Segregacija fosforja po kristalnih mejah v železovih zlitinah

Grain boundary segregation of phosphorus in iron alloys

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A. UVOD

Mehanske lastnosti kovin in zlitin se lahko drastično poslabšajo zaradi obogatitve rezidualnih elementov po kristalnih mejah. Dobro je znan primer popustne krhkosti. Nizko legirana jekla, ki jih žarimo ali počasi hladimo skozi interval temperatur 350—600 °C, često pokažejo povišanje prehodne temperature žilavi-krhki lom. Razlog za popustno krhkost je ravnotežna segregacija nečistoč in legirnih elementov po kristalnih mejah[1, 2]. Prisotnost tujih atomov na kristalnih mejah zmanjša kohezijo kristalnih mej.

Nečistoči, ki sta prvenstveno odločilni za popustno krhkost malo legiranih jekel, sta P in nekoliko manj Sn. Zato smo raziskali interkristalno ravnotežno segregacijo P v več ternarnih in kvarternarnih zlitinah na osnovi železa.

B. EKSPERIMENTALNO DELO

Več preizkušancev (dolžina 35 mm, premer 3,7 mm) postavimo na nosilec v UHV (ultra visok vakuum) komoro (sl. 1). Tlak v sistemu je bil $1{,}33 \cdot 10^{-7}$ Pa. Z manipulatorjem postavimo po en vzorec v napravo za lomljenje, ki je hlajena s tekočim dušikom na približno —100 °C. Nato zlomimo preizkušanec z udarcem kladiva in prelom postavimo pred valjasti zrcalni analizator. V tem položaju lahko dobimo sliko prelomne površine s pomočjo sekundarnih elektronov. Opravimo elementarno analizo s spektroskopijo Augerovih elektronov (AES). Majhen premer elektronskega snopa okoli 5 µm omogoča, da se izvrši Augerova analiza različnih delov preloma. Slika 2 prikazuje Augerov spekter, posnet na transkristalnem delu preloma. Preizkušanec je bil iz zlitine Fe-P z 0,17 % P. Poleg pika za železo se na njem razločijo še P pik, ki predstavlja volumsko koncentracijo tega elementa in nizki piki za C in O, katerih poreklo je absorbcija. Slika 3 prikazuje AES spekter, značilen za interkristalen prelom. Visoki pik pri 120 eV pripada segregiranemu P. Razmerje med višino P pika in višino Fe pika (pri 650 eV) je merilo koncentracije P. Zaradi kalibracije smo raziskali ravnotežno površinsko segregacijo P na

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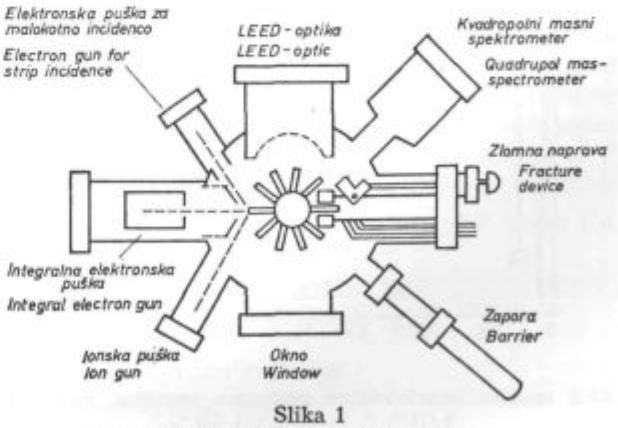
INTRODUCTION

The mechanical properties of metals and alloys can be degraded drastically by the enrichment of residual atoms in the grain boundaries. A well known example is temper embrittlement. Low alloy steels that are tempered or slowly cooled through the temperature range 350—600 °C often exhibit an increase in their ductile-brittle transition temperature. The reason for this temper embrittlement is equilibrium grain boundary segregation of impurities and alloying elements.[1, 2] The presence of these atoms in the grain boundaries lowers the grain boundary cohesion.

The impurities primarily responsible for the temper embrittlement in low alloy steels are P and to a less extent Sn. Therefore we have investigated the equilibrium grain boundary segregation of P in several ternary and quaternary iron-based alloys.

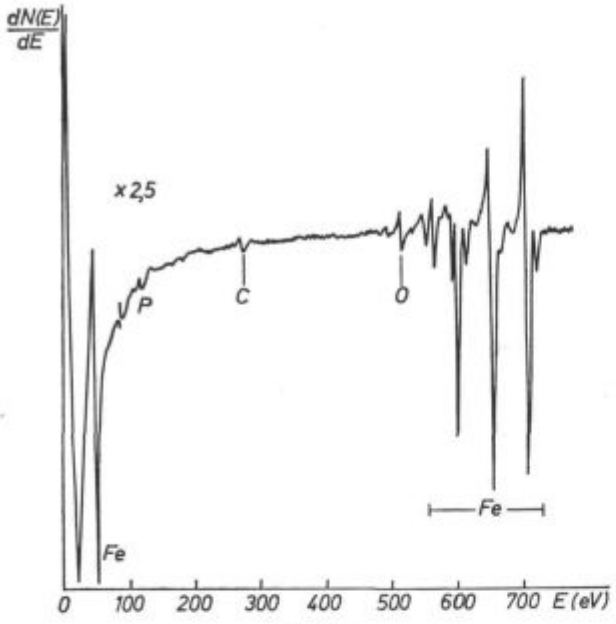
EXPERIMENTAL

Several specimens (length 35 mm ∅ 3,7 mm) are mounted on the holder inside the UHV-chamber. (Fig. 1) The base pressure of the system is $1.33 \cdot 10^{-7}$ Pa. With the manipulator one specimen is inserted into the fracture device which is cooled with liquid nitrogen to about —100 °C. Then this specimen is fractured by impact with a hammer and the fracture surface is aligned in front of



Slika 1
UHV komora z LEED in AES.

