Vpliv oligoelementov na nekatere lastnosti zelo čistega železa in jekla

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A. UVOD

Do danes je zbrano zelo veliko informacij o vplivu elementov, ki nastopajo kot primesi v kovinah, in posebno v jeklih. To je predvsem posledica težav, ki jih povzročajo primesi pri izdelavi in uporabi kovinskih delov. Zaradi tega izrazi, kot npr. »oligoelementi« takoj vzbujajo v zavesti metalurgov misli o škodljivem vplivu, kar v splošnem ni nujno in je odvisno od tega, za katere lastnosti gre. Ugoden vpliv nekaterih primesi na določeno lastnost materiala običajno spregledamo. Številni taki primeri so bili odkriti ob pojavu težav pri izdelavi ali uporabi kovinskih delov, izdelanih iz zelo čistih surovin. Praktiki pa so le bili zmožni identificirati škodljive elemente in izdelati učinkovite ukrepe za kompenzacijo njihove prisotnosti. Pri tem so delavnice in obrati imeli vlogo laboratorijev, ker je delo potekalo v industriji.

V poskusih, ki naj bi pojasnili vlogo določenega oligoelementa ali grupe elementov, običajno delamo z laboratorijskimi šaržami jekla iste osnovne sestave, ki mu potem dodajamo točno določene količine oligoelementov, oz. določenega oligoelementa. Pri takem načinu dela običajno ne upoštevamo prisotnosti običajnih primesi v osnovnem materialu, npr. jeklu, in pri tem predpostavljamo, da njihov vpliv lahko zanemarimo. V naslednjem enostavnem primeru bomo videli, da na ta način lahko pridemo do napačnih sklepov.

Prvotno smo v raziskavah vpliva različnih nečistoč na mehanske lastnosti železa uporabljali kot osnovni material običajno elektrolitsko železo. Tako so bile določene prehodne temperature pri raziskavah vpliva žvepla in različnih ostalih nečistoč na udarno žilavost. Nepričakovano se je pokazalo, da je bila prehodna temperatura približno 250 °C, in sicer neodvisno od vsebnosti žvepla v območju 20—50 ppm. (Vse koncentracije se v nadaljevanju nanašajo na količino mase). Navidezno očividen zaključek je bil, da žveplo v koncentracijah do 50 ppm nima vpliva na žilavost čistega železa. Še bolj presenetljiva je bila ugotovitev, da je prehodna temperatura precej nižja, približno enaka sobni temperaturi, ko smo v istih poskusih kot osnovni material namesto običajnega elektrolitskega železa uporabili zelo čisto železo, ki smo ga izdelali po lastnem rafinacijskem postopku. Poleg tega smo ugotovili, da je prehodna temperatura precej občutljiva na vsebnost žvepla, saj

Influences of residuals on some properties of high purity iron and steel

A. INTRODUCTION

Up to the present time, a vast amount of information has been gained about the influence of trace elements in metals, particularly in steels. This is mostly the result of troubles caused by such elements in the manufacture and in the current use of metal parts. Because of the way metallurgists have got acquainted with trace elements, the term »residual« quite commonly imply adverse effects. However, depending on the properties under consideration this is not necessarily true because the influence of a given residual element is usually overlooked if it is favorable: a number of such cases have been discovered when the use of raw materials of high purity instead of common ones resulted in various kinds of difficulties either in the manufacture or in the subsequent use of the parts. Nevertheless, men in the practice have been able to identify in many cases harmful elements and to devise efficient measures in order to counterbalance their presence: working on an industrial scale, the workshop is their laboratory.

Furthermore, in order to better interpret the role of particular element or group of elements in a given steel, it is a common procedure to use laboratory scale heats whose base composition is defined by the steel, the contents of some elements being suitably altered. Doing so, the important fact is that people disregard the usual residuals of the base steel, assuming that their influence can be neglected. A simple example will show how this can lead to erroneous conclusions.[1]

In order to test the influence of various impurities on the mechanical properties of iron, commercial electrolytic iron was used at first as the base material. The transition temperature of the impact strength was determined in the presence of various impurities and among others, of sulphur. Surprisingly it proved to be almost independent of the sulphur content in the range which had been considered, that is 20 to 50 ppm: it amounted approximately to 250 °C. The apparently obvious conclusion was that underneath 50 ppm, sulphur does not influence the brittleness of pure iron.

