# Popustna krhkost konstrukcijskih jekel zaradi nečistoč

# Impurity induced temper embrittlement of structural steels

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## A. REVERZIBILNA POPUSTNA KRHKOST (RTE)

Najboljši primer za poslabšanje lastnosti kristalnih mej zaradi nečistoč je RTE konstrukcijskih jekel, zato ker so segregacijske značilnosti in njihovo razmerje do krhkosti zelo skrbno in natančno raziskani in tudi zato, ker ima krhkost tako značilne in splošne karakteristike, da daje predstavo tudi o tem, kar lahko pričakujemo v drugih sistemih zlitin in lastnosti[1, 3, 4]:

— prvič, segregacijski pojav je zelo kompleksen, ker segregira skupaj in podobno cela vrsta elementov, od neželjenih do namerno dodanih zlitinskih elementov;

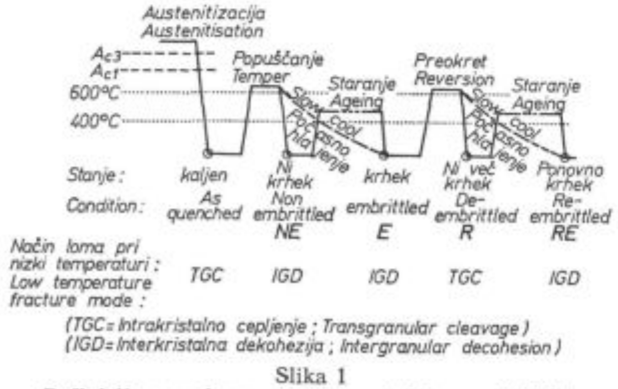
— dalje, razmerje med segregacijo in krhkostjo je kompleksno; slednjo določa konkurenčen efekt sestave kristalnih mej in volumske sestave;

— tretjič, segregacije spreminjajo različne uporabne lastnosti istega jekla.

RTE se pojavi v značilni obliki, ko se kaljeno in popuščeno jeklo stara ali se počasi ohlaja skozi temperaturno območje med 400 in 600 °C (sl. 1). Značilno za krhkost je:

— povišanje prehodne temperature žilavi-krhki lom (TT) pri udarnem preizkusu, ne da bi se opazno spremenile natezne lastnosti pri temperaturi ambienta;

— zaradi nje se spremeni način preloma pri nizki temperaturi od intrakristalnega cepljenja na interkristalen krhek prelom;



Slika 1

**Definicija pogojev za toplotno obdelavo pri RTE.**

Fig. 1

**Definition of the heat treatment conditions in RTE.**

## A. REVERSIBLE TEMPER EMBRITTLEMENT (RTE)

The best example of impurity-induced impairment of grain boundary properties is certainly that of RTE of structural steels, since it is the phenomenon in which the segregation pattern and its relations with embrittlement have been studied very thoroughly and accurately, and also because its properties exhibit typical and general characters which shed light on what can be expected from other alloy systems and properties[1, 3, 4]:

— first, the segregation process itself is quite complex since a wide variety of elements, unwanted residuals as well as intentionally added species segregate together and in a mutually dependent way;

— next, the relationhip between segregation and brittleness is also complex since the latter is determined by the concurrent effects of grain boundary composition and bulk microstructure;

— thirdly, these very same segregations alter a wide variety of other engineering properties of the same steel.

RTE in its typical form appears when a quenched and tempered low-alloy steel is aged, or slowly cooled through the temperature range 400—600 °C, fig. 1. It is characterized by:

— an increase in the ductile-brittle transition temperature (TT) in impact tests without any apparent loss in room-temperature tensile properties;

— the concomitant change of the low temperature fracture mode from transgranular cleavage to intergranular brittle fracture;

— its reversible character, that is, the possibility to de-embrittle the steel by reheating it above the embrittling range (say, 650 °C) and cooling it rapidly to room temperature, then to re-embrittle it again, and so forth.

### 1. Segregation of embrittling impurities

This embrittlement is basically induced by the segregation to the high angle grain boundaries of the $\alpha$-phase of non metallic impurities »I« of groups IV A and V A of the periodic table, P, Sb, Sn, Si, (As?), fig. 2, and it is generally observed[5, 6] that the embrittlement, i. e. the transition temperature shift $\Delta$TT increases quasi linearly with the concentration of impurities segregated at the boun-

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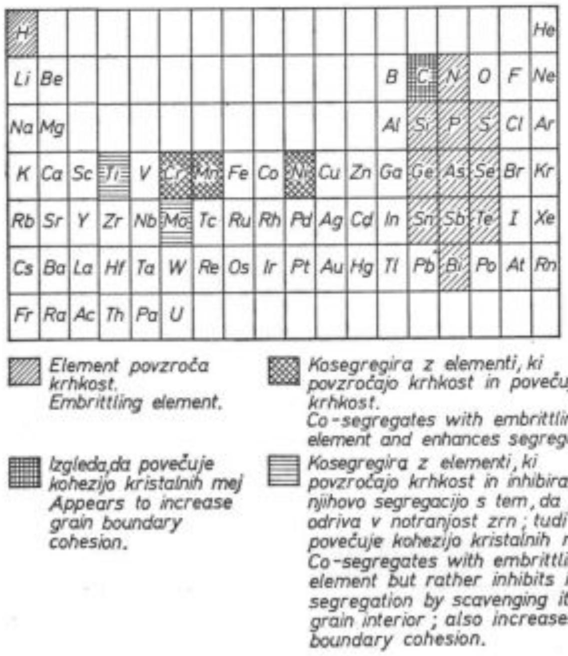
— krhkost je reverzibilne narave, zato se lahko krhkost odpravi iz jekla z ogrevanjem nad področje krhkosti (npr. 650 °C) in hitrim ohlajanjem na temperaturo ambienta, nato pa se lahko ponovno ustvari in tako dalje.