Fig. 1
UHV-chamber with LEED and AES.



Slika 2

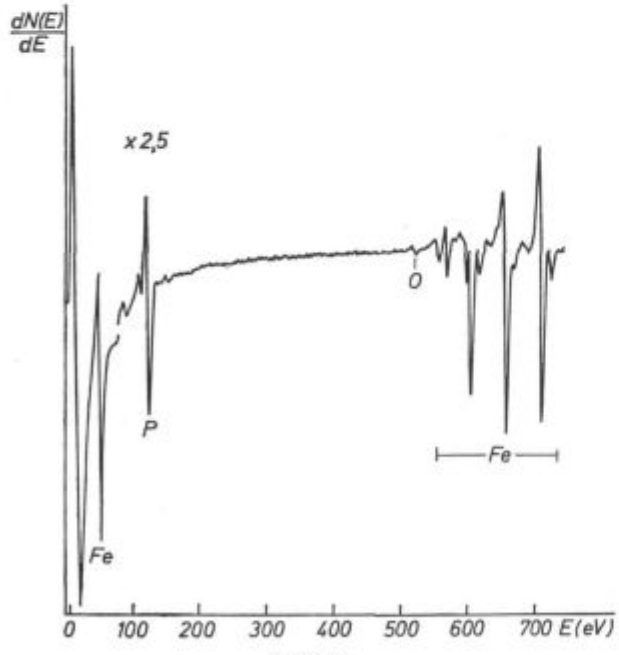
AES spekter transkristalne prelomne površine, zlitina z 0,173 % P, žarjena pri 420 °C.

Fig. 2

AES-spectrum of a transgranular fracture surface, alloy with 0.173 % P, annealed at 420 °C.

monokristalih iz zlitine Fe — 1 % P s pomočjo difrakcije elektronov z nizko energijo (LEED) in AES meritvami.

Na sliki 4 smo kombinirali LEED odseve P na (100) površini z ustreznim AES spektrom. LEED



Slika 3

AES spekter interkristalne prelomne površine, zlitina z 0,173 % P, žarjena pri 420 °C.

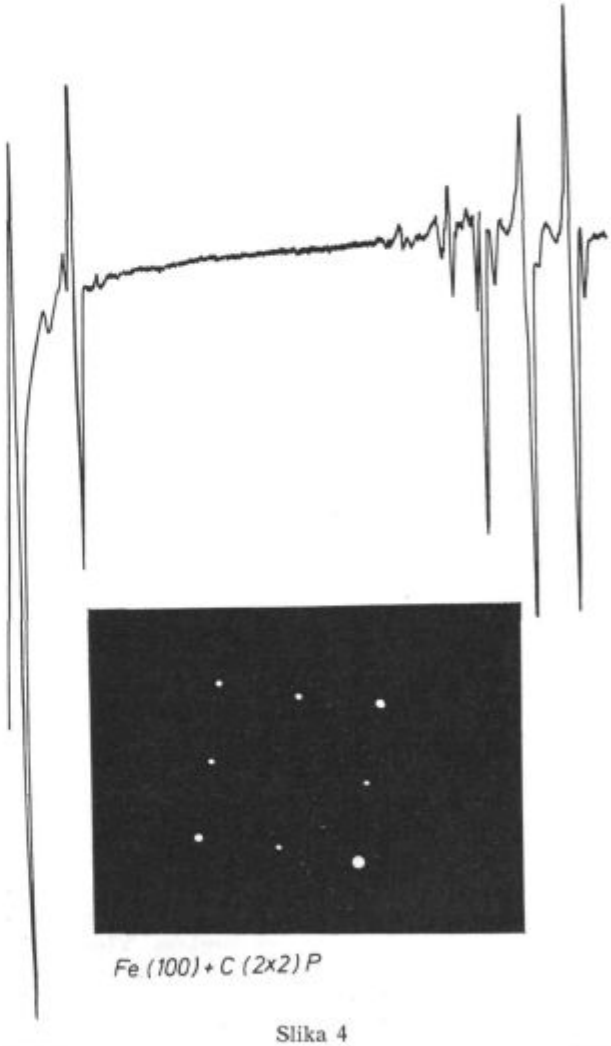
Fig. 3

AES-spectrum of an intergranular fracture surface, alloy with 0.173 % P, annealed at 420 °C.

the cylindrical mirror analyser. In this position a secondary electron image of the fracture surface can be obtained and by Auger electron spectroscopy (AES) elemental analysis is performed. The small electron beam diameter of about 5 μm allows to separate Auger analysis of different parts of the fracture surface.

Fig. 2 presents an Auger spectrum taken on a transgranular part of a fracture surface. The specimen was an Fe-P alloy containing 0.17 % P. Besides the iron peaks one can detect the P peak representing the bulk content of P and the small peaks of C and O which are caused by adsorption. The AES-spectrum characterising intergranular fracture of the same sample is given in Fig. 3. The high peak at 120 eV is due to segregated P. The ratio of the peak height of P to that of Fe (at 650 eV) provides a measure of the P concentration.

