# *Popustna krhkost utopnega jekla za delo v vročem s 5 % kroma*

# *Temper Embrittlement of 5 wt.-% Cr Hot Work Die Steel*

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**ASM/SLA: Q26s, N8a, TSk**

*Raziskali smo vpliv parametrov popuščanja na udarno žilavost in lomne značilnosti utopnega jekla za delo v vročem Č.4751 s postmartenzitno mikrostrukturo.*

*Prevladujoči dejavnik, ki kontrolira razvoj krhkosti, je segregiranje fosforja na mejah zrn in na drugih medplastjih v kovini. Segregacijski učinek fosforja spremlja kosegregacija silicija skupaj s sočasno precipitacijo karbidov.*

## 1. UVOD

Orodno jeklo s sekundarnim utrjevanjem z 0,4 % C, 5 % Cr, 1,3 % Mo, 0,4 % V in 1 % Si (Č.4751) se uporablja predvsem za orodja in utope, ki obratujejo pri povišanih temperaturah, ker združuje dobro obstojnost trdote z veliko obrabno odpornostjo, zadostno žilavost ter majhno občutljivost na pokanje v vročem. Jeklo Č.4751 kaže efekt sekundarnega utrjevanja, ako je popuščano pri temperaturah okrog 500° C, ugotovljeno pa je bilo tudi, da s pričetkom sekundarnega utrjevanja sovpada znaten padec žilavosti. Mehanizem pojava je povezan s precipitacijo karbidov $M_6C$ in MC iz martenzita, kot tudi z atermalno transformacijo zaostalega avstenita. Ugotovljeno je bilo[1], da to krhkost lahko skoraj odpravimo z odstranjevanjem silicija iz jekla in zdi se, da je posledica vpliva silicija na precipitacijo karbidov med letvicami martenzita.

Ako pa jeklo Č.4751 popuščamo nekaj ur v temperaturnem območju med 550° C in 600° C, opazimo določen zastoj v pričakovani evoluciji žilavosti[2]. Mikrostrukturni izvor te krhkosti do sedaj še ni bil zadovoljivo pojasnjen, zato smo ga podrobno raziskali.

## 2. EKSPERIMENTALNI DEL

Majhno količino jekla Č.4751, trgovske kvalitete, smo pretalili v 20-kg vakuumski peči, ga ulili v ingot ter le-tega v vročem izvaljali v palico, premera 15 mm. Kemična sestava jekla je prikazana v **tabeli 1**.

**Tabela 1:** Kemična sestava preiskanega jekla v ut. %

| C | Si | Mn | P | S | Cr | Mo | V | Al |
|---|---|---|---|---|---|---|---|---|
| 0,39 | 0,93 | 0,30 | 0,023 | 0,014 | 5,86 | 1,12 | 0,28 | 0,038 |

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*The influence of tempering parameters on impact energy and fracture characteristics of Č.4751 hot work die steel with post-martensitic microstructure has been investigated.*

*The dominant factor controlling the evolution of brittleness is the segregation of phosphorus on grain boundaries as well as on other interfaces in metal. The segregation effect of phosphorus is accompanied by cosegregation of silicon together with simultaneous carbide precipitation.*

## *1. INTRODUCTION*

*Secondary hardening tool steel with 0,4 % C, 5 % Cr, 1,3 % Mo, 0,4 % V and 1 % Si (Č.4751) is used primarily for tools and dies which operate at elevated temperatures because it associates good hardness retention with high resistance to wear, sufficient toughness and little susceptibility to heat checking. Č.4751 steel exhibits secondary hardening effect when tempered around 500° C and a sharp drop in toughness, coincident with the onset of secondary hardening, was observed too. The mechanism involved is associated with precipitation of $M_6C$ and MC type carbides from the as-quenched martensite and also due to athermal transformation of retained austenite. It has been established[1] that this embrittlement can be almost eliminated by removal of silicon and it seems that the embrittlement resulted from the influence of silicon on interlath carbide precipitation.*

*But when Č.4751 steel is tempered at temperature range of 550° C to 600° C for a few hours some standstill in the expected evolution of toughness is observed[2]. The microstructure origins of this embrittlement have not been clarified yet that is why we investigated them thoroughly.*

## *2. EXPERIMENTAL*

*A small quantity of commercial Č.4751 steel was remelted in a 20 kg vacuum-induction furnace, then it was cast in an ingot and hot-rolled to a 15 mm rod. The chemical composition of the steel is shown in **Table 1**.*

***Table 1:** Chemical composition of the investigated steel, wt. — %*

| C | Si | Mn | P | S | Cr | Mo | V | Al |
|---|---|---|---|---|---|---|---|---|
| 0,39 | 0,93 | 0,30 | 0,023 | 0,014 | 5,86 | 1,12 | 0,28 | 0,038 |

*Charpy V-notch specimens were machined from the rod, which was previously normalized and soft annealed*

Iz palice, ki je bila normalizirana in mehko žarjena 2 uri pri temperaturi 800° C, smo izdelali Charpyjeve preizkušance z V zarezo. Preizkušanci so bili v vakumski peči avstenitizirani 15 min. pri 960° C, kaljeni v toku plinastega dušika pri tlaku 0,5 MPa, nato dvakrat popuščeni po 2 uri pri 710° C, z vmesnim podhlajevanjem pri −196° C, ter nazadnje dodatno popuščeni v temperaturnem območju od 450 do 660° C 2 uri, 5 ur oziroma 24 ur, s končnim ohlajanjem v vodi.