## 1. Segregacija nečistoč, ki povzročajo krhkost

Krhkost povzroča segregacija nemetalnih nečistoč »I« iz skupin IV A in V A periodičnega sistema: P, Sb, Sn, Si (As?) (sl. 2) na velikokotnih mejah α faze. Ugotovljeno je bilo[5, 6], da krhkost, oz. premik prehodne temperature ΔTT, raste skoraj linearno s koncentracijo nečistoč, ki so obogatene na meji (sl. 3). Na osnovi te čisto empirične odvisnosti se lahko definira neka »krhkostna moč« $EP_I$ za vsako nečistočo I kot naklon črt v odvisnosti med povečanjem prehodne temperature in atomskim procentom I na kristalni meji. Na sliki 3 vidimo, da je EP za Sb in Sn mnogo večji kot za P. Podobne odvisnosti so ugotovili za različna malo legirana jekla, npr.: 1,5 Ni-Cr in 1,5 Mn-Cr-Ni-Mo jekla[6] (16 NC 6 in 16 MCND 6 po francoskih standardih) (sl. 4). Tolažilno je, da črte povprečnih kvadratnih korenov v teh diagramih sekajo vertikalno os pri vrednostih, ki so točno enake izmerjenim vrednostim za nekrhko stanje vsakega jekla brez interkristalnega preloma, pri katerem so le zelo nizke segregacije P. To obnašanje ni specifično samo za malo legirana jekla, ugotovljeno je bilo tudi v martenzitnem 13 % Cr nerjavnem jeklu[7, 8] (sl. 5). Tipično RTE so dokazali tudi v feritnem litem železu[9]. Segregacije, ki nastopajo

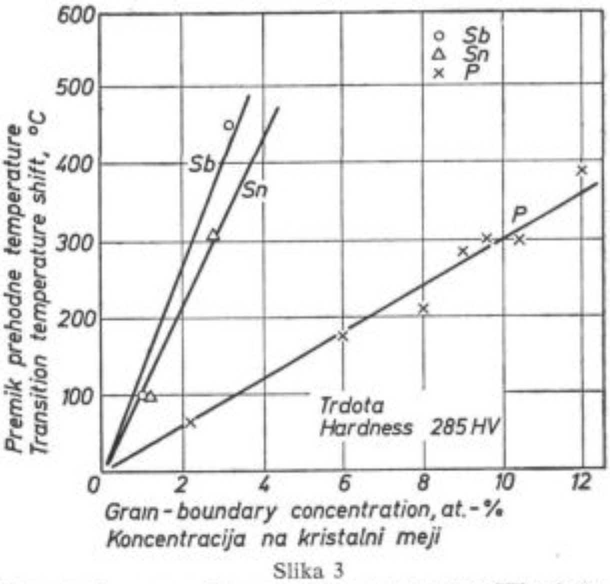


Slika 2

**Periodni sistem s prikazom vloge različnih elementov v RTE (po ref. 1, modificirano)**

Fig. 2

**Periodic chart showing the role various elements play in RTE (after ref. 1, modified).**



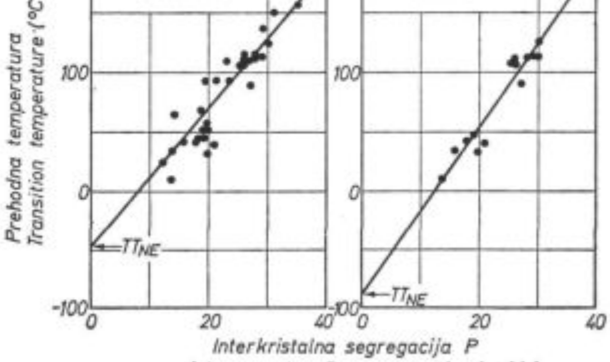
Slika 3

**Sprememba v premiku prehodne temperature TT z interkristalno segregacijo metaloidov v Ni-Cr malolegiranih jeklih (3340) (po ref. 5).**

Fig. 3

**Variation of transition temperature shift TT with intergranular segregation of metalloids in Ni-Cr low alloy steels (3340) (after ref. 5).**

dary, fig. 3. On the basis of this purely empirical relationship, an »embrittling potency« $EP_I$ can be defined for each impurity I as the slope of these lines, i. e. the increase in transition temperature per atomic percent of I at the boundary. Fig. 3 shows that the EP of Sb and Sn is much larger than that of P. Similar relationships have been obtained with various low alloyed steels, e. g. 1.5 Ni-Cr and 1.5 Mn-Cr-Ni-Mo steels (16 VC 6 and 16 MCND 6 respectively according to the French standards[6], fig. 4, and it is quite comforting that the mean square root lines shown on these dia-

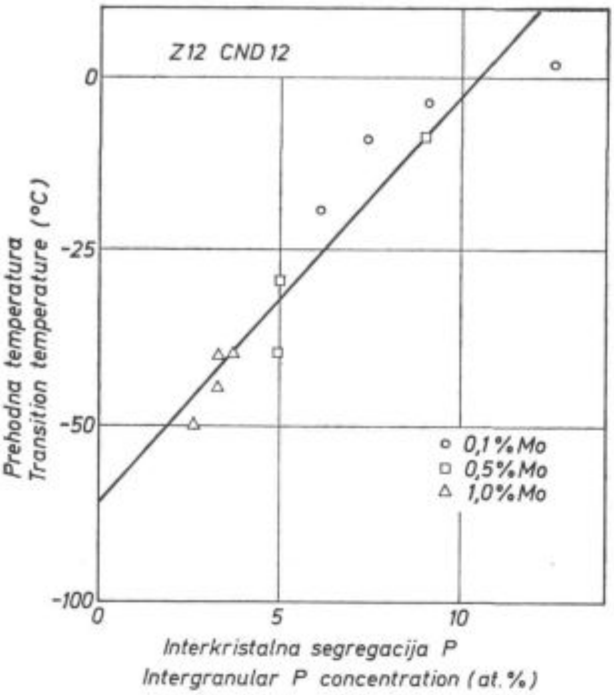


Slika 4

**Sprememba prehodne temperature TT z interkristalno segregacijo fosforja v Ni-Cr in Mn-Cr-Ni-Mo malolegiranih jeklih (po ref. 6).**

Fig. 4

**Variation of transition temperature TT with intergranular segregation of phosphorus in Ni-Cr and Mn-Cr-Ni-Mo low alloy steels (after ref. 6).**



Slika 5

**Sprememba prehodne temperature TT z interkristalno segregacijo fosforja v 12 % Cr martenzitnem nerjavnem jeklu z različnimi dodatki molibdena (po ref. 8).**

Fig. 5

**Variation of transition temperature TT with intergranular segregation of phosphorus in 12 % Cr martensitic stainless steel containing various Mo additions (after ref. 8).**

v RTE, so neravnotežnega tipa. Začetna segregacija namreč raste, ko se dviga temperatura staranja (sl. 6 levo) in sledi temperaturna odvisnost koeficienta volumske difuzije. Maksimalna (stalno stanje) interkristalna koncentracija pri tem pada (sl. 6 desno), in to razlaga reverzibilnost krhkosti pri visokih temperaturah feritnega območja.