For calibration we investigated the equilibrium surface segregation of P on an Fe-1 % P single



Slika 4

LEED odsevi segregiranega P na Fe (100) in ustrezni AES spekter.

Fig. 4

LEED-pattern of segregated P on Fe (100) and corresponding AES-spectrum.

odsevi kažejo, da je nastala zelo lepo razvita c (2 × 2) struktura, ki ustreza pokritju s polovico sloja P atomov. Zato ustreza razmerje višin pikov $A_P(120)/A_{Fe}(650) = 1$ stopnji prekritja $\Theta = 0{,}5$ in površinski koncentraciji $\Delta = 6 \cdot 10^{14}$ atomov P/cm². Vendar je ta kalibracija veljavna le za naše posebne merilne pogoje.

1. Interkristalna segregacija P v α železu

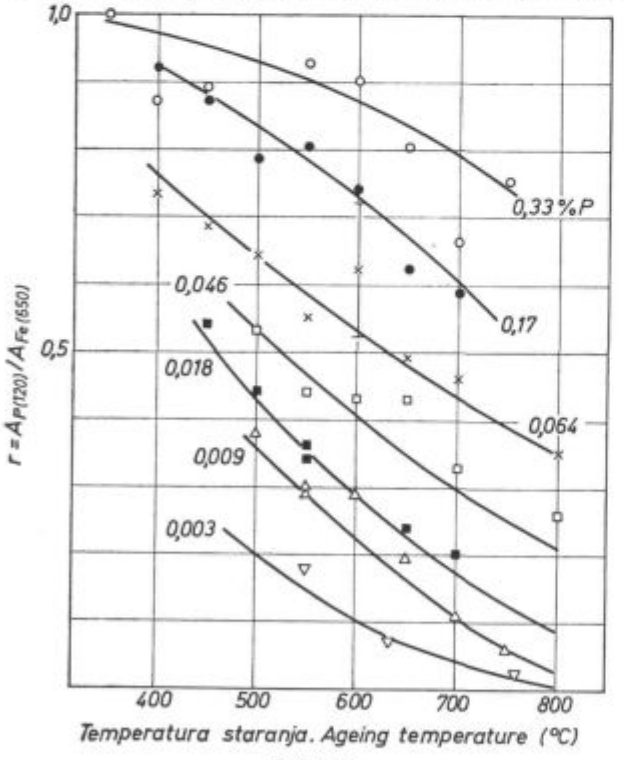
Pripravili smo 7 binarnih zlitin Fe-P s sestavo, ki je prikazana v tabeli 1.

Tabela 1: Sestava zlitin (%)

Table 1: Alloy composition (%)

Zlitina Alloy	P	Mn	S	Si	C	N	Sb
Sm 915	0.003	0.027	0.04	0.009	0.001	0.001	0.001
Sm 916	0.009	0.017	0.04	0.006	0.001	0.001	0.001
Sm 917	0.018	0.028	0.04	0.007	0.001	0.001	0.001
Sm 918	0.046	0.016	0.04	0.007	0.001	0.001	0.001
Sm 919	0.064	0.028	0.04	0.007	0.001	0.001	0.001
Sm 920	0.170	0.027	0.04	0.006	0.001	0.001	0.001
Sm 921	0.330	0.019	0.04	0.006	0.001	0.001	0.001

Preizkušance smo žarili pri različnih temperaturah v območju med 400 in 800 °C. Slika 5 prikazuje spremembe v interkristalni koncentraciji P v odvisnosti od temperature uravnoteženja. Obo-



Slika 5

Interkristalna koncentracija P v odvisnosti od temperature žarjenja za zlitine Fe-P.

Fig. 5

Grain boundary concentration of P as a function of aneal-ing temperature for Fe-P alloy.

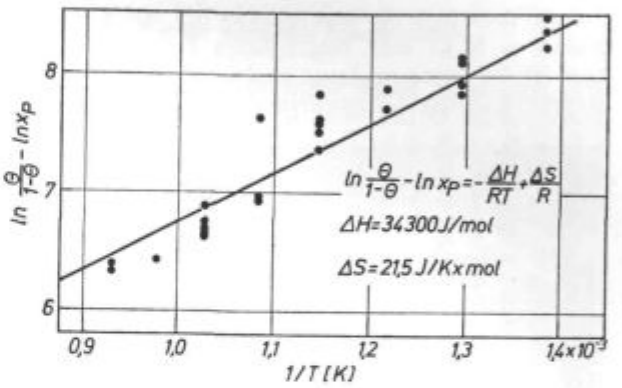
crystal performing low energy electron diffraction (LEED) and AES measurements.

Fig. 4 combines the LEED-pattern of P on the (100) surface with the corresponding AES-spectrum. The LEED pattern indicates the formation of a very well developed c (2 × 2) structure. This structure implies a coverage of 1/2 monolayer P. Therefore the peak height ratio $A_P(120)/A_{Fe}(650) = 1$ corresponds to the degree of coverage $\Theta = 0.5$ and a surface concentration $\Delta = 6 \cdot 10^{14}$ P-atoms/cm². However, this calibration is valid only for our special measuring conditions.

Grain boundary segregation of P in α-iron

Seven binary Fe-P alloys were prepared, their composition is given in Table 1.