Merjenja žilavosti pri sobni temperaturi so bila opravljena z vsaj petimi Charpyjevimi preizkušanci za vsako temperaturo popuščanja, medtem ko je bila Brinellova trdota merjena na vsakem preizkušancu.

Mikrofraktografske preiskave prelomnih površin Charpyjevih preizkušancev smo opravili z vrstičnim elektronskim mikroskopom JEOL JSM-35 (SEM), medtem ko smo mikrostrukturo preiskali s presevnim elektronskim mikroskopom JEOL FX (TEM), ki je bil opremljen z analizatorjem karakterističnih rentgenskih žarkov (EDS).

Opravili smo tudi elektrolitsko izolacijo karbidov, izolat pa je bil analiziran z rentgensko difrakcijsko tehniko.

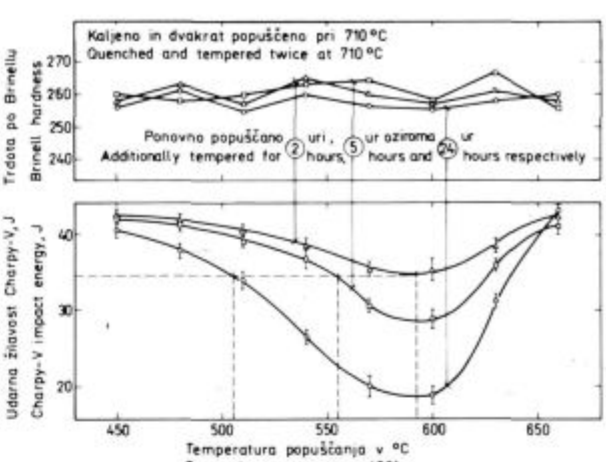
## 3. REZULTATI

V diagramu na **sliki 1** so prikazane odvisnosti med udarno žilavostjo in temperaturo dodatnega popuščanja, različno dolge čase popuščanih Charpyjevih V-preizkušancev, ki so bili pred tem kaljeni ter dvakrat popuščeni pri 710° C, z vmesnim podhlajevanjem v tekočem dušiku.

Podhlajevanje med začetnim dvojnim popuščanjem je bilo potrebno, da bi se izognili vplivu morebitnega zaostalega avstenita.

Medtem ko trdota jekla ostaja navidezno neodvisna od parametrov popuščanja, pa Charpyjeva udarna žilavost po 24-urnem popuščanju pri 600° C pade od začetnih 42 J na vsega okrog 20 J. Močan padec Charpyjevih vrednosti pri jeklu, ki je bilo 5 ur, zlasti pa 24 ur popuščano pri 600° C, je verjetno posledica razvoja reverzibilne popustne krhkosti, kot je bilo ugotovljeno v eni prejšnjih raziskav[3].

Segregacije, ki nastopajo pri reverzibilni popustni krhkosti, so ravnotežnega tipa. Začetna segregacija




**Slika 1:**
Vpliv dodatnega popuščanja na trdoto in udarno žilavost jekla Č.4751, ki je bilo pred tem kaljeno in dvakrat popuščeno pri 710° C, z vmesnim podhlajenjem v tekočem dušiku

***Fig. 1***
*Influence of additional tempering on hardness and impact energies of steel Č.4751 which has been previously quenched and tempered twice at 710° C with intermediate undercooling in liquid nitrogen.*

*at 800° C for 2 hours. Specimens were then austenitized at 960° C for 15 min. in a vacuum furnace, quenched in a flow of gaseous nitrogen at a pressure of 0,5 MPa, tempered twice at 710° C for 2 hours with intermediate undercooling at — 196° C, then additionally tempered in a temperature range of 450° C to 660° C for 2 hours, 5 hours and 24 hours respectively and finally cooled in water.*