Then, the same measurements were made using the first batches of a just started production of refined iron. The still great surprise was that je naraščala za približno 10 °C za vsak ppm žvepla. Nadalje se je pokazalo, da je vpliv žvepla odvisen od prisotnosti drugih nečistoč. Glavne rezultate lahko rezimiramo v naslednji obliki:

1. Prehodna temperatura čistega železa kontinuirno narašča z vsebnostjo žvepla in doseže približno 600 °C pri 60 ppm S.

2. Ogljik, če je raztopljen v osnovi, močno zmanjša vpliv žvepla. Tako npr. pri 30 ppm ogljika narašča prehodna temperatura za vsak ppm žvepla samo za 3 °C.

3. Kaže, da oligoelementi, ki so prisotni v elektrolitskem železu, razen žvepla in ogljika, ne vplivajo na obnašanje železa.

Dodatek žvepla do približno 20/25 ppm povečuje prehodno temperaturo. Pri večji vsebnosti žvepla se prehodna temperatura skoraj ne spreminja.

Do sedaj ni bila možna jasna razlaga teh rezultatov, predvsem pa je nepojasnjena interakcija med žveplom in ostalimi oligoelementi. Omenjeni rezultati pa jasno kažejo, da nekontrolirana prisotnost primesi lahko povzroči težave. Če se povrnemo k industrijskim jeklom, kaže, da raziskave vpliva različnih elementov lahko privedejo do napačnih rezultatov, kar je odvisno od vsebnosti in vrste primesi, ki so prisotne v osnovnem materialu. To je eden izmed vzrokov, zaradi katerih se vedno znova pojavlja problem nečistoč v kovinah kljub številnim in zelo koristnim rezultatom, ki so že doseženi v metalurški industriji.

Za boljše razumevanje teh problemov je bil že zdavnaj dan predlog, da se k tovrstnim raziskavam pristopa na naslednji način:

Najprej je treba pripraviti osnovni material zahtevane nominalne sestave, in sicer z uporabo čim bolj čistih elementov. Vsebnost nečistoč mora biti tako majhna, da jo zanesljivo lahko zanemarimo. Osnovni sestavi potem dodajamo točno določene količine ustreznih oligoelementov. Navidez je to zelo enostavno, dejansko pa nastopa cela vrsta vprašanj, ki jih tukaj ne moremo obsežno obravnavati. Zadostuje ugotovitev, da vsebnost primesi nikoli ni dovolj majhna, da bi jo lahko »zanesljivo zanemarili«. Celo v ekstremno čistih materialih vedno ostaja odprto vprašanje vpliva prisotnih primesi. To pomeni, da priprava ustreznega jekla osnovne sestave zahteva uporabo ekstremno čistih materialov, ki jih praviloma ni na tržišču in jih moramo zato skrbno pripraviti s posebnimi postopki.

B. PRIPRAVA ZELO ČISTEGA ŽELEZA IN JEKLA[1–8]

V skladu s temi izvajanji smo razvili takšne posebne postopke v našem laboratoriju. Najprej smo razvili postopek za pripravo zelo čistega železa. Potem smo se lotili priprave čistega kroma in niklja v zvezi z nerjavnimi jekli. Glede na to, da

the transition temperature was much lower, near room temperature. Furthermore, it was quite sensitive to the sulphur content, increasing by some 10 °C per ppm of sulphur. However, subsequent experiment have shown that the influence of sulphur may be greatly modified in the presence of other impurities. On the whole, the main results could be summarized as follows:

1. In refined iron, the transition temperature increases continuously as the sulphur content goes up, reaching eventually some 600 °C with 60 ppm of sulphur.

2. Carbon, if dissolved in the matrix considerably moderates the influence of sulphur. For instance, with a carbon content of 30 ppm, the transition temperature increases only by 3 °C per ppm of sulphur.

3. Apart from sulphur and carbon, the residual elements which are present in electrolytic iron do not seem to influence the behaviour of the metal. Now, if sulphur is added, it increases the transition temperature as far as its content does not go beyond about 20/25 ppm; then, as mentioned previously, the transition temperature remains practically constant.

