S primerom, ki ga označujemo z reverzibilno popustno krhkostjo jekla, je pokazano, kako je na ta ali drugačen način možno vplivati na normalne lastnosti jekla. Razen empiričnih podatkov je zelo malo znanega o mehanizmih medsebojnega delovanja segregacij in drugih vrst poškodb na kristalnih mejah. V večini primerov ni jasno niti to, ali se njihovi vplivi enostavno seštevajo ali pa drug drugega izrazito poudarjajo. Popolnoma jasno je tudi, da na to vprašanje ni splošnega odgovora. Znano je, da se vpliv različnih vrst nečistoč v različnih jeklih različno odraža, saj so tudi posamezne lastnosti na specifičen način odvisne od mikrostrukture kovine.

Znani primeri kažejo, da se isti efekti pokažejo v različnih materialih. Avtorjevo mnenje je, da spektakularen razvoj metod in naprav za površinsko analizo ne bo le širil seznama škodljivih pojavov zaradi primesi, ampak bo pomagal odkriti tudi primere sestavljenih (»množičnih«) segregacij in posebej še tiste legirne elemente, katerih prisotnost koristno vpliva na uporabne lastnosti kovin.

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growth along grain boundaries at both ends of the range of growth rates and alternating stress intensities, but for entirely diferent reasons:

— at larger ΔK, i.e. at larger K_{max} a static type of brittleness closely akin to plain temper embrittlement is involved;

— in the vicinity of the threshold ΔK_o it would rather be an environment-controlled effect more akin to segregation-enhanced hydrogen embrittlement.

The example of fatigue strikingly illustrates the variety of combinations of harmful effects by which impurity segregation can affect a given engineering property.

E. CONCLUSION

Although selective this review has shown that a wide variety of elements can segregate in grain boundaries of iron-base alloys of current technological interest and severely affect their properties. Only in a minority of cases have beneficial effects been observed. The example of what has been called reversible temper embrittlement of steels has revealed itself particularly instructive since we have been able to show throughout this paper that **all** their usual properties are critically affected in one or another way. However, besides the empirical evidence available very little is known on the mechanisms of interaction between segregations and other types of damage of grain boundaries: it is not even clear yet in most cases whether these effects are additive or synergistic. It is quite certain that there is no universal answer which is already evident in the fact that different types of steel exhibit widely varying response with respect to each type of sollicitation since the corresponding properties are also controlled by the material's microstructure in a specific manner.

Nevertheless, the available examples have shown that effects of the same type can be expected in different materials and it is the author's opinion that the immediate consequence of the spectacular development of modern surface analysis techniques will be not only to lengthen the list of phenomena associated with the segregation of detrimental impurities but also to reveal the importance of multiple segregations and especially that of beneficial alloying elements the majority of which remains to be found.

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