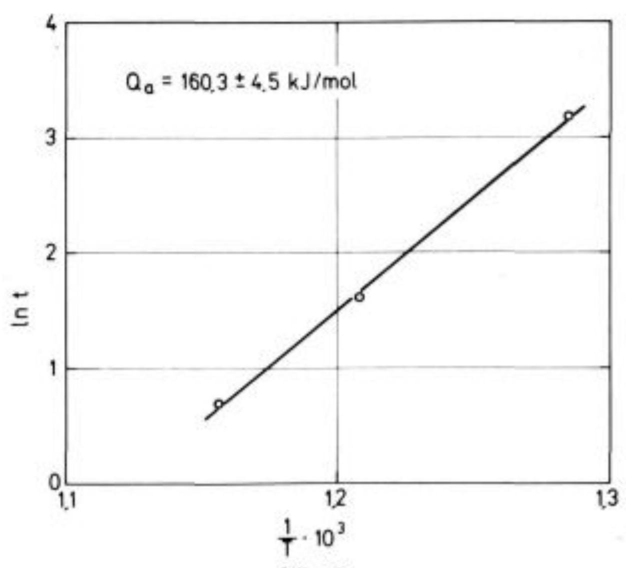
*At least five Charpy V-notch specimens were tested at room temperature for each tempering temperature, while the Brinell hardness was measured on every specimen. The microfractographic examination on fracture surfaces of Charpy specimens was carried out in the JEOL JSM-35 scanning electron microscope (SEM), while the microstructure was investigated in transmission electron microscope JEOL FX (TEM) equipped with energy dispersive spectroscopy (EDS). The electrolytic isolation of carbides was also carried out and the isolate was analyzed with X-ray diffraction technique.*

## *3. RESULTS*

*Charpy V-notch energy versus tempering temperatures curves as obtained for specimens additionally tempered for various periods, after quenching and double tempering at 710° C with intermediate undercooling in liquid nitrogen, are shown in **Fig. 1**. Undercooling in between the initial double tempering was necessary to avoid the influence of eventual retained austenite.*

*The hardness of steel remains virtually independent of the tempering parameters, whereas the Charpy V-notch impact energy drops from initial value of 42 J to only about 20 J after tempering 24 hours at 600° C. The drastic drop in the Charpy values of steel after tempering for 5 hours but particularly 24 hours at 600° C is probably partly due to reversible temper embrittlement, as established in one of earlier investigations[3].*

*The segregations involved in reversible temper embrittlement are of equilibrium type, namely when the ageing temperature is risen, the initial segregation rate increases following the temperature dependence of the bulk diffusion coefficient, while the maximum i. e. steady*




**Slika 2:**
Izvrednotenje aktivacijske energije za segregiranje fosforja z uporabo Arrheniusove enačbe

***Fig. 2***
*Evaluation of the activation energy of segregation of phosphorus according to the Arrhenius equation.*

namreč z dviganjem temperature žarjenja raste ter sledi temperaturni odvisnosti koeficienta volumske difuzije. Maksimalna, to je stacionarna interkristalna koncentracija pri tem pada, in to razlaga reverzibilnost krhkosti pri visokih temperaturah feritnega območja, kot je bilo tudi ugotovljeno v že citirani referenci[3].

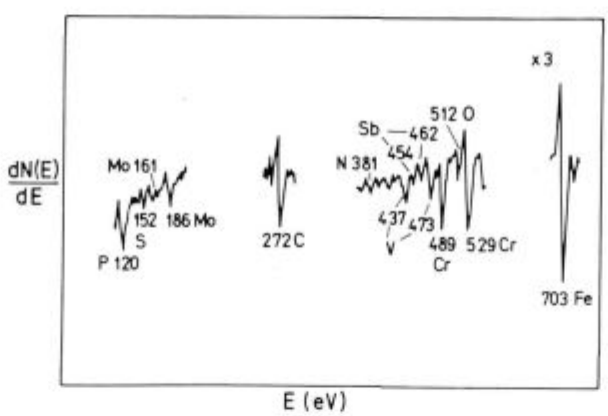
Udarna žilavost je sorazmerna intenziteti segregacij, enak nivo segregacij je bil zato dosežen s popuščanjem, bodisi 2 uri pri 592° C bodisi 5 ur pri 555° C bodisi 24 ur pri 505° C. Ako predpostavimo, da še celo po 24 urah popuščanja ni dosežena končna največja intenziteta segregacije, potem je levi del diagrama na sliki 1 mogoče uporabiti za določitev aktivacijske energije za volumsko difuzijo oligoelementa, ki kontrolira razvoj krhkosti. Iz naklona premice v dvojnem logaritemskem diagramu časa popuščanja proti recipročni vrednosti temperature popuščanja, prikazanem na **sliki 2**, je bila izračunana aktivacijska energija približno 160 kJ/mol, kar je zelo blizu aktivacijski energiji za difuzijo fosforja v feritu. Zares je že bilo potrjeno z Augerjevo spektroskopijo, da v jeklih podobne vrste segregira zlasti fosfor. Romhányi s sodelavci[4] je v orodnem jeklu s 5 % kroma, ki je bilo avstenitizirano pri 1100° C, kaljeno in popuščano 2 uri pri 600° C, našel na mejah kristalnih zrn do 6 % fosforja in 1 % žvepla, pa tudi sledove dušika in antimona. Augerjev spekter, prikazan na **sliki 3**, dokazuje, da so segregacije fosforja in žvepla v soodvisnosti z obogatitvijo s kromom (8 do 9 %), vanadijem (približno 2 %) in molibdenom (3 do 5 %). Nadalje je opazen izrazit ogljikov pik (8 do 9 %) z deloma karbidno strukturo. Augerjevi piki kažejo rahlo lokalno fluktuacijo, vendar pa bi lahko poudarili soodvisnosti med kromovim pikom ter vsoto segregiranega fosforja in žvepla.