It has not been possible to clearly explain all these results, particularly the interaction between sulphur and residual elements. Nevertheless, they show how uncontrolled trace elements may prove troublesome. Turning back to industrial steels, it appears that, depending on the residuals which are present in base steel, experiments on the influence of various elements can lead to erratic results. This is one of the reasons why the problem of trace elements in metals is permanently reopened, in spite of the many results which are so valuable in the metallurgical industries.

As an aid towards a better understanding of these problems, it has long been proposed to go a way which can be described as follows.

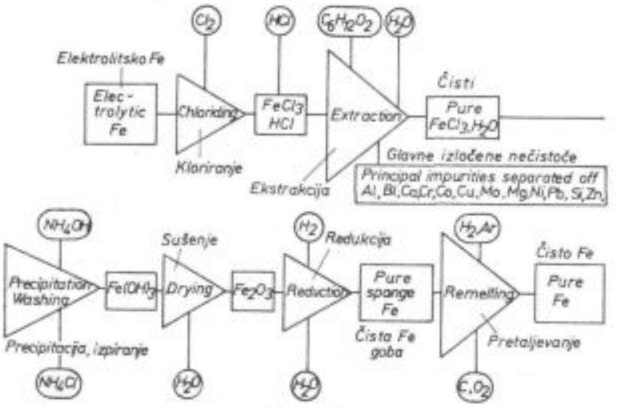
Considering the constituents of a steel whose contents are explicitly specified, a base material of the same nominal composition is prepared using pure elements. The impurity contents must be so low that they are certainly negligible. Then, well controlled amounts of suitable elements can be added to this base steel. Apparently, this is a very simple procedure. Actually, it raises a number of questions which cannot be discussed at length here. Suffice it to say that it is never easy to assert that residual impurities are »certainly negligible«. Even in extremely pure materials, the influence of these elements remains always questionable. This means at least that the preparation of suitable base steels requires materials of exceptionnally high purity. As a general rule, they are not available as commercial products so they must be prepared by carefully controlled procedures.

se lahko nabavi zelo čist silicij, se sedaj ukvarjamo s postopkom za pridobivanje zelo čistega mangana. Razvoj postopka za pripravo vsakega zelo čistega elementa temelji na dveh osnovnih zahtevah:

1. postopek mora omogočiti izdelavo elementa zahtevane čistoče,

2. postopek mora zagotoviti izdelavo zadosti velike količine materiala.

Izhajajoč iz v literaturi opisanega postopka rafinacije, v vsakem konkretnem primeru najprej s preliminarnimi poskusi ugotovimo, koliko ta postopek omogoča izpolnitev omenjenih zahtev. Običajno so potrebne manjše prilagoditve ali celo precejšnje spremembe. Nato organiziramo manjše obrate za normalno proizvodnjo po tako razvitem postopku.



Slika 1

Shema postopka pridobivanja čistega železa

Fig. 1

General principle of the refining procedure for iron.

Na sl. 1 vidimo shemo postopka pridobivanja zelo čistega železa[4]. Izhodni material je običajno elektrolitsko železo, ki ga s pomočjo klora prevedemo pri 300—350 °C v $FeCl_3$. Železov klorid potem raztopimo v konc. HCl. Najpomembnejši del rafinacijskega postopka je dvojna ekstrakcija z butil acetatom ($C_6H_{12}O_2$). V prvi stopnji železov klorid prehaja v organsko fazo. Pri tem večina nečistoč ostane v kisli raztopini, ki jo nato dekantiramo in dolijemo čisto vodo. V drugi stopnji železov klorid prehaja nazaj v vodno raztopino. Tako dobimo zelo čisto vodno raztopino železovega klorida. Z amoniakom nato precipitiramo železo v obliki Fe-hidroksida, ki ga zelo skrbno približno 10 krat izpiramo s čisto vodo, da odstranimo amonijev klorid. Po sušenju dobljeni železov oksid reduciramo z vodikom v železovo gobo, ki je po vsebnosti vseh nečistoč, razen ogljika in kisika, zelo čista. Gobo lahko potem neposredno uporabimo kot zelo čisto železo v vseh primerih, v katerih so dopustne manjše primesi ogljika in kisika. Ta rafinacijski postopek smo uporabljali v našem laboratoriju pri obsežnih raziskavah vpliva različnih nečistoč na krhkosti železa[1, 2].