The samples were annealed at different temperatures within 400—800 °C range. Fig. 5 demonstrates the grain boundary concentration of P in de-



Slika 6

Ovrednotenje proste entalpije segregacije po Mc Leanovi enačbi.

Fig. 6

Evaluation of the free enthalpy of segregation of P according to the Mc Lean equation.

pendence on equilibration temperature. The grain boundary enrichment increases with decreasing temperature and with increasing bulk concentration. According to our calibration the maximum coverage with P on one side of a fractured grain boundary is 1/2 monolayer. If we assume an equal distribution of segregated P on both sides we can conclude that the maximum content of P in a grain boundary is one monolayer.

The grain boundary segregation of P obeys the Langmuir — Mc Lean equation:

$$\ln \frac{\Theta}{1-\Theta} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln X_P$$

ΔH — segregation enthalpy

ΔS — segregation entropy

X_P — bulk concentration of P

A logarithmic plot of our results vs. reciprocal temperature according to this equation is shown

gatitev po mejah raste, ko se znižuje temperatura in raste volumska koncentracija. V skladu z našo kalibracijo je največje pokritje s P na eni strani prelomljene kristalne meje 1/2 enega sloja atomov. Če predpostavimo, da je enaka porazdelitev fosforja na obeh straneh, lahko zaključimo, da največja koncentracija P na meji ustreza enemu sloju atomov. Segregacija P na meji ustreza Langmuir-Mc Leanovi enačbi:

$$\ln \frac{\Theta}{1-\Theta} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln X_P$$

ΔH — entalpija segregacije

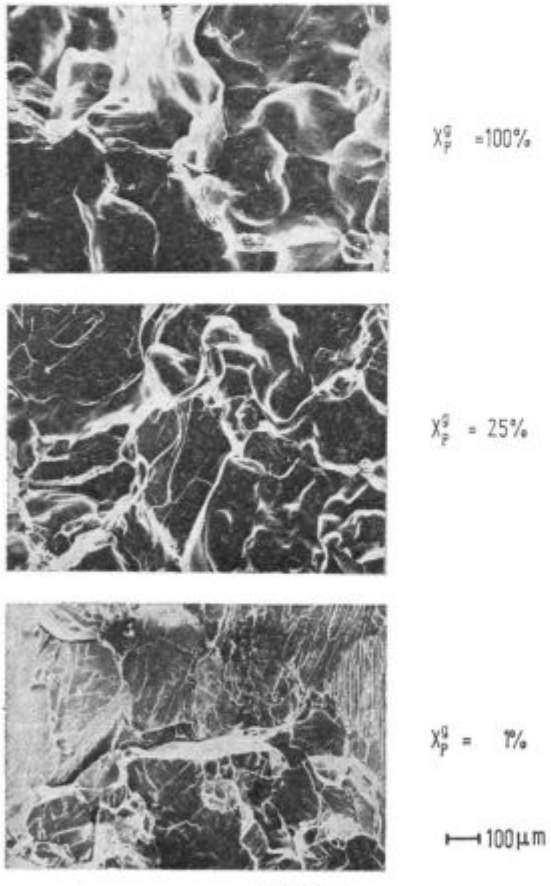
ΔS — entropija segregacije

X_P — volumska koncentracija P

Logaritmičen prikaz naših rezultatov v odvisnosti od recipročne temperature skladno s to enačbo je prikazan na sliki 6. Iz tega diagrama smo ocenili, da je prosta entalpija segregacije:

$\Delta G = \Delta H - T\Delta S = -34300 - 21{,}5\ T$ (kJ/mol).

Prosta entalpija za segregacijo pri 600 °C je približno — 53 kJ/mol. Segregacija P povzroča krhkost (sl. 7). Vrsta preloma se drastično spremeni iz intrakristalnega v interkristalni, ko raste koncen-

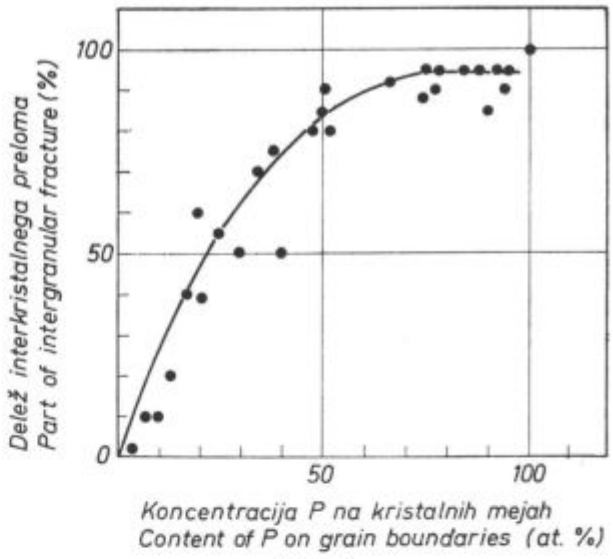


Slika 7

SEM mikrofraktografije vzorcev z različno interkristalno koncentracijo P.

Fig. 7

SEM-fractographs of specimens with different grain boundary concentration of P.



Slika 8

Sprememba interkristalne koncentracije P in Cr v odvisnosti od temperature za Fe-P in Fe-Cr-P zlitine.

Fig. 8

Variation of intergranular concentration of P and Cr with annealing temperature for Fe-P and Fe-Cr-P alloys.

in Fig. 6. From this diagram we estimated the free enthalpy of segregation to be

$\Delta G = \Delta H - T.\Delta S = -34300 - 21{,}5.T$ kJ/mole).