Že omenjene spremembe v udarni žilavosti se odražajo tudi na morfologiji prelomnih površin. Po dvakratnem popuščanju 2 uri pri 710° C, z vmesnim podhlajevanjem v tekočem dušiku, je frakturna površina Charpyjevih preizkušancev transgranularna, drobno jamičasta, torej duktilna, kakršna je prikazana na **sliki 4**. Po dodatnem popuščanju 24 ur pri 600° C se pot napredovanja razpok spremeni, prelom postane intergranularen vzdolž meja primarnih avstenitnih zrn **(slika 5)**, čeprav so opaženi tudi kvazicepilni detajli ter posamični duktilni grebeni **(slika 6)**.

*state grain boundary concentration decreases. This accounts for the "reversibility" of embrittlement at higher temperatures of the ferritic range, as observed also in the already quoted reference[3].*

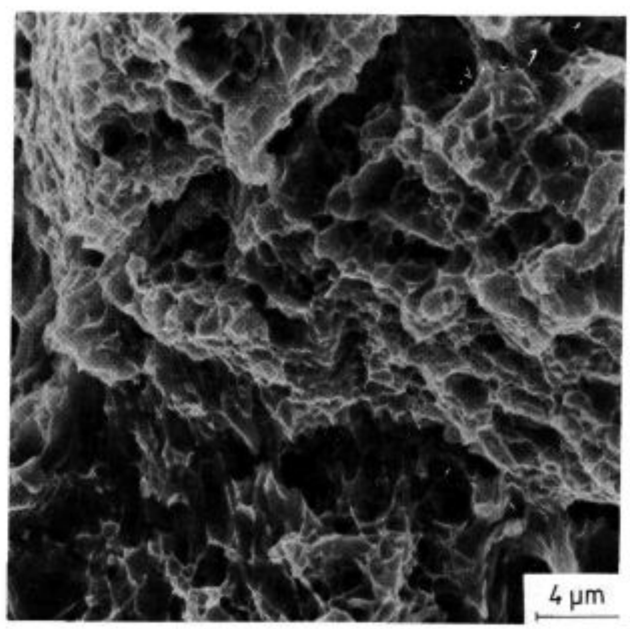
*The impact energy is proportional to the level of segregation and the same level of segregation is therefore achieved after tempering for 2 hours at 592° C or 5 hours at 555° C or 24 hours at 505° C. If the assumption is considered that the final maximal level of segregation is not attained even after 24 hours of tempering, then the left side of the diagram shown in Fig. 1 could be used for the determination of the activation energy for bulk diffusion of residuals, which controls the development of embrittlement. An activation energy of about 160 kJ/mol was derived from the slope of a log-log plot of time vs. reciprocal tempering temperature in* ***Fig. 2****, which is very close to that for bulk diffusion of phosphorus in ferrite. It was already confirmed indeed by the Auger spectroscopy, that particularly phosphorus segregates in such type of tool steel. Romhányi and coworkers[4] found up to 6 % of phosphorous and 1 % of sulphur as well as traces of nitrogen and antimony on the grain boundaries in 5 wt. — % chromium tool steel, austenitized at 1100° C, quenched and tempered at 600° C for 2 hours. The Auger spectrum shown in* ***Fig. 3*** *proved, that the segregation of phosphorus and sulphur is in correlation with the enrichment of chromium (8—9 %), vanadium (approx. 2 %) and molybdenum (3—5 %). Further, the strong carbon peak (8—9 %) with partly carbide structure is remarkable. The Auger peaks exhibit slight local fluctuaction, but the correlation of the chromium peak with the sum of phosphorus + sulphur segregated should be underlined.*

*The already mentioned changes in the impact values are also reflected in fracture surfaces morphology. After tempering twice at 710° C for 2 hours with intermediate*