## 2. **Vpliv kovinskih dodatkov**

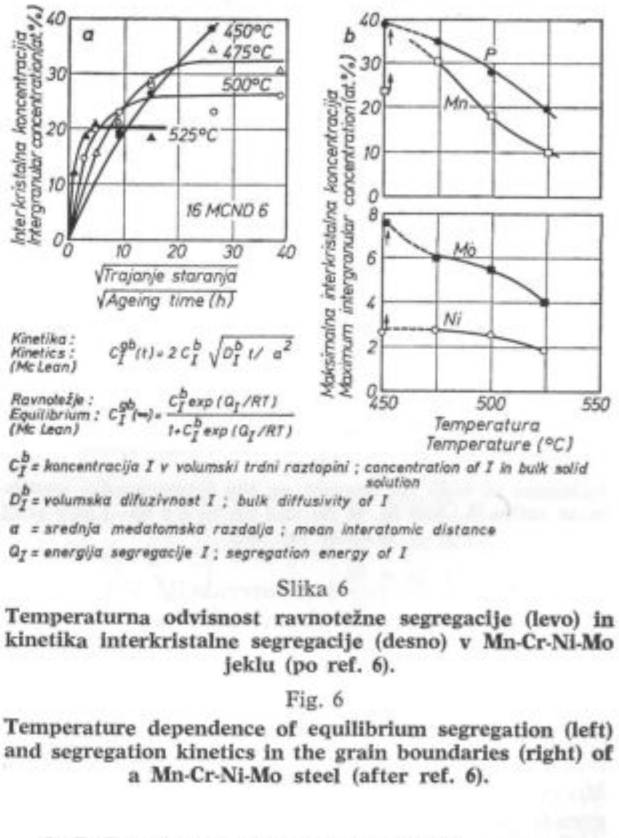
Vpliv dodatka prehodnih kovin »M«: Cr, Mn, Ni in Mo je bistven, da bi razumeli RTE. Ti elementi namreč sodelujejo v treh osnovnih značilnostih pojava: spreminjajo segregacijo nečistoč I, direktno vplivajo na kohezijo kristalnih mej in kontrolirajo mikrostrukturo.

Vsi kovinski elementi lahko kosegregirajo z nečistočami (sl. 6 desno).

a) V nekaterih primerih se segregacija obeh vrst atomov medsebojno pospešuje, kot prikazuje sl. 7[10]. Količina niklja na kristalnih mejah raste s količino Sb na kristalnih mejah in v matriksu. Vendar segregacija Ni povečuje segregacijo Sb, ker hitrost bogatenja Sb na mejah $\beta_{Sb}$ ne bi naraščala strmo v odsotnosti Ni, ampak bi verjetneje padala počasi, kot kaže črtkana črta, ki ustreza ravnotežni binarni segregaciji po Mc Leanovi enačbi[2]. Lahko se pokaže[1, 2] s pomočjo enostavnega termodinamičnega modela, da je vzrok za ta sinergistični

grams intercept the vertical axes at values exactly equal to the measured values of the non-embrittled conditions of each steel, in which no intergranular fracture was observed and very low P segregations were effectively expected. This type behaviour is not specific to low alloyed steels, and has been observed in martensitic 13 % Cr stainless steels[7, 8], fig. 5. Typical RTE has been shown to occur in ferritic cast iron[9] also.

The segregations involved in RTE are of the equilibrium type since when the ageing temperature is raised the initial segregation rates increase fig. 6 left, following the temperature dependence of the bulk diffusion coefficient, while the maximum (steady state) grain boundary concentrations decrease, fig. 6 right, which accounts for the »reversibility« of embrittlement at higher temperatures of the ferritic range.



Kinetika:
Kinetics:
(Mc Lean)
$C_I^{gb}(t) = 2\,C_I^b\,\sqrt{D_I^b\,t/\,a^2}$

Ravnotežje:
Equilibrium:
(Mc Lean)
$C_I^{gb}(\infty) = \dfrac{C_I^b \exp(Q_I/RT)}{1 + C_I^b \exp(Q_I/RT)}$

$C_I^b$ = koncentracija I v volumski trdni raztopini; concentration of I in bulk solid solution
$D_I^b$ = volumska difuzivnost I; bulk diffusivity of I
$a$ = srednja medatomska razdalja; mean interatomic distance
$Q_I$ = energija segregacije I; segregation energy of I

Slika 6

**Temperaturna odvisnost ravnotežne segregacije (levo) in kinetika interkristalne segregacije (desno) v Mn-Cr-Ni-Mo jeklu (po ref. 6).**

Fig. 6

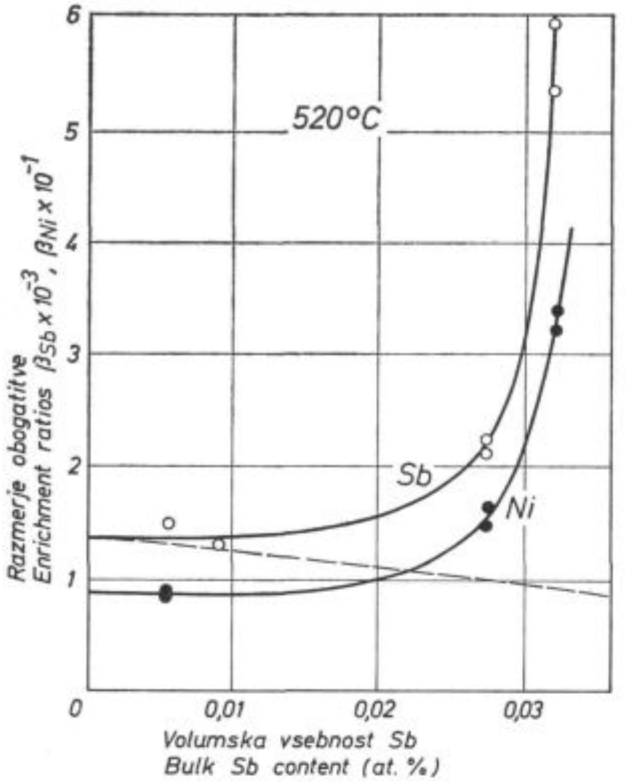
**Temperature dependence of equilibrium segregation (left) and segregation kinetics in the grain boundaries (right) of a Mn-Cr-Ni-Mo steel (after ref. 6).**

## 2. **Influence of metallic additions**

The behaviour of the transition metal additions »M«, Cr, Mn, Ni, Mo is essential to the understanding of RTE since they are involved in three basic features of phenomenon: they alter the segregation of the impurities I, they directly affect the cohesion of grain boundaries, and they control the microstructure.