B. PREPARATION OF HIGH PURITY IRON AND STEEL[1–8]

Working along these lines, such procedures have been developed in our laboratory. The initial step was the preparation of iron. Then, in view of studying stainless steels nickel and chromium have been dealt with. As high purity silicon can be purchased, the case of manganese is now being considered.

For each element, the procedure to be developed is selected in accordance with two general rules:

1. it must be able to yield a product of the required purity.

2. it must be applicable to fairly large quantities of material.

Taking in each particular case a refining process which has been described in the litterature, preliminary tests show how far it can satisfy these requirements. Some simple adjustments or more important modifications are usually necessary. Then small shops are organized for a regular production according to a well defined procedure.

Figure 1 shows the general principle of the process for iron[4]. The starting material is a commercial electrolytic iron. It is attacked by chlorine at a temperature of about 300/350 °C and transformed into iron chloride. Then $FeCl_3$ is dissolved into a concentrated solution of hydrochloric acid. The most important part of the refining process is now a double liquid-liquid extraction with butylacétate ($C_6H_{12}O_2$). In a first step, the iron chloride goes into the organic phase whereas most of the impurities remain in the acid solution. The latter one is decanted and replaced by pure water. In the second step of the process, the iron chloride goes back into the aqueous phase. In this way, one gets a solution of very pure iron chloride. Then, iron hydroxide is precipitated by means of ammonia. It is carefully washed with very pure water: about 10 operations are necessary to remove most of the ammonium chloride. After drying the iron oxide is reduced to iron sponge by means of hydrogen.

Apart from the carbon and oxygen contents, the sponge iron is very pure. It can be used in cases when some carbon and oxygen can be tolerated. This is what has been done in our laboratory in an extensive investigation of the influence of various elements upon the brittleness of iron[1, 2].

Now, if carbon and oxygen must be avoided, or if the metal has to be obtained in a solid form, the iron sponge will be melted in a silver water-cooled boat by induction heating. In the present state of the technique we currently produce bars up to about 1200 g which are 50 cm in length. With a new equipment which has just been tested, bars of 4 kg have been melted; it should be possible to go up to 10 kg.

Če se zahteva zelo velika čistoča tudi glede vsebnosti ogljika in kisika ali če moramo imeti kompakten kos zelo čistega železa, železovo gobo pretalimo v vodno hlajeni srebrni ladjici v indukcijski peči. Na sedanji stopnji razvoja tega postopka uspešno izdelujemo palice, dolžine 50 cm, s težo približno 1200 g. Nova oprema, ki smo jo pravkar preizkusili, omogoča izdelavo 10-kilogramskih palic, vendar smo do sedaj dosegli izdelavo 4-kilogramskih palic.

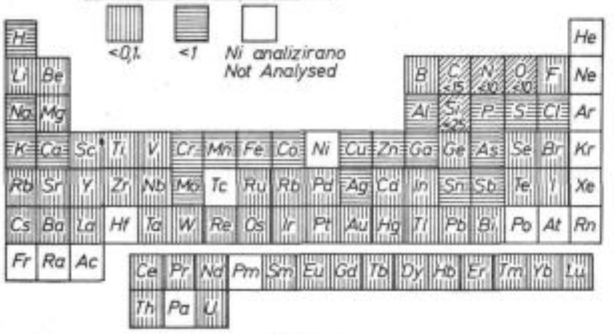
Čeprav je naš postopek rafinacije podoben conski rafinaciji, je v bistvu povsem drugačen, saj odstranitev ogljika in kisika dosežemo z interakcijo staljenega metala z atmosfero v peči. Nadalje, indukcijska tuljava se premika vzdolž železne palice z razmeroma veliko hitrostjo 12 cm/min v obe smeri. S tako consko homogenizacijo izboljšamo homogenost izdelka. Ogljik in kisik iz železa reagirata v atmosferi argona. Tako odstranimo ogljik v obliki CO, preostali kisik odstranimo s čistim vodikom. Standardni postopek sestoji iz 60 prehodov, po 30 v vsako smer.