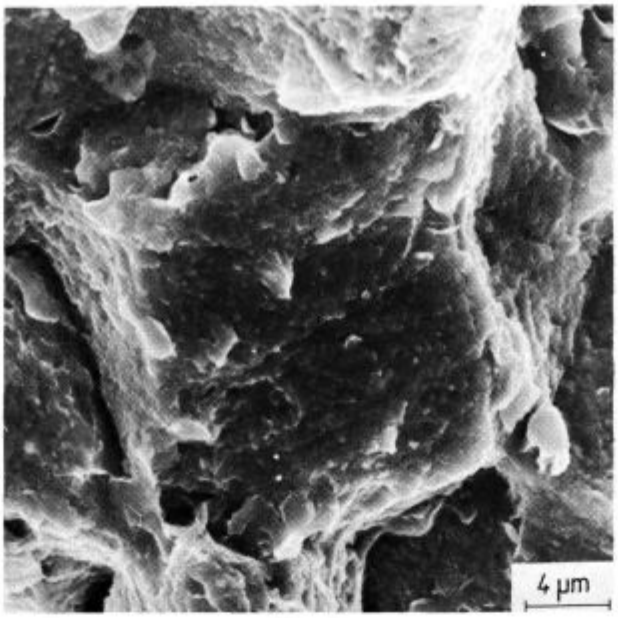

**Slika 3:**
Augerjev spekter intergranularne prelomne površine jekla s 5 % kroma, avstenitiziranega pri 1100° C, kaljenega ter popuščenega pri 600° C (Lit. 4)

***Fig. 3***
*Auger spectrum of the intergranular fracture surface of steel with 5 wt. — % chromium, austenitized at 1100° C, quenched and tempered at 600°C (Ref. 4).*



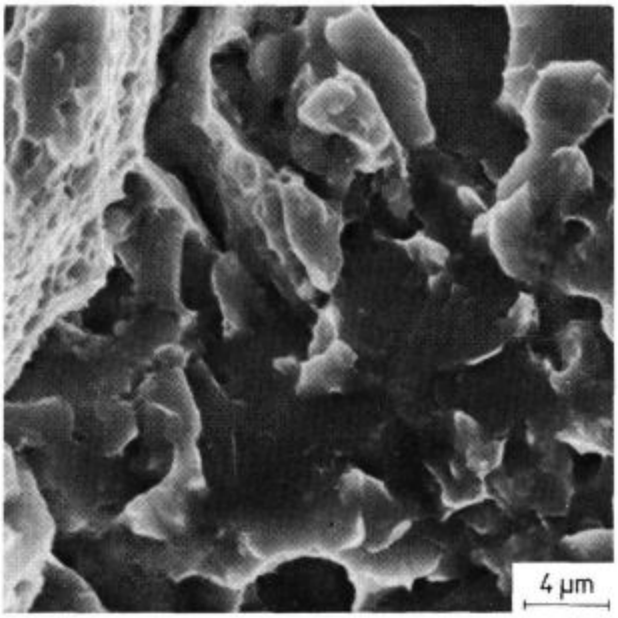

**Slika 4:**
Fraktografski posnetek Charpyjevega preizkušanca, kaljenega in dvakrat popuščenega pri 710° C, z vmesnim podhlajenjem v tekočem dušiku

***Fig. 4***
*Fractographs of Charpy specimen, quenched and tempered twice at 710° C with intermediate undercooling in liquid nitrogen.*




**Slika 5:**
Fraktografski posnetek Charpyjevega preizkušanca, kaljenega in dvakrat popuščenega pri 710° C, z vmesnim podhlajenjem, nato dodatno popuščenega 24 ur pri 600° C. Interkristalno krhko

***Fig. 5***
*Fractographs of Charpy specimen, quenched and tempered twice at 710° C with intermediate undercooling, then additionally tempered at 600° C for 24 hours. Intercrystalline brittle.*




**Slika 6:**
Fraktografski posnetek Charpyjevega preizkušanca, kaljenega in dvakrat popuščenega pri 710° C, z vmesnim podhlajenjem, nato dodatno popuščenega 24 ur pri 600° C. Kvazicepilno s posamičnimi duktilnimi grebeni

***Fig. 6***
*Fractographs of Charpy specimen, quenched and tempered twice at 710° C with intermediate undercooling, then additionally tempered at 600° C for 24 hours. Quasi-cleavage and single ductile tearing.*

V literaturi[5–8] so bili kot najvažnejši identificirani precipitati v kaljenem in pri povišanih temperaturah popuščenem orodnem jeklu s 5 % kroma, navedeni $M_2C$, $M_7C_3$ ter $M_6C$. Okuno[7] je ugotovil, da so v orodnem jeklu H-13, kaljenem v olju in popuščenem pri 600° C, le karbidi MC in $M_6C$, karbide $M_7C_3$ v obliki aglomeriranih zrn najdemo po popuščanju pri višjih temperaturah, med 600 in 650° C.