All metallic elements can co-segregate with the impurities, fig. 6 right.

a — In some cases the segregations of both types of atoms enhance each other, as demonstrated by fig. 7[10]. The Ni build-up at the boundaries efekt v tem, da je kemična interakcija med atomi M in I (po kristalnih mejah) prednostno privlačnostna v primerjavi z atomi Fe-I.*



Slika 7

**Vpliv volumske vsebnosti Sb na razmerja interkristalne obogatitve $\beta_{Ni}$ in $\beta_{Sb}$ za Ni in Sb v jeklu s 5 Ni in 1,5 Cr (po ref. 10).**

Fig. 7

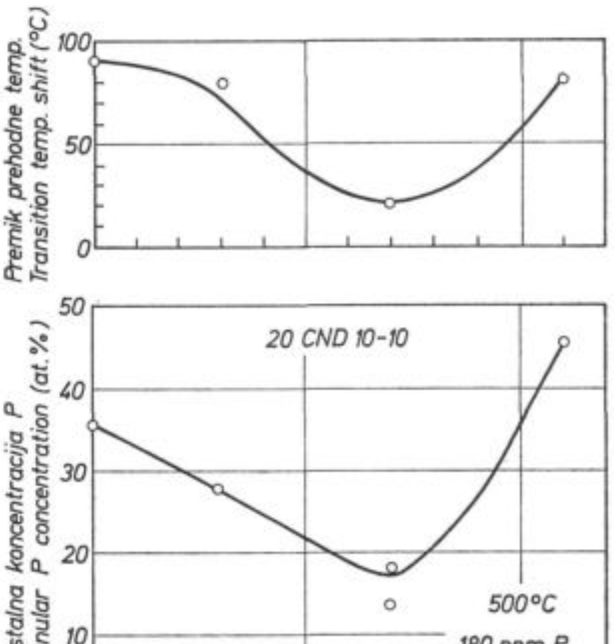
**Influence of bulk Sb content on the intergranular enrichment ratios $\beta_{Ni}$ and $\beta_{Sb}$ of Ni and Sb in a 5 Ni—1.5 Cr steel (after ref. 10).**

Nasprotno, ko postane interakcija M-I močnejša, postane njen učinek močnejši v notranjosti zrn. Ta efekt se upira prejšnjemu, nečistoča lahko ujame prehodno kovino v matriksu in zato se zmanjša segregacija[14]. Tako Mo pobere del raztopljenega fosforja z izločanjem fosfida (Mo, Fe)$_3$P in zato potlači segregacijo P do dodatkov 0,7 % Mo (sl. 8). To deloma razlaga zmanjšanje krhkosti zaradi molibdena v malo legiranih jeklih[15, 16]. Podoben efekt opažamo v jeklu s 13 % Cr (sl. 5), kjer povečanje vsebnosti molibdena od 0,1 % do 1 % zmanjša oboje, segregacijo P in krhkost po vseh žarjenjih[8].

b) Segregirani zlitinski elementi tudi neposredno vplivajo na intrakristalen prelom. Tako je v seriji malo legiranih jekel vrste 20 CND 10—10, v katerih se lahko doseže različni nivo Mo segregacije[15, 16], porušeno linearno razmerje med P

increases with the Sb content of the matrix and grain boundaries, but the Ni segregation also enhances that of Sb since the Sb enrichment ration $\beta_{Sb}$ at the boundaries would not increase steeply in the absence of Ni but would rather decrease slowly as shown by the dotted line according to Mc Lean's equation for binary equilibrium segregation[2]. It could be shown[1, 2], with the help of simple thermodynamic models that his synergistic effect is due to the fact that the chemical interactions between M and I atoms (in the grain boundaries) are preferentially attractive with respect to the Fe-I ones.*

Conversely, as the M-I interaction becomes larger, its effect in the grain interior becomes more critical: this effect opposes the former since the impurity can now be trapped in the matrix by the transition metal, causing its segregation to decrease[14]. In effect, Mo scavenges part of the soluble



Slika 8

**Vpliv volumske vsebnosti Mo na premik prehodne temperature in interkristalno segregacijo P v Cr-Mo-Ni (20 CND 10—10) jeklih (po ref. 15 in 16).**

Fig. 8

**Influence of bulk Mo content on the transition temperature shift and intergranular P segregation in Cr-Ni-Mo (20 CND 10—10) steels (after ref. 15, 16).**

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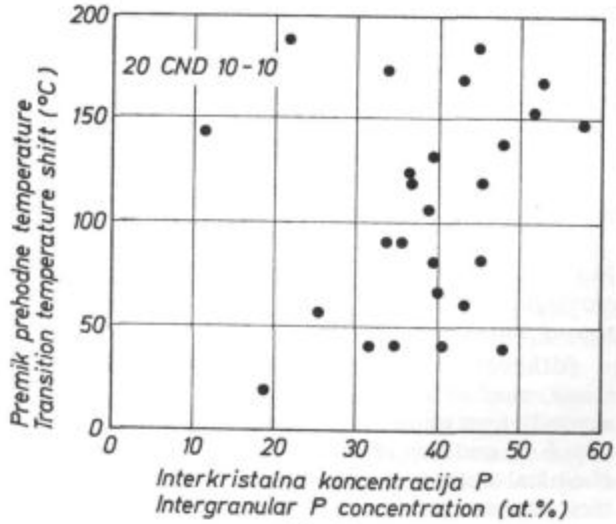
* Čeprav je bil ta dokaz izpeljan na osnovi enostavnega modela regularne raztopine[11], se smatra, da je njegova kvalitativna veljavnost splošna. To je bilo pred kratkim potrjeno z uporabo Gibbsove absorpcijske izoterme[13].

* Although this demonstration was originally carried out on the basis of a simple regular solution model[11] its qualitative validity was claimed to be general, which has recently been confirmed using only the Gibbs adsorption isotherm[13].



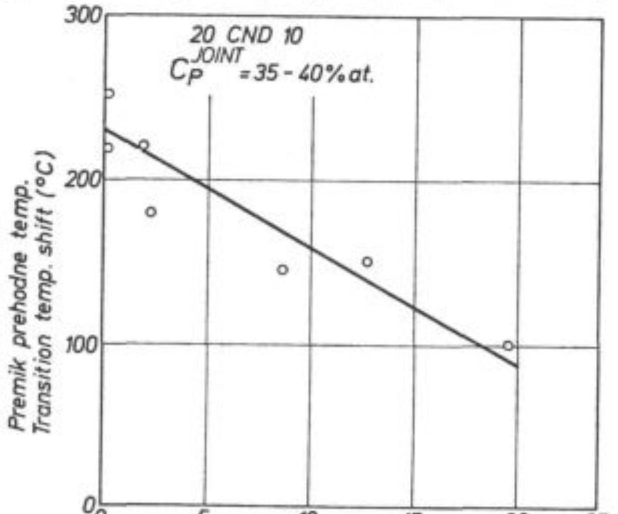
Slika 9

**Odsotnost linearnega razmerja med TT in interkristalno koncentracijo P v različnih jeklih z Mo vrste 20 CND 10—10 (po ref. 15 in 16).**