Da bi lahko ugotavljali učinkovitost rafinacijskega postopka, smo namenili posebno pozornost razvoju ustreznih analitskih metod za določanje vsebnosti najbolj kritičnih nečistoč[5, 8].

V sodelovanju z osmimi francoskimi laboratoriji[6] smo potem izvedli obsežen analitsko-raziskovalni program raziskav. Tako smo določili vsebnost 76 elementov v vzorcih, ki so bili izdelani iz 6 palic zelo čistega železa. Dobljene rezultate smo analizirali glede na:

1. reproduktivnost rafinacijskega postopka s primerjavo vsebnosti primesi v posameznih palicah,
2. homogenost posamezne palice in
3. kvaliteto različnih analitskih metod.

Vsebnost nečistoč v izhodnem elektrolitskem železu se je spreminjala v precej širokem območju. Tako smo za posamezne elemente dobili naslednje območje, oz. vrednosti (v ppm mase): Ti =



Slika 2

Mejne vsebnosti nečistoč v čistem železu

Fig. 2

Limits of impurity contents in refined iron.

Although similar to a zone-refining process, our treatment is in fact quite different. Actually, the removal of carbon and oxygen is due solely to interactions of the metal with the surrounding atmosphere. Furthermore, the heating coil moves along the bar at a relatively high speed of 12 cm/min in either direction. This is a zone-levelling procedure which improves the homogenity of the product. Carbon is eliminated by combination with the internal oxygen in an atmosphere of argon. Then, oxygen is removed in an atmosphere of pure hydrogen. In the standard procedure, 60 passes are performed, 30 in each direction.

Clearly, the validity of a refining technique is never better than the efficiency of the corresponding analytical testing methods. Therefore, a great effort has been made in our laboratory in order to develop suitable methods whereby the contents of the most critical impurities could be determined[5, 8]. Then, an extensive program of analysis has been carried out in cooperation with eight other French laboratories[6]. The contents of 76 elements have been determined in specimens taken out of six different bars. The results have been interpreted in terms:

1. of reproducibility of the production process from one bar to the other.
2. of homogeneity of each bar.
3. of validity of the various analytical methods.

In the starting electrolytic iron, the impurity contents exhibit wide variations. We have obtained for instance the following results (contents in ppm: Ti = 10—50; Cr = 0.5—12; Ni = 6—50, with: S $\simeq$ 35; Mn $\simeq$ 12; Co $\simeq$ 9.

In the iron sponge, the carbon and oxygen contents may be as high as 15 and 500 ppm respectively. For the other elements the composition is the same as in the subsequently remelted metal.

The table of figure 2 summarizes the results concerning 76 elements which have been analysed in 6 remelted bars[6]. Comparing with the values indicated for the sponge iron we see, in particular, that the contents of Ti, Cr, Mn, Co, Ni, are now well below 1 ppm. Only the contents of C, N, O, and Si exceed 1 ppm. However, the indicated limits also reflect the sensitivity limits of the analytical methods. For instance in the case of C and O, subsequent analysis by activation methods have disclosed contents near or underneath 1 ppm.

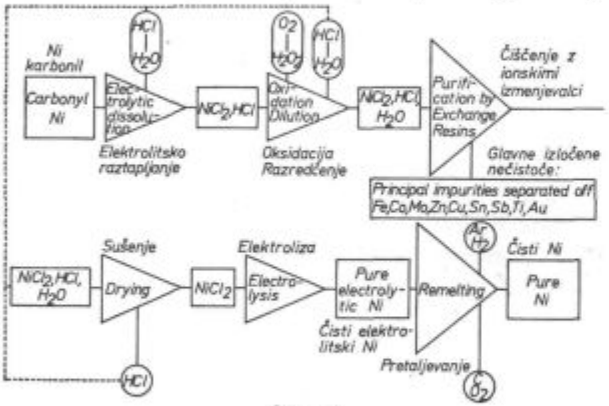
Furthermore, since the time when the table has been established, the quality of our production has been improved. This concerns particularly silicon whose content was relatively high in the six bars because some silica had entered the iron hydroxide during the washing proces. Using water free of silica and teflon containers has allowed to avoid contamination the oxide.