Tip precipitatov je bil določen z uporabo TEM in EDS analize, kot tudi z rentgensko difrakcijsko tehniko, upoštevaje pri tem citirane podatke, nanašajoče se na termično zgodovino jekla. Rentgenska difrakcija elektrolitskega izolata odkrije v jeklu, ki je bilo kaljeno in med dvakratnim popuščanjem pri 710° C še podhlajeno, karbide $M_7C_3$ in $M_6C$ v enakem deležu. Elektronski posnetek mikrostrukture tega vzorca jekla, prikazan na **sliki 7**, kaže značilno substrukturo visoko popuščenega martenzita, sestavljeno iz malih podzrn, nanizanih vzdolž prvotnih martenzitnih igel, vrste precipitatov v glavnem vzdolž meja podzrn in redke precipitate v letvicah martenzita.

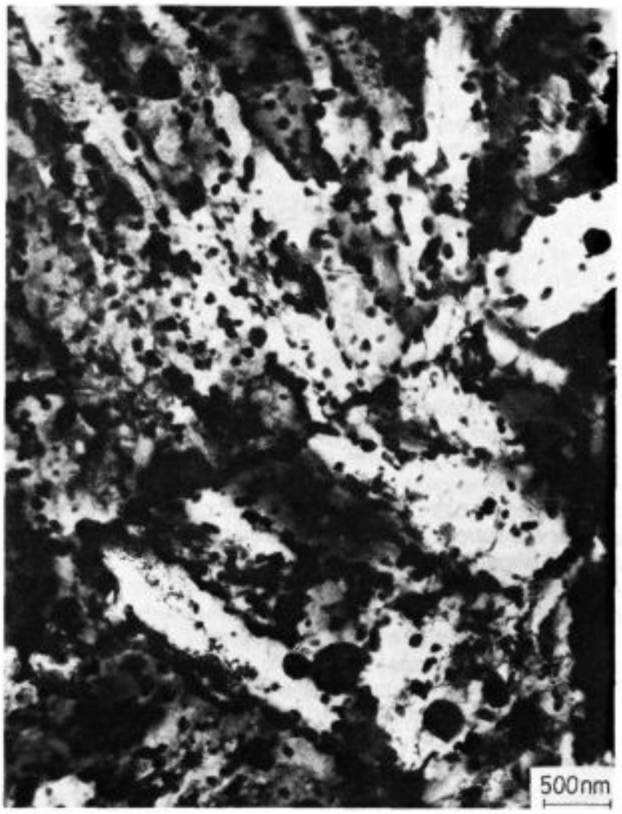
Po dodatnem popuščanju istega jekla 24 ur pri 600° C smo ugotovili majhen porast količine karbidov $M_6C$, posledično pa je bila zmanjšana količina karbidov, vrste $M_7C_3$. Posamični precipitati $M_6C$ so bolj grobi, vendar pa število precipitatov vzdolž meja podzrn ter vzdolž letvic ostaja skoraj nespremenjeno **(slika 8)**. Relativno majhna razlika v količini in obliki karbidov ne more biti odgovorna za povsem drugačno morfologijo preloma, povzročeno z dodatnim popuščanjem jekla 24 ur pri temperaturi 600° C. Pri EDS analizi smo pozornost usmerili zlasti na precipitate na mejah podzrn in med letvicami, ker bi lahko bili povezani s potjo razpoke. Tipični EDS spekter precipitata v jeklu, ki je bilo po kaljenju in dvakratnem popuščanju pri 710° C, z vmesnim podhlaje-

*undercooling in liquid nitrogen, the fracture surface is small dimpled and transgranular, therefore ductile* ***(Fig. 4)****. After an additional tempering at 600° C for 24 hours, the cracks propagation path changed and an intergranular fracture along preaustenite grain boundaries* ***(Fig. 5)*** *quasi-cleavage fracture details and single ductile tearing are observed too* ***(Fig. 6)****.*

*In references[5–8] the main precipitates present in as quenched and at elevated temperature tempered 5 wt. – % chromium tool steel were identified as $M_2C$, $M_7C_3$ and $M_6C$. Okuno[7] established that in oil quenched and at 600° C tempered H-13 tool steel only carbides MC and $M_6C$ are found, $M_7C_3$ carbides in shape of agglomerated grains are found after tempering at higher temperatures between 600° C and 650° C.*

*The type of precipitates was established using TEM and EDS analysis as well as X-ray diffraction technique, also considering the quoted data relating to the thermal history of the steel. X-ray diffraction of electrolytic isolate revealed in steel, as quenched and tempered twice at 710° C with intermediate undercooling, $M_7C_3$ and $M_6C$ carbides in equal portion. Electron micrographs of this specimen in* ***Fig. 7*** *show a characteristic substructure of high-tempered martensite, consisting of small subgrains arranged along the former martensite needles, rows of precipitates mainly along the subgrain boundaries and rare intralath precipitates.*