The free enthalpy of segregation at 600 °C is about —53 kJ/mole.

Segregation of P causes embrittlement (Fig. 7). The fracture mode changes drastically from transgranular to intergranular with increasing grain boundary concentration of P. In Fig. 8 the part of intergranular fracture is plotted in dependence on the grain boundary concentration of P.

We also investigated the depth profile of segregated P in the grain boundary by means of Ar-sputtering and field ion microscopy[3]. The experiments proved that P is enriched mainly in the first layer.

Grain boundary segregation of P in an Fe-Cr alloy

Commercial steels are multicomponent systems in which interactions occur between several impurities and alloying elements. Guttmann[4] developed a model describing the segregation in multicomponent systems, putting forward the idea of »synergistic cosegregation«, i. e. enhanced segregation by attractive interaction of segregating species. Some authors have assumed cosegregation of Cr and P in steels[5].

The grain boundary segregation of P for an Fe-Cr alloy containing 2.2 % Cr and 0.047 % P was measured in order to clarify the role of Cr in the segregation behaviour of P. In Fig. 9 the normalized Auger peak height ratios of P and Cr are plotted vs. temperature. The grain boundary concentration of Cr lies only slightly above the bulk

tracija fosforja. Na sliki 8 smo prikazali razmerje med deležem interkristalnega preloma in interkristalno koncentracijo fosforja.

Raziskali smo tudi globinski profil segregiranega P s pomočjo razprševanja z argonom na kristalni meji in s poljsko ionsko mikroskopijo[3]. Preizkus je pokazal, da je fosfor obogaten predvsem v prvem sloju.

2. Segregacija P po mejah v zlitini Fe-Cr

Komercialna jekla so večkomponentni sistemi, v katerih prihaja do interakcij med različnimi nečistočami in zlitinskimi elementi. Guttmann[4] je razvil model, ki opisuje segregacijo v večkomponentnih sistemih, in oblikoval zamisel o »sinergistični kosegregaciji«, to je povečani segregaciji zaradi privlačnostne interakcije segregiranih elementov. Nekateri avtorji so predpostavili kosegregacijo Cr in P v jeklih[5].

Izmerili smo segregacijo P na kristalni meji v zlitini Fe-Cr z 2,2 % Cr in 0,074 % P z namenom, da pojasnimo vlogo Cr v segregacijskem obnašanju P. Na sl. 9 je prikazano razmerje med višino normaliziranega Augerovega pika za P in Cr in temperaturo. Interkristalna koncentracija Cr je le malo nad volumsko koncentracijo. Izmerjena interkristalna koncentracija P se v temperaturnem območju med 500 in 800 °C dobro ujema s tistimi, ki so bile izmerjene v ekvivalentni Fe-P binarni zlitini (sl. 9). Zato lahko zaključimo, da je interakcija med Cr in P le zelo šibka.

3. Tekmovalni efekt med P in C

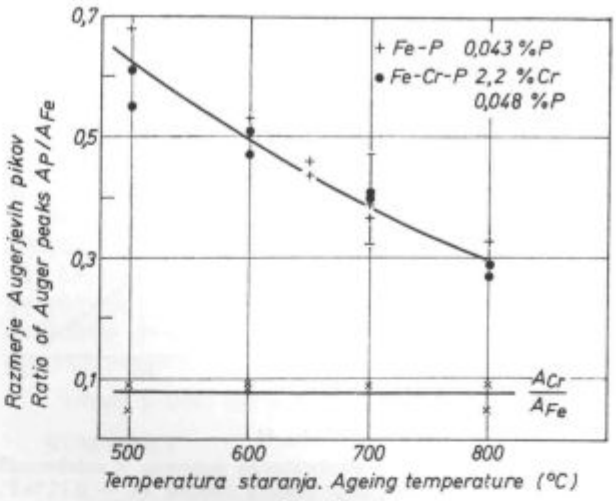
Tauber in Grabke[6] sta dognala, da zaradi tekmovanja v interkristalni segregaciji dušik in ogljik odrineta S, segregiran v železu.

Raziskali smo vpliv C in N na segregacijo P. Vzorce iz binarne Fe-P zlitine smo naogljičili v toku zmesi CH_4/H_2 pri 600 °C. Raznotežje pri določeni temperaturi in določen parcialni tlak CH_4 proti H_2 vodi do točno določene aktivnosti ogljika v kovini. V takih vzorcih oba elementa, ogljik in fosfor, segregirata po kristalnih mejah.

Slika 10 kaže razmerje normaliziranih višin pikov za P in C v odvisnosti od volumske koncentracije ogljika. Z naraščanjem koncentracije ogljika pada interkristalna koncentracija P in raste koncentracija C.

Naši rezultati kažejo, da je P odrinjen s kristalne meje zaradi odbojne C-P interakcije.

Rezultat te odbojne reakcije je sprememba v načinu preloma, ki jo prikazuje slika 11. Povečano volumsko koncentracijo ogljika spremlja zmanjšanje deleža interkristalnega preloma, kar seveda kaže, da je material manj krhek. Fe-P vzorci kažejo več interkristalnega preloma kot vzorec, ki vsebuje C, celo če je v obeh primerih enaka koncentracija fosforja na kristalni meji.



Slika 9

Delež interkristalnega preloma v odvisnosti od interkristalne koncentracije P.