Fig. 9

**Absence of a linear relationship between TT and intergranular P segregation in various Mo-bearing 20 CND 10—10 steels (after ref. 15, 16).**

segregacijo in krhkostjo (sl. 9), drugače povedano, krhkostna moč P ni več konstantna. Vendar se pokaže, če upoštevamo segregirano koncentracijo Mo $C_{Mo}^{gb}$ kot novo spremenljivko, da za določeno P segregacijo porast prehodne temperature zaradi povečanja krhkosti ΔTT regularno pada, ko raste $C_{Mo}^{gb}$ (sl. 10); bolj splošno, krhkostna moč P stalno pada, ko se povečuje $C_{Mo}^{gb}$ (sl. 11). Zanimiva je



Slika 10

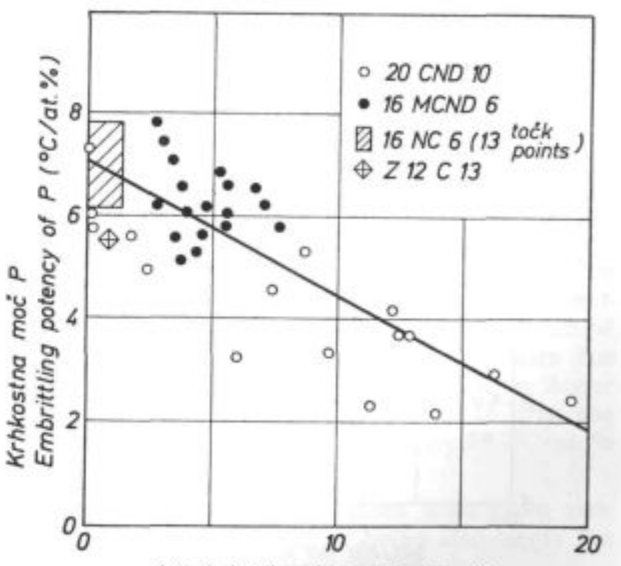
**Vpliv segregiranega Mo na krhkost jekel vrste 20 CND 10—10 (izraženo s TT) pri konstantni P segregaciji (po ref. 15 in 16).**

Fig. 10

**Influence of segregated Mo on embrittlement of 20 CND 10—10 steels (as measured in terms of TT) at constant P segregation (after ref. 15, 16).**

phosphorus by precipitating a phosphide (Mo, Fe)$_3$P and therefore depresses the segregation of P up to additions of 0.7 % Mo, fig. 8, which partly accounts for the de-embrittling effect of Mo in low alloyed steels[15, 16]. A similar effect is observed in 13 % Cr steels, fig. 5, where the increase in Mo content from 0.1 % to 1 % lowers both the P segregation and embrittlement resulting from each embrittling treatment[8].

b — The segregated alloying elements also have a direct influence on the grain boundary fracture. Thus in a series of low alloyed 20 CND 10—10 steels where various levels of Mo segregation can be produced[15, 16], the linear relationship between P segregation and embrittlement is totally destroyed, fig. 9, in other words the embrittling potency of P is not constant any more. However, when the segregated Mo content $C_{Mo}^{gb}$ is considered as a new variable it appears that for a given P segregation the embrittlement ΔTT regularly decreases with increasing $C_{Mo}^{gb}$, fig. 10, and more generally that the embrittling potency of P steadily decreases as $C_{Mo}^{gb}$ increases, fig. 11. It is interesting to note that besides very thoroughly investigated 2 1/4 Cr-1 Ni-1 Mo steel (20 CND 10, open circles in fig. 11), several steels of quite different compositions including 13 % Cr martensitic stainless obey this correlation with a satisfactory experimental scatter, considering that existing on transition temperatures and Auger measurements, and the influence of other alloying elements as will be discussed below.



Slika 11

**Sprememba krhkostne moči P (EP$_r$) z interkristalno segregacijo segregiranega Mo (po ref. 6, 8, 15 in 16).**

Fig. 11

**Variation of the embrittling potency of P, EP$_r$, with the intergranular concentration of segregated Mo (after ref. 6, 8, 15, 16).**

ugotovitev, da ustreza tej korelaciji poleg skrbneje raziskanega jekla 2 1/4 Cr-Ni-1 Mo (20 CND 10, prazni krogci na sl. 11), cela vrsta jekel z različno sestavo, vključno s 13 % Cr martenzitnim nerjavnim jeklom. Pri tem so odstopanja eksperimentalnih meritev temperature in rezultatov Augerjeve analize povsem sprejemljiva ob upoštevanju vplivov drugih legirnih elementov, kar bomo obravnavali v nadaljevanju.

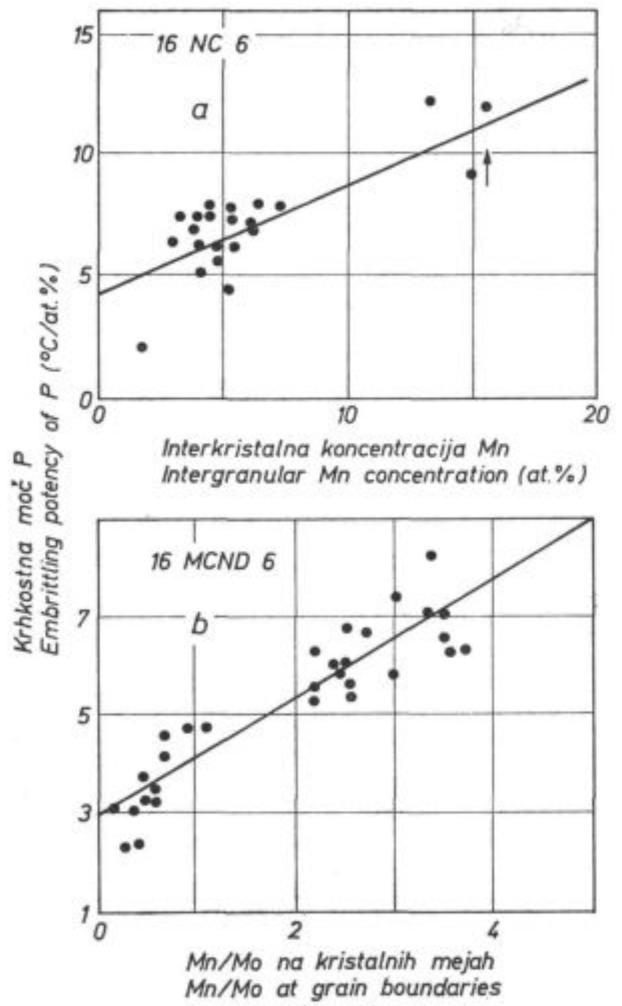
Fizikalna vsebina te čisto empirične odvisnosti še ni znana.

Lahko si predstavljamo, da[3, 15, 16]

— Mo učinkovito zmanjšuje krhkostni efekt P;

— Mo poveča kohezijo kristalnih mej, kot to stori C v čistem železu[17, 18, 19];

— tretja možnost je, da Mo pospešuje koristno segregacijo C s kosegregacijo zaradi močne Mo-C interakcije.