*After additional tempering of the same steel for 24 hours at 600° C a small increase of the quantity of $M_6C$ carbides and consequential decrease of the quantity of $M_7C_3$ precipitates are found. Some $M_6C$ precipitates are coarser, however the number of precipitates along lath and subgrain boundaries remains nearly unchanged* ***(Fig. 8)****. The relatively small difference in quantity and size of carbides couldn't be responsible for*

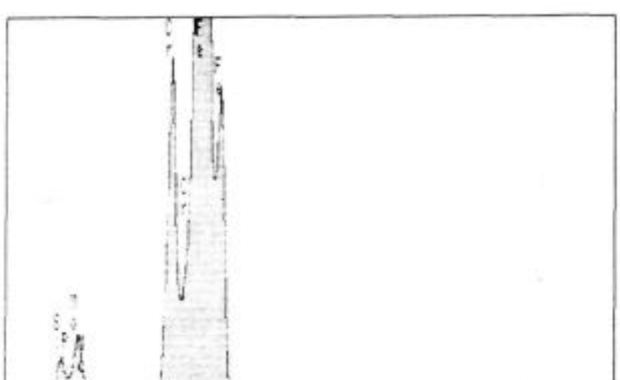



**Slika 7:**
TEM mikrografski posnetek jekla Č.4751, kaljenega in dvakrat popuščenega pri 710°C, z vmesnim podhlajenjem v tekočem dušiku.

***Fig. 7***
*TEM micrographs of steel Č.4751, quenched and tempered twice at 710°C with intermediate undercooling in liquid nitrogen.*


**Slika 8:**
TEM mikrografski posnetek jekla Č.4751, kaljenega in dvakrat popuščenega pri 710°C, z vmesnim podhlajenjem, nato dodatno popuščenega 24 ur pri 600°C

***Fig. 8***
*TEM micrographs of steel Č.4751, quenched and tempered twice at 710°C with intermediate undercooling, then additionally tempered at 600°C for 24 hours.*



**Slika 9:**
Značilni EDS rentgenski spekter medplastja martenzita letvica/karbid v jeklu Č.4751, kaljenem in dvakrat popuščenem pri 710°C, z vmesnim podhlajenjem, nato dodatno popuščenem 24 ur pri 600°C

***Fig. 9***
*Characteristic EDS X-ray spectrum of martensite lath/carbide interface in steel Č.4751, quenched and tempered twice at 710°C with intermediate undercooling, then additionally tempered at 600°C for 24 hours.*

*the completely different fracture morphology produced by the additional tempering of steel for 24 hours at 600°C.*

*At EDS X-ray analysis the attention was focused on precipitates at lath and subgrain boundaries, because they could be connected to the crack path. A typical EDS spectrum for a precipitate in steel, quenched and tempered twice at 710°C with intermediate undercooling then additionally tempered at 600°C for 24 hours, is shown in* ***Fig. 9****. It is characteristic for chromium rich carbide but it is not clear whether iron and molybdenum are detected from carbide phase or from the matrix. By focusing the beam to the martensite lath/carbide interface, the strong peak of silicon and phosphorus was regularly detected. The peak of sulphur could be covered with that of molybdenum. For this reason it is not possible to detect an eventual segregation of sulphur at grain boundaries.*

## *4. DISCUSSION*

*Temper embrittlement of Č.4751 tool steel is easily provoked when the high-tempered steel with post-martensitic microstructure is additionally tempered for a few hours at 600°C.*

*Fracture morphology of additionally tempered steel changes from transcrystalline and ductile into mixed mode i. e. intercrystalline and quasi-cleavage transcrys-*

vanjem, še dodatno popuščeno 24 ur pri temperaturi 600° C, je prikazan na **sliki 9**. Spekter je značilen za s kromom bogat karbid, čeprav ni jasno, ali sta železo in molibden detektirana iz karbidne faze ali iz osnove. S fokusiranjem snopa na mejo martenzita letvica/površina karbida smo redno zabeležili močan silicijev in fosforjev pik. Pik, ki pripada žveplu, bi bil lahko prekrit z molibdenovim pikom. Iz tega razloga ni mogoče zaznati morebitnih segregacij žvepla na mejah zrn.

## 4. RAZPRAVA

Popustno krhkost orodnega jekla Č.4751 lahko povzročimo tako, da pri visokih temperaturah popuščeno jeklo s postmartenzitno mikrostrukturo dodatno popuščamo nekaj ur pri temperaturi 600° C. Morfologija preloma dodatno popuščenega jekla se spremeni od transkristalne duktilne v mešano obliko, to je interkristalno ter kvazicepilno transkristalno. Med duktilnim in krhkim jeklom pa nismo opazili nobene pomembne razlike, nanašajoče se na morfologijo ter sestavo karbidnih precipitatov.