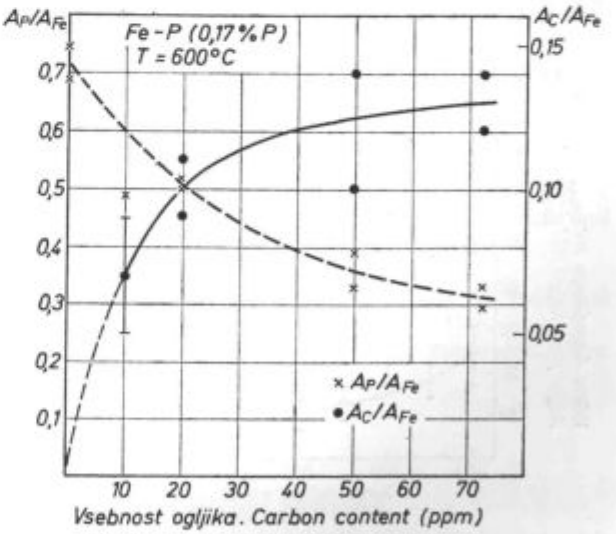
Fig. 9

Percentage of intergranular fracture as a function of P-grain boundary concentration.

concentration. The detected grain boundary concentrations of P within 500—800 °C temperature range are in good agreement with the values for an equivalent Fe-P binary alloy (Fig. 9). One can conclude that the interaction between Cr and P is only very weak.

Competition effect between P and C

The existence of competition effect in grain boundary segregation has been established by Tauber and Grabke[6] who found that sulfur in iron segregated can be displaced by nitrogen and carbon.

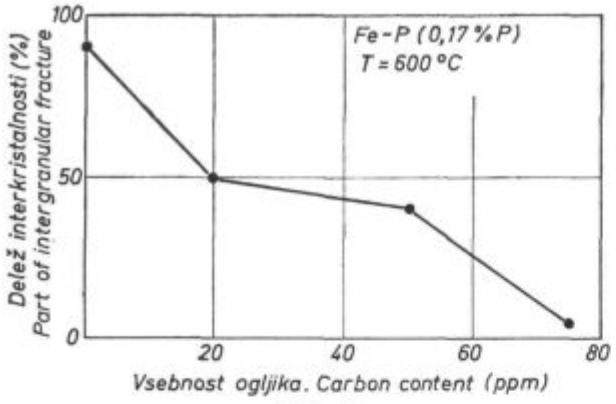


Slika 10

Spremembe interkristalne koncentracije P in C v odvisnosti od vsebnosti ogljika (zlitina Fe — 0,17 % P žarjena pri 600 °C).

Fig. 10

Variation of intergranular concentration of P and C with carbon bulk concentration (Fe — 0.17 % P alloy, annealed at 600 °C).



Slika 11

Sprememba deleža interkristalnega preloma v odvisnosti od volumske koncentracije ogljika (zlitina Fe — 0,17 % P, žarjena pri 600 °C).

Fig. 11

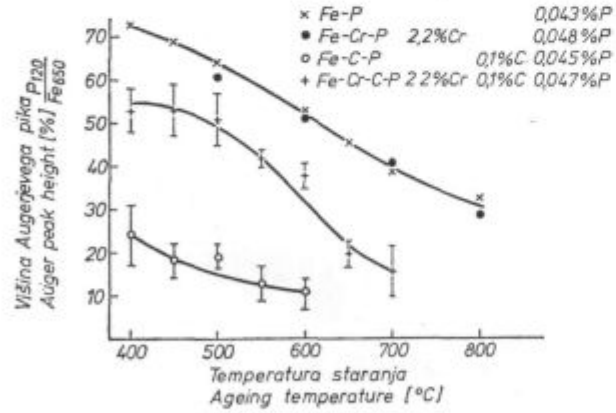
Variation of the percentage of intergranular fracture with carbon bulk concentration (Fe — 0.17 % P alloy, annealed at 600 °C).

Rezultat dodatka ogljika je torej ne samo odrinjenje P, ampak tudi povečanje interkristalne kohezije zaradi prisotnosti ogljika na kristalni meji. Naj omenimo še, da smo dobili kvalitativno enake rezultate v odrivnem efektu za N-P interakcijo, vendar je bil pozitivni efekt dušika na kohezijo manj poudarjen.

4. Segregacija P po kristalnih mejah v sistemu Fe-Cr-C-P

Ogljikova jekla ne kažejo popustne krhkosti zaradi fosforja. To razlagajo z odrivnim efektom ogljika. Dodatek Cr ali drugih legirnih elementov pa lahko privede do krhkosti v malo legiranih in v visoko legiranih jeklih.

Pregledali smo segregacijo P v štirikomponentnem sistemu Fe-Cr-C-P. Zlitina je imela 2,2 %



Slika 12

Sprememba interkristalne koncentracije P v odvisnosti od temperature žarjenja v zlitinah Fe-P, Fe-C-P, Fe-Cr-P in Fe-Cr-C-P.

Fig. 12

Variation of grain boundary concentration of P with anealing temperature in Fe-P, Fe-C-P, Fe-Cr-P and Fe-Cr-C-P alloys.

Now we have investigated the influence of C and N on P-segregation. Samples of the binary Fe-P alloys were carburized in flowing CH_4/H_2 mixtures at 600 °C. Equilibration at a given temperature and fixed partial pressure ratio of CH_4 to H_2 lead to a well defined carbon activity within the bulk.