Similar procedures have been devised for nickel and chromium. For nickel, the procedure

$=10$—50; $Cr = 0,5$—12; $Ni = 6$—50; $S \simeq 35$; $Mn \simeq 12$; $Co \simeq 9$. V železovi gobi vsebnosti ogljika in kisika lahko dosežeta 15, oz. 500 ppm. Vsebnost ostalih elementov je bila skoraj enaka kot v pretaljenih palicah.

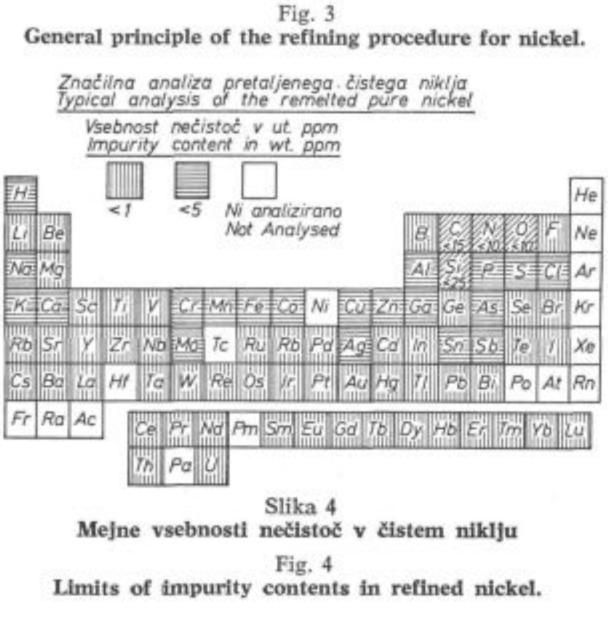
Tabela na sl. 2 kaže rezultate[6] analize šestih palic glede na 76 elementov. Primerjava z analizo železove gobe kaže, da so vsebnosti Ti, Cr, Mn, Co in Ni sedaj precej pod 1 ppm. Samo vsebnosti C, N, O, in Si so večje od 1 ppm. Vendar je treba pri tem upoštevati, da nastopajo omejitve, ki jih narekujejo meje občutljivosti uporabljenih analitskih metod. Tako so npr. aktivacijske metode analize pokazale, da je vsebnost ogljika in kisika približno 1 ppm ali pod 1 ppm. Medtem smo že izboljšali kvaliteto naše proizvodnje zelo čistega železa, posebno glede na vsebnost silicija. Vsebnost silicija je bila v omenjenih šestih palicah razmeroma velika zaradi onesnaženja Fe-hidroksida s SiO_2 pri izpiranju z vodo. Izpiranje z vodo, ki ni vsebovala SiO_2 in uporaba teflonskih posod sta pripomogla, da smo se izognili temu onesnaženju.

Podobna postopka smo razvili za pridobivanje Ni in Cr. Postopek za pridobivanje čistega niklja



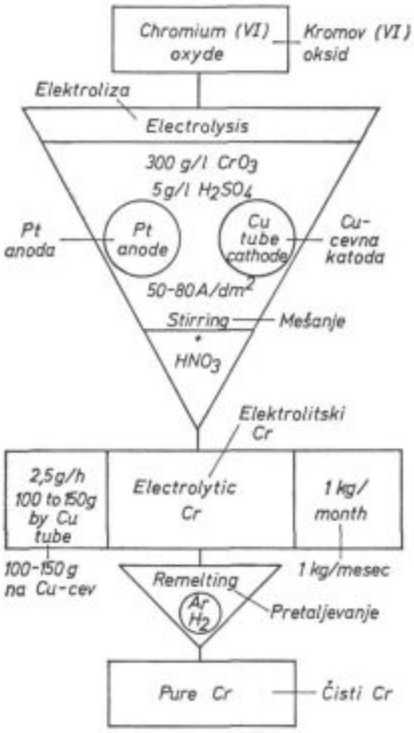
Slika 3
Shema postopka pridobivanja čistega niklja

Fig. 3
General principle of the refining procedure for nickel.



Slika 4
Mejne vsebnosti nečistoč v čistem niklju

Fig. 4
Limits of impurity contents in refined nickel.