Slika 12

**Vpliv segregiranega Mn(a) in Mo + Mn (b) na krhkostno moč P (po ref. 6).**

Fig. 12

**Influence of segregated Mn (a) and Mn + Mo (b) on the embrittling potency of P (after ref. 6).**

The physical significance of this purely empirical correlation is not known yet. It can be thought that[3, 15, 16]:

— Mo effectively counteracts the embrittling effect of P;

— Mo intrinsically improves the cohesion of grain boundaries as C does in pure Fe[17, 18, 19];

— a third possible mechanism would be that Mo promotes the beneficial segregation of C through a co-segregation process driven by a strong Mo-C interaction.

Although it cannot be decided yet which of these mechanisms (or combination of these) is actually operating it is interesting to note that Ti, which is another transition metal with both high chemical activity and high cohesive energy, exhibits the same two effect on Sb-induced embrittlement as Mo does on that due to P, i.e. Ti scavenges the impurity in the bulk and lowers its embrittling effect at the boundaries[20].

A behaviour opposite to that of Mo and Ti is that of Mn whose segregation induces an apparent enhancement of the embrittling potency of P, fig. 12.a,[6] and in a steel containing both Mo and Mn the embrittling potency of P is a complex function of the segregation of both elements, fig. 12b, decreasing with the former and increasing with the latter. In the case of Mn again it is not known yet whether its deleterious effect exerts itself intrinsically on the cohesion of the boundaries or only in the presence of P atoms there but it has already been suggested in the past that Mn could be an embrittler in the same sense as the non metallic residuals although to a smaller extent. It should be borne in mind however, that the alloying elements Mn, Mo, Ni, Cr, etc. do not segregate by themselves to the grain boundaries[3, 11] but need the promoting action of the non metals P, Sn, Sb which makes it very difficult to analyze their specific effect.

Another source of complexity is that carbon controls the amount of carbide-forming metals (Cr, Mo, Ti) in solid solution and therefore their beneficial (Mo, Ti) or deleterious (Cr) action on impurity segregation and embrittlement. Thus in Ni-Cr steels the segregation of P, Sb and Ni is considerably larger at low C than at 0.4 % C, fig. 13[21, 22], due to the enlancing effect of Cr which is cancelled out at a larger C content because the majority of Cr is then in carbide form. Similarly, the beneficial effect of Mo disappears at higher (1.1 %) Mo addition in 20 CND 10—10 steels, fig. 8,[15, 16] because in that case the kinetics of Mo-rich carbides precipitation are accelerated to such an extent that virtually all the active (soluble) Mo is precipitated and both the P segregation and embrittlement resume their values in Mo free steels. A similar effect can be induced in the very good 0.7 % Mo steel by increasing the ageing time or temperature to 3300 hrs and 550 °C, respectively[15, 16].

Ni se še mogoče odločiti o tem, kateri od teh mehanizmov (ali kombinacija mehanizmov) je dejansko dejaven. Zanimivo, da tudi Ti, ki je prehodna kovina z veliko kemično aktivnostjo in veliko kohezijsko energijo, pokaže podobna efekta na krhkost zaradi Sb kot Mo v primeru krhkosti zaradi P, torej Ti veže nečistočo v matriksu in zmanjšuje njen krhkostni vpliv na mejah[20].

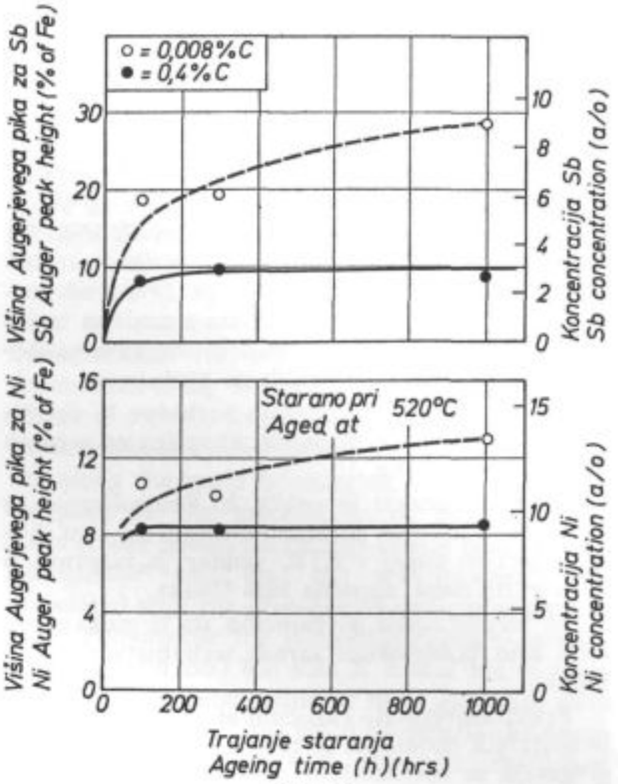
Mangan ima nasproten vpliv od Ti in Mo, segregacija mangana namreč navidezno povečuje krhkostno moč P (sl. 12a)[6]. Zato je v jeklu, ki vsebuje Mo in Mn krhkostna moč P kompleksna funkcija segregacije obeh elementov (sl. 12b) in se zmanjšuje s prvim elementom in povečuje z drugim. Še ni znano, ali se škodljivi vpliv mangana uresničuje le na koheziji mej ali samo v prisotnosti P atomov na mejah. V preteklosti je že bilo izraženo, da bi mangan lahko povzročal krhkost na enak način, čeprav v manjšem obsegu kot nekovinski reziduali. Upoštevati pa je potrebno, da legirni elementi Mn, Mo, Ni, Cr itd. ne segregirajo sami po sebi na kristalne meje[3, 11], ampak potrebujejo pospeševalni učinek nekovin P, Sn in Sb, zaradi česar je zelo težko opredeliti njihov specifični vpliv.

Nov vir zapletenosti je v tem, da v jeklih ogljik kontrolira količino karbidotvornih elementov (Cr, Mo, Ti), ki so v trdni raztopini in je zato odločilen tudi za njihov koristni (Mo, Ti) ali škodljivi (Cr) učinek na segregacijo in krhkost. V Ni-Cr jeklih so segregacije P, Sb in Ni večje pri nizkem C kot pri 0,4 % C (sl. 13)[21, 22] zaradi pospeševalnega vpliva Cr, ki pa je izničen pri večjih množinah C, zato ker je večina Cr v karbidni obliki. Podobno izgine koristen vpliv Mo pri večjem dodatku Mo (1,1 %) v jeklu 20 NCD 10—10[15, 16] (sl. 8). Vzrok je v tem, da je kinetika precipitacije karbidov, bogatih z Mo, tako pospešena, da je skoraj ves aktivni (raztopljeni) Mo precipitiran. Zato segregacija in krhkost dobita ponovno enake vrednosti, kot v jeklih brez Mo. Do podobnega pojava pride v dobrem 0,7 % Mo jeklu, če se podaljša čas žarjenja na 3300 ur ali se temperatura dvigne na 550 °C[15, 16].