In such samples both carbon and phosphorus segregate to the grain boundaries.

Fig. 10 shows the normalized peak height ratios of P and C as a function of carbon bulk concentration, with increasing carbon concentration the grain boundary concentration of P decreases and the grain boundary concentration of C increases.

Our results prove that P is displaced from the grain boundary due to repulsive C-P interaction.

The effect of this displacement reaction is a change in fracture mode which is seen in Fig. 11. Increasing carbon bulk concentration is accompanied by a decrease in the amount of intergranular fracture indicating that the material is now less brittle. The Fe-P specimens show more intergranular fracture than the specimens containing C, even if the grain boundary concentration of P is the same.

Therefore, the effect of carbon addition is not only a displacement of P but also an increase in grain boundary cohesion resulting from the presence of carbon in the grain boundary. It should be mentioned that we obtained qualitatively the same results for N-P interaction with respect to the displacement effect, but the positive effect of nitrogen on cohesion was less pronounced.

Grain boundary segregation of P in the Fe-Cr-C-P system

Plain carbon steels do not show temper embrittlement by phosphorus. This can be explained by the displacement effect of C. However, the addition of Cr and other alloying elements can lead to an embrittlement of low alloyed and high alloyed steels.

We have examined P segregation in the four component system Fe-Cr-C-P. The alloy contained 2.2 % Cr, 0.1 % C and 0.048 % P. The grain boundary concentration of P as a function of annealing temperature is given in Fig. 12. The diagram also shows the corresponding results for Fe-C-P, Fe-Cr-P and Fe-P alloys. All alloys contain nearly the same amount of P in the bulk. The grain boundary concentration of P is high in all cases. expect for the alloy Fe-C-P where carbon can displace P from the grain boundary. This displacement obviously does not occur in the Fe-Cr-C-P alloy. An interpretation of this result in terms of Cr-P cosegregation is not possible. We propose another explanation.

The precipitation of chromium carbides diminishes the concentration of dissolved C. This prevents the displacement of P by C. Chromium

Cr, 0,1 % C in 0,048 % P. Koncentracija P na kristalni meji je prikazana kot funkcija temperature žarjenja na sliki 12. Diagram prikazuje tudi ustrezne vrednosti za zlitine Fe-C-P, Fe-Cr-P in Fe-P. Vse zlitine imajo približno enako volumsko koncentracijo P. Interkristalne koncentracije P so visoke v vseh primerih, izjema je zlitina Fe-C-P, kjer ogljik odriva P s kristalnih mej. Odrivanja očitno ni v zlitini Fe-Cr-C-P. Interpretacija teh ugotovitev ni mogoča na osnovi kosegregacije, zato predlagamo drugo razlago.

Precipitacija kromovih karbidov zmanjša koncentracijo raztopljenega C. To prepreči, da bi ogljik odrinil fosfor. Kromovi karbidi precipitirajo po mejah in po volumnu. Zato se opazi povečan Augerov signal za Cr na interkristalnih prelomih, kjer je prisoten tudi ogljik. Prisotnost kromovih karbidov po mejah je bila potrjena z metalografskimi raziskavami in z razpršilnimi preizkusi. Naši preizkusi razlagajo dejstvo, da so popustni krhkosti podvržena malo legirana jekla, ki vsebujejo karbidotvorne elemente, na primer Cr, Mo, Mn itd., medtem ko ogljikova jekla niso krhka tudi pri relativno visokih količinah P.

C. REZIME

1. P segregira po Mc Leanovi enačbi. Delež interkristalnega preloma raste s koncentracijo P po kristalnih mejah.

2. Med Cr in P je le zelo rahla interakcija. Opazili nismo nobene kosegregacije.

3. C odriva P s kristalnih mej in s tem povečuje interkristalno kohezijo.

4. V prisotnosti kroma ni odrivnega efekta C. Izločanje Cr karbidov zmanjšuje koncentracijo raztopljenega C, zato pride do segregacije P in krhkosti.

5. Izsledki razlagajo dejstvo, da v ogljikovih jeklih ni krhkosti zaradi P. Vendar lahko P inducira popustno ali lezno krhkost v malo legiranih jeklih, ki vsebujejo Cr ali druge karbidotvorne elemente.

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RAZPRAVA

Ph. Aubrun, Sollac, Florange

Ali je normalno, da jekla za globoko vlečenje z visoko mejo plastičnosti in z 0,06 % C in 0,08 % P ne kažejo nobene krhkosti?

H. Erhart

To vprašanje razlagajo naše meritve. Krhkost zlitine Fe-P se zmanjša z dodatkom majhnih količarbides precipitate in the bulk as well as in the grain boundaries. Therefore, an enhanced Auger signal of Cr is observed for the grain boundary fracture surfaces, but carbon is also present. The existence of chromium carbides in the grain boundaries was confirmed by metallographic investigations and sputtering experiments.

Our experiments explain the fact that low alloyed steels containing carbide forming elements like Cr, Mo, Mn etc. exhibit temper embrittlement by phosphorus while plain carbon steels do not embrittle even if they contain relatively high P-concentrations.

SUMMARY

1. P segregates according to the Mc Lean equation. The part of intergranular fracture increases with P-grain boundary concentration.

2. There is only a very weak interaction between Cr and P. No cosegregation is observed.

3. C displaces P from the grain boundaries and improves intergranular cohesion.

4. The displacement effect of C is suspended by the presence of Cr. The precipitation of Cr-carbides diminishes the concentration of dissolved C, so that P-segregation and embrittlement occurs.