Slika 5
Shema postopka pridobivanja čistega kroma

Fig. 5
General principle of the refining procedure for chromium.

has reached a state of development comparable to that for iron. The only difference is that no extensive program of analysis has not been yet carried out.

As suggested in figure 3, commercial carbonyl nickel is first dissolved electrolytically in a dilute solution of hydrochloric acid. Then, the solution is purified by means of iron exchange with suitable resins, namely:

— resin DOWEX 50 W × 8 Form H+ 100—200 mesh

— resin DOWEX 1 × 8 Form Cl− 200—400 mesh.

The pure nickel chloride is then electrolyzed to pure nickel. The nickel cathodes are eventually melted into bars in a water-cooled silver boat as in the case of iron.

The limits of the impurity contents are given in the table of figure 4. On the whole, they are larger than in the case of iron. But this is mainly due to the fact that they are based mainly on the only results of our laboratory[7, 8]: the »safety limits« are not so well known as in the case of iron where they have been carefully discussed by several laboratories.

The production of chromium has been started a few months ago. It has not yet reached the regular pace arrived at for iron and nickel. Figure 5 shows the general principle of the refining process; figure 6 is a table of some, still preliminary, analytical results.

je dosegel približno enako stopnjo razvoja kot za železo. Razlika je le v tem, da še nismo izvedli obsežnega programa primerjalnih kemičnih analiz, kot v primeru železa.

Kot vidimo iz sheme na sl. 3, tehnični karbonilni nikelj elektrolitsko raztopimo v razredčeni HCl. Raztopino potem očistimo z ionskimi izmenjevalci, tj. z ustreznimi smolami, in sicer:

— smola DOWEX 50 W × 8 Form H^+ z granulacijo 100—200 mesh,

— smola DOWEX 1 × 8 Form Cl^- z granulacijo 200—400 mesh.

Iz tako dobljenega čistega nikljevega klorida pridobivamo čisti nikelj z elektrolizo. Če je to potrebno, Ni katode potem pretalimo v vodno hlajeni srebrni ladjici, kot v primeru železa. Mejne vsebnosti posameznih elementov primesi so, kot kaže tabela na sl. 4, nasploh večje kot v čistem železu. Vendar je to posledica dejstva, da imamo v tem primeru na razpolago le rezultate kemijske analize iz našega laboratorija[7, 8]. »Varne meje« niso torej tako dobro znane, kot v primeru železa, kjer je pri analitskem delu sodelovalo več različnih laboratorijev.

S proizvodnjo čistega kroma smo začeli šele pred nekaj meseci, zato postopek še ni standardiziran, kot pri železu in niklju. Splošno shemo rafinacijskega postopka za krom vidimo na sl. 5, preliminarne analize pa kaže tabela na sl. 6.

C. VPLIV SELENA NA KINETIKO $\alpha \rightarrow \gamma$ IN $\gamma \rightarrow \alpha$ PREMENE ŽELEZA[11, 12]

Priprava čistih materialov seveda ni bil naš končni cilj, temveč le prvi in nujni korak pri raziskavah vpliva nečistoč v jeklu, kar je neposredno povezano s praktičnimi problemi[3]. Po drugi strani pa so čisti materiali izredno pomembni za temeljne raziskave, kot lahko vidimo iz naslednjega primera. V okviru raziskav o tvorbi in možnih modifikacijah različnih vključkov v jeklu smo smatrali za potrebno, da znova preverimo nekatere dele ravnotežnega diagrama železo—selen[9, 10]. V ta namen smo uporabili različne metode, med njimi tudi termično analizo z adiabatnim kalorimetrom[11, 12].

Osnovni princip aparature je razviden iz sheme na sl. 7. Preizkušanec E je v trdnem ali tekočem stanju v posebni celici, katere zunanje in notranje stene skrbno vzdržujemo pri enaki temperaturi. Tako smo popolnoma preprečili prenos toplote skozi stene od vzorca, oz. k njemu. Z grelnim elementom F_a dovajamo natančno določeno količino toplote preizkušancu E, katerega temperaturo merimo s termoelementom G. Ker je sistem toplotno izoliran, lahko natančno merimo količino dovedene toplote, ki je potrebna za določeni dvig temperature preizkušanca, oz. za kristalno premeno. Žal isti postopek ni možno uporabiti pri ohlajanju, ker ohlajanje toplotno izoliranega si-