## 3. Vpliv mikrostrukturnih parametrov

Mikrostruktura je važen parameter, ki kontrolira krhkost pri določeni sestavi kristalnih mej, čeprav obe vrsti parametrov med seboj na splošno nista odvisni. V določenem jeklu občutljivost raste od feritno perlitne, do mikrostrukture iz popuščenega bainita in je največja v popuščenem martenzitu.

Raste tudi s trdoto, ki se lahko spreminja s spremembo začetnih pogojev žarjenja. Rezultati Mulforda in sod.[21] kažejo pri uporabi enakih kalibracijskih faktorjev za določanje intergranularne koncentracije iz Augerovih podatkov, kot so bili uporabljeni v ref. 6, 15 in 16, da raste krhkostna moč P z 0,03 °C/at. % na Vickersovo enoto[16] (sl. 14).



Slika 13

**Vpliv C na segregacijo Sb in Ni v 3,5 Ni—1,7 Cr jeklih (po ref. 22).**

Fig. 13

**Influence of C on the segregations of Sb and Ni in 3.5 Ni —1.7 Cr steels (after ref. 22).**

## 3. The influence of microstructural parameters

Microstructure is also an important parameter controlling the extent of embrittlement for a given composition of grain boundaries, although the two categories of parameters are not mutually dependent in general.

In a given steel the susceptibility increases from ferrite-pearlite to tempered bainite, and is at a maximum in tempered martensite.

It also increases with hardness which can be varied e. g. by varying the initial tempering treatment: from the results of Mulford et al.[21] it can be shown, using the same calibration factors for deriving intergranular concentrations from Auger data as those employed in ref. 6, 15, 16, that the embrittling potency of P increases by 0.03 °C/at. % per Vickers point[16], fig. 14.

Embrittlement also increases with grain size. The effect of this parameter being also larger the larger is the embrittlement itself[23].

The influence of grain size on fracture which is also observed although to a smaller extent in the case of cleavage, is essentially explained in terms of the mechanics of crack propagation[23, 3, 11, 24]. It has been shown both experimentally and analytically[11] that grain size cannot affect segregation in temper brittle steels. Such a direct

Krhkost se povečuje z velikostjo zrn in je vpliv tega parametra tem večji, čim večja je krhkost[23]. Vpliv velikosti zrn na prelom, ki je bil tudi zabeležen, čeprav v manjši meri, v primerih cepilnih prelomov, razlagamo z mehaniko propagacije razpoke[23, 3, 11, 24]. Dokazano je bilo eksperimentalno in analitično[11], da velikost zrn ne vpliva na segregacijo v jeklih, ki so krhka zaradi popuščanja. Da tak neposreden vpliv, ki zahteva, da skupna količina nečistoč, ki so segregirane po kristalnih mejah, ni zanemarljiva v primerjavi z nazivno vsebino, bi lahko ugotovili le pri zelo majhnih velikostih zrn, katerih pa v jeklih ne srečujemo.

Morfologija interkristalnih karbidov in drugih delcev je tudi važen dejavnik, ki vpliva na začetek in širjenje razpoke.

Legirni elementi in ogljik, ki kontrolirajo vse te mikrostrukturne parametre, imajo pri tem drugo odločilno vlogo v RTE, vendar je razprava o teh efektih zunaj namena tega članka.

Za rezime lahko povzamemo, da je mehanizem RTE zelo kompleksen zaradi treh bistvenih razlogov.

Prvič, segregacije različnih elementov, nečistoč in metalnih dodatkov, so medsebojno odvisne. Segregacije se spreminjajo z M-I kemičnimi interakcijami na mejah in v matriksu, to pa ima nasproten učinek na absolutno velikost segregacije. Poleg tega precipitacija legiranih karbidov, ki permanentno spreminja sestavo trdne raztopine, premakne ravnotežje matriks/meja in menja kinetiko segregacije.

Drugič, kohezija same kristalne meje je odvisna od splošne kemijske sestave mej, torej od nečistoč, zlitinskih elementov in ogljika.

Tretjič, mikrostrukturni parametri močno vplivajo na razmerje segregacija-krhkost.

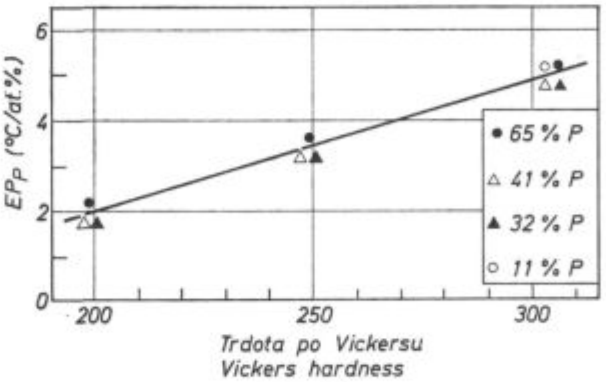
## B. ENOSTOPENJSKA POPUSTNA KRHKOST (OSTE) JEKEL Z ZELO VELIKO TRDNOSTJO

Čeprav podoben prejšnji obliki krhkosti, je ostal ta pojav relativno dolgo nejasen in šele pred kratkim je bil mehanizem prepričljivo pojasnjen[25]. Za izdelavo jekel, ki imajo visoko mejo plastičnosti (1400 $MN/m^2$) in imajo nekaj plastičnosti, se kaljeni martenzit žari eno do dve uri pri temperaturi pod 400 °C. Ta temperatura zmanjša trdoto in pričakovali bi ustrezno povečanje žilavosti. Pokaže pa se anormalni minimum žilavosti pri sobni temperaturi po žarjenju pri približno 350 °C (sl. 15), ki je navadno povezan s spremembo načina preloma od duktilnega transkristalnega na interkristalen prelom vzdolž mej avstenitnih zrn. Ker se ta izguba žilavosti ujema s premeno $\varepsilon$ karbidov v ploščičasti cementit po kristalnih mejah, je bilo to sprejeto kot razlaga mehanizma krhkosti. Kasneje se je pokazalo, da zelo čista talina ni občutljiva za zmanjšanje žilavosti[26] in da je krhkost pove-

effect, which requires that the total amount of segregated impurities is not negligible with respect to the nominal content, would be observed only at very small grain sizes for which the steels are not very susceptible anyhow.

The morphology of intergranular carbides and other particles is also an important factor influencing crack initiation and propagation.

The alloying elements and carbon play here another determining role in RTE by controlling all these microstructural parameters but the discussion of such effects is out of the scope of this paper.