5. The observations explain the fact that in plain carbon steels no embrittlement by P occurs. However, in low alloyed steels with Cr or other carbide forming elements temper embrittlement or creep embrittlement can be induced by P.

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DISCUSSION

Ph. Aubrun, Sollac, Florange

Is it normal that steels for deep drawing with high limit of elasticity and with 0.06 % C and 0.08 % P do not show any fragility.

H. Erhart

This observation is well explained by our measurements. The embrittlement of Fe-P alloys

čin C zaradi tekmovanja med P in C na kristalnih mejah (sl. 10 in 11). 0.06 % C je zadosti, da se prepreči krhkost zaradi segregacije P v nelegiranem jeklu.

S. Engineer, Thyssen, Edelstahlwerke, Krefeld

Imam vprašanje glede vaše predzadnje slike. Ali se lahko razlaga tako, da se v jeklu z 0.3 % C ne pojavi krhkost zaradi fosforja?

H. Erhart

Ta razlaga je veljavna le za jekla, ki nimajo elementov karbidotvorcev. Segregacija P po kristalnih mejah se izvrši v tekmovanju z obogatitvijo s C. Dodatek elementov, ki niso karbidotvorci, na pr.: Ni, Si itd., ne zmanjša količine raztopljenega C. V takih zlitinah je majhna občutljivost za krhkost.

Dodatek elementov karbidotvorcev, npr. Cr, Mn, itd., zmanjša količino raztopljenega C in vodi k manj poudarjenemu izpodrinjenju P s C. To dokazuje sl. 12. Intenziteta segregacije P v zlitini Fe-Cr-C-P je mnogo večja kot v zlitini Fe-C-P. Jekla, ki imajo zadostne količine elementov karbidotvorcev, so podvržena krhkosti zaradi P, četudi je vsebnost C velika.

C. Goux, ESNM, Saint Etienne

Omenili ste, da ogljik in dušik povečujeta trdnost kristalnih mej v železu. Ali mogoče veste za druge elemente, ki imajo podoben učinek, na primer bor?

H. Erhart

Ni nam znano, ali so poleg C in N še drugi elementi, ki lahko povečajo kohezijo kristalnih mej. Tudi dosedaj ni jasen vpliv bora. Pri nas nismo raziskovali segregacijskega ponašanja bora in njegovega vpliva na interkristalno kohezijo.

F. Vodopivec

Razumel sem, da se lahko segregacija fosforja razvije do enega sloja fosforja ali fosfida po kristalnih mejah. Težko si predstavljam, kakšne so mehanske lastnosti takega železa. Ali nam lahko o tem poveste kaj več?

H. Erhart

Pri relativno visokih koncentracijah fosforja in po toplotni obdelavi v določenem intervalu temperature se lahko kristalne meje nasitijo z enim slojem fosforja. To je pokazala spektroskopija Augerovih elektronov in se lahko potrdi s poljsko ionsko mikroskopijo. Po kristalnih mejah ni prisoten fosfid, temveč dvodimenzionalen sloj atomov (ali ionov) fosforja. Prav gotovo je kohezija takih kristalnih mej zelo majhna in je material zelo krhek.

is reduced by addition of low amounts of C due to competition between C and P in the grain boundaries (fig. 10, 11). 0.06 % C is sufficient to prevent embrittlement caused by P segregation in an unalloyed steel.

S. Engineer, Thyssen, Edelstahlwerke, Krefeld

I have a question to your second last slide. Could one interpret it in such a way, that in a steel with 0.3 % C embrittlement due to phosporus does not occur?

H. Erhart

This interpretation is correct only for steels containing no carbide forming elements. Grain boundary segregation of P occurs in competition with enrichment by C. The addition of non-carbide forming elements, like Ni, Si, etc., does not reduce the amount of dissolved C. In such alloys the susceptibility to embrittlement is low.

The addition of carbide forming elements like Cr, Mn, etc., reduces the amount of dissolved C leading to a less pronounced displacement of P by C. This is demonstrated in fig. 12. The segregation level of P in Fe-Cr-C-P alloy is much higher than in Fe-C-P alloy. Steels containing sufficient amounts of carbide forming elements show embrittlement due to P — even if the carbon concentration is high.

C. Goux, ESNM, Saint Etienne

You have mentioned that carbon and nitrogen improve the strength of grain boundaries in iron. Do you know if there are other elements which have the same effect, possibly boron?

H. Erhart

We do not know whether there are other elements beside C and N which can improve the cohesion of grain boundaries. Also the effect of boron is not clear as yet. Neither the segregation behaviour of B nor its effect to grain boundary cohesion were investigated by us.

F. Vodopivec

I have understood that the segregation of phosphorus could develop to a monolayer of phosphorus or phosphide at the grain boundaries. I can hardly form an idea of the mechanical properties of such iron. Could you give us more details?

H. Erhart

For relatively high phosphorus concentrations and after heat treatment within certain temperature range the grain boundaries of iron or steel can become saturated with a monolayer of phosphorus. This was found by Auger-electron spectroscopy and could be confirmed by field-ion-microscopy. It is not a phosphide which is present at the grain boundary, but a virtually two dimensional layer of phosphorus atoms (or ions). Certainly the cohesion of such grain boundaries is very low and the material is very brittle.