Iz rentgenske EDS analize sledi, da vsebnost molibdena v trdni raztopini ni bila bistveno spremenjena z dodatnim popuščanjem nekaj ur pri 600° C. Po drugi strani je očividno, da prisotnost molibdena v trdni raztopini ni v celoti preprečila segregiranja fosforja na notranjih površinah. Segregiranje fosforja se pojavlja vzporedno s segregiranjem silicija, aktivacijska energija za volumsko difuzijo silicija v feritu (258 kJ/mol) pa je mnogo višja od aktivacijske energije za volumsko difuzijo fosforja v feritu (167 kJ/mol). Ako bi segregacije obeh elementov, silicija in fosforja, imele enak učinek, bi pričakovali, da bo kinetika porajanja krhkosti kontrolirana z difuzijo počasnejšega silicija na meje kristalnih zrn. Dejstvo, da je kinetika krhkosti kontrolirana z difuzijo fosforja, bi lahko razložili na dva načina, bodisi tako, da ima segregiranje silicija le manjši vpliv na energijo loma, bodisi z naravo segregiranja silicija, ki naj bi bila drugačna od fosforjeve, namreč neodvisna od volumske difuzije.

Stopnjevanje krhkosti zaradi sočasne prisotnosti fosforja in silicija v jeklu je omenjeno tudi v referencah 1 in 8. Ugotovljeno je bilo še, da bi silicij lahko vplival na tvorbo karbidov, vrste $M_6C$ (ref. 5). Segregiranje silicija ter precipitiranje karbidov $M_6C$ na mejah in v medplastjih smo opazili tudi mi. Tega pa še ne moremo imeti za dokaz, da segregiranje silicija vpliva tudi na tvorbo karbidov $M_6C$, saj smo našli na mejah zrn in med letvicami martenzita tudi karbidne precipitate, vrste $M_7C_3$.

## 5. SKLEPI

Popustna krhkost visoko popuščenega orodnega jekla Č.4751 s postmartenzitno mikrostrukturo je nastala zaradi segregiranja fosforja na primarnih mejah avstenitnih zrn, kot tudi na različnih drugih medplastjih. Posledica tega je interkristalni oziroma krhek transkristalni prelom jekla.

Sočasno s segregiranjem fosforja je bilo opaženo tudi segregiranje silicija. Segregiranje silicija ter izločanje karbidov ima sicer lahko pomembno vlogo v procesu nastajanja krhkosti, vendar pa ugotovljena aktivacijska energija, približno 160 kJ/mol, izhajajoča iz časovno-temperaturne odvisnosti poslabšanja žilavosti zaradi dodatnega popuščanja, dokazuje, da je difuzija fosforja v feritu odločujoči dejavnik, ki kontrolira kinetiko krhkosti.

*talline respectively. No significant distinction in morphology and composition of carbide precipitates is observed between ductile and brittle state of steel. From EDS X-ray analysis ensues that the content of molybdenum in solid solution was not substantially modified at the additional tempering for a few hours at 600° C. On the other hand, it is evident that the presence of molybdenum in solid solution did not prevent entirely the interfacial segregation of phosphorus. The segregation of phosphorus occurs simultaneously with that of silicon. The activation energy of bulk diffusion of silicon in ferrite (258 kJ/mol) is much greater than that for bulk diffusion of phosphorus (167 kJ/mol). If the segregation of both elements, silicon and phosphorus, had the same effect one would expect that the kinetics of embrittlement would be controlled by the diffusion of the slower silicon towards grain boundaries. The fact that the kinetics of embrittlement is controlled by the diffusion of phosphorus could be explained in two ways, either the segregation of silicon has only a minor effect on fracture energy or that the nature of silicon segregation is different from that of phosphorus, i. e. independent of bulk diffusion. An enhanced embrittlement due to the simultaneous presence of phosphorus and silicon in steel is quoted also in ref. 1 and 8. It was also found that silicon could even affect the formation of carbides of $M_6C$ type[5]. The presence of a segregation of silicon and precipitates of the $M_6C$ carbide at boundaries and interfaces was also observed in this work. This could not be considered as evidence that the segregation of silicon did affect the formation of $M_6C$ carbide, since precipitates of $M_7C_3$ carbide were found on grain boundaries and martensite lath interfaces.*

## *5. CONCLUSIONS*

*Temper embrittlement of Č.4751 tool steel with high-tempered post-martensitic microstructure was produced by segregation of phosphorus at preaustenite grain boundaries as well as at other different interfaces. This further caused intercrystalline or transcrystalline brittle fracture mode respectively.*

*A segregation of phosphorus was observed simultaneously with that of silicon. The segregation of silicon and precipitation of carbides may play an important role in embrittlement process, however the activation energy of about 160 kJ/mol derived from time-temperature relationship of toughness reduction because of additional tempering proves that the diffusion of phosphorus in ferrite is a dominant factor controlling the kinetics of embrittlement.*

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