Slika 14

**Vpliv trdote na krhkostno moč P v 3,5 Ni—1,7 Cr jeklih (po ref. 6, ki uporablja podatke iz ref. 21).**

Fig. 14

**Influence of hardness on the embrittling potency of P in 3.5 Ni—1.7 Cr steels (after ref. 6 using data of ref. 21).**

In summary, the mechanism of RTE appears extremely complex for esentially three reasons.

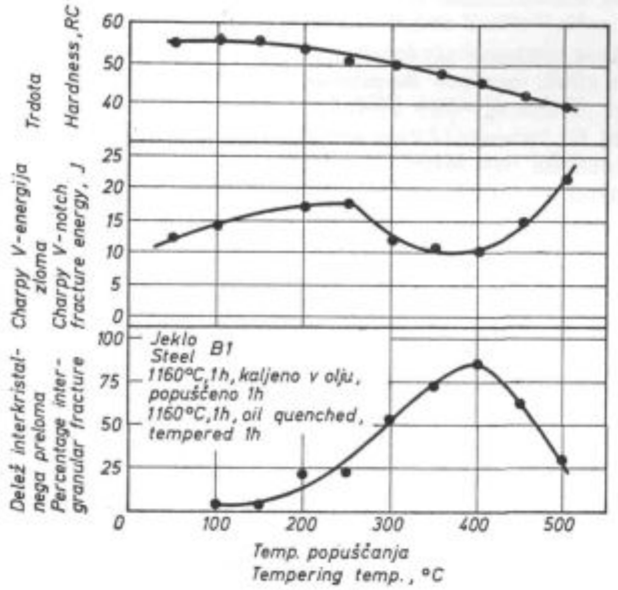
First, the segregations of various elements, impurities I and metallic additions M are mutually dependent. They vary with the M-I chemical interactions at the boundaries and in the matrix, which have opposite effects on the absolute segregation level. Moreover, the precipitation of alloyed carbides which permanently alters the composition of the solid solution displaces the matrix/boundary equilibria and changes the segregation kinetics.

Secondly, the cohesion of the boundary is a function of the overall chemical composition of the boundary in respect to impurities, alloying elements, and carbon.

Thirdly, the microstructural parameters strongly affect the segregation-embrittlement relationship.

## B. ONE-STEP TEMPER EMBRITTLEMENT (OSTE) OF VERY HIGH STRENGTH STEELS

Although akin to the former, this phenomenon has remained virtually unexplained even longer and only recently has its mechanism been quite zana s prisotnostjo nečistoč, ki so odgovorne za reverzibilno popustno krhkost (P, Sn, Sb, v nekaterih primerih pa tudi S, N in Mn). Segregacije teh elementov po kristalnih mejah so opredelili z Augerovo elektronsko spektroskopijo[25, 27], vendar so bile interkristalne koncentracije mnogo manjše od tistih, ki jih srečamo pri RTE. Razlog za to je, da so segregacije pri OSTE nastale v avstenitu pred kaljenjem in zato žarjenje v področju ferita nanje sploh ne vpliva, nizka temperatura in kratko trajanje namreč ne ustvarijo nobenega nakopičenja na kristalnih mejah[25, 28]. Segregacija je premajhna, da bi povzročila zaznavno krhkost, če po kristalnih mejah ne bi bilo ploščastih karbidov, ki delujejo kot zavora proti drsenju in tako pomagajo, da nastanejo razpoke v že oslabljenih kristalnih mejah. Oba pojava morata biti prisotna, da pride do krhkosti, to kaže odsotnost krhkosti v zelo čistem jeklu in v kaljenem stanju. Prvič ni segregacij, drugič pa ni ploščičastih karbidov po mejah. Visoka trdnost materiala tudi pospešuje krhkost. Pri višjih temperaturah žarjenja (>370—400 °C) globulitizacija cementita in mehčanje feritnega matriksa odpravita krhkost.* Šele pri višji temperaturi (≥450 °C) in/ali pri daljših žarjenjih se ponovno pojavi interkristalna krhkost v obliki RTE, to pot zaradi ponovne segregacije v feritnem področju.



Slika 15

**Enostopenjska popustna krhkost: sprememba trdote, žilavosti in oblike preloma s temperaturo žarjenja pod 540 °C v jeklu vrste 4340 (po ref. 27).**

Fig. 15

**One-step temper embrittlement: variation of hardness, toughness and fracture appearance with tempering temperature below 500 °C in a 4340 steel (after ref. 27).**

convincingly explained[25]. To obtain steels which have high yield strength (1400 MN/m$^2$) but also possess some ductility, the as-quenched martensite is tempered for one or two hours at temperatures below 400 °C. This tempering causes a decrease in hardness so one would expect a corresponding increase in toughness. However, the room temperature toughness exhibits an anomalous minimum around 350 °C, fig. 15, which is usually associated with the change in failure mode from ductile transgranular fracture to brittle intergranular decohesion along the prior austenite grain boundaries. Since this toughness loss coincides with the transformation of ε-carbides to plate-like cementite along the grain boundaries, this was formely accepted as the mechanism of embrittlement. Later it was shown that a high purity heat was not susceptible[26] and that the embrittlement was associated with the presence of impurities such as those responsible for reversible temper embrittlement (P, Sn, Sb) but also N, S and Mn in some instances. The segregation of these elements were actually observed at the grain boundaries by Auger Electron Spectroscopy[25, 27]. However, the intergranular concentrations observed were much smaller than those encountered in RTE. This is because the segregations responsible for OSTE have occurred in austenite phase prior to quenching and are virtually unaffected by the tempering treatment in ferrite range, whose short duration and low temperature are unable to give rise to any appreciable diffusive build-up at the boundaries[25, 28]. This segregation would be too small to induce appreciable embrittlement were it not for the presence of the plate-like carbides along the boundaries which act as slip barriers and help initiate cracks at already weakened boundaries. Both phenomena are necessary for the embrittlement to occur as shown by the absence of embrittlement in the high purity heat and in the as-quenched condition of impure heats, respectively associated with the absence of segregated impurities and of plate-like carbides at the boundaries. Ebrittlement is also favored by very high strength of the material. For higher tempering temperatures (> 370—400 °C) globularization of cementite and general softening of the matrix take place causing the embrittlement to vanish.* It is only at higher temperatures (≥ 450 °C) and/or for longer tempering times that intergranular embrittlement will re-appear in the form of RTE due to the onset of segregation in the ferritic range itself.

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* Ta krhkost ni reverzibilna, zato je ni mogoče ponovno ustvariti s ponovnim žarjenjem pri 350 °C, razen če jeklo avstenitiziramo in kalimo, da nastane ponovno martenzit.

* This embrittlement is not »reversible« in the sense that it cannot be induced again by re-tempering at 350 °C unless the steel is austenitized and quenched again to form martensite.

*Zahvala*

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