Značilne analize pretaljenega čistega kroma
Typical analysis of the remelted pure chromium

Vsebnost nečistoč v ut. ppm
Impurity content in wt. ppm

O	N	S	C	Si
15	15	<10	<20	<10

Na	K	Ca	Mn	Fe	Co	Cu	Zn	Ni	Ga	As	Sb	W	Pb	Al
0,03	<0,2	<10	0,001	<20	1,7	1,1	<1,7	<2	<0,003	0,01	0,14	0,13	<10	<10

Slika 6
Mejne vsebnosti nečistoč v čistem kromu

Fig. 6
Limits of impurity contents in refined chromium.

D. INFLUENCE OF SELENIUM ON THE KINETICS OF THE $\alpha \rightarrow \gamma$ AND $\gamma \rightarrow \alpha$ TRANSFORMATIONS OF IRON[11, 12]

As pointed out previously, preparing pure metals is not our end goal: it is only a preliminary, necessary step, before we can investigate the influence of trace elements in steels, which is a question closely related to practical problems[3]. On the other hand, pure materials are also invaluable in fundamental research, as can be shown by the following example.

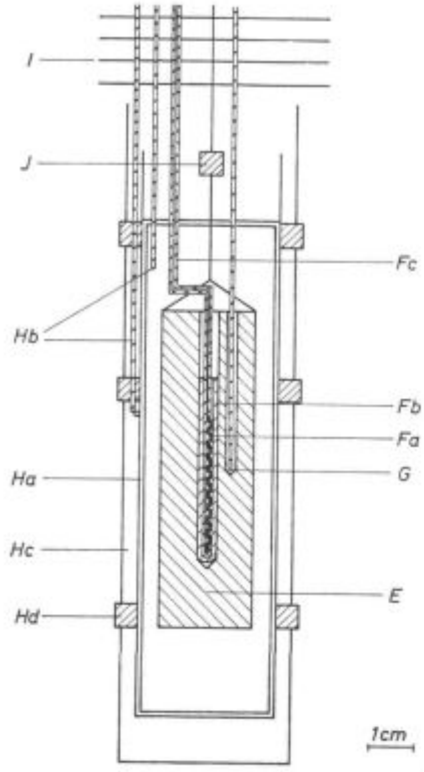
As part of a research program concerning the formation and the possible modification of various inclusions in steels, we felt necessary to verify some parts of the iron-selenium equilibrium diagram[9, 10]. Various methods have been used for this purpose and among them, thermal analysis with an adiabatic calorimeter[11, 12].

The basic principle of the device can be explained by the schematic representation of figure 7. The specimen E which can be either solid or liquid is placed in a special cell whose inside and outside walls can be rigorously maintained at the same temperature. This means that any heat flow through the walls of the cell, towards the specimen or from the specimen can be prevented. Thanks to a heating element F_a, well known quantities of heat can be injected into the specimen whose temperature is measured by a thermocouple G. Consequently, as there is no heat loss through the walls of the cell, the amount of heat which is needed to increase the temperature of the specimen or to bring about a transformation can be measured accurately.

Unfortunately, the same procedure does not work on cooling as heat loss of the specimen can be achieved only by heat loss through the walls of the cell: the device is no more adiabatic. However, carefully controlling the difference in the temperatures of the inside and outside walls of the cell, it is possible to determine, at least approximately, the heat loss of the specimen.

stema ni možno. Vendar je s skrbno kontrolo razlike temperatur zunanje in notranje stene možno vsaj približno določiti toplotne izgube preizkušanca.

Najprej smo opravili številne meritve, potrebne za preizkus in umerjanje aparature. Pri meritvah na srebru smo slučajno opazili, da je tališče neodvisno od količine dovedene toplote, tj. od hitrosti taljenja. Z drugimi besedami, temperatura na medfazni površini talina/trdna snov je vedno enaka in ustreza temperaturi ravnotežja talina/trdna snov. Pri taljenju temperatura medfazne površine ni odvisna od hitrosti, s katero se medfazna površina premika vzdolž preizkušanca.



Slika 7

Merilna celica adiabatnega kalorimetra
E — preizkušanec, F_a — grelni element (volfram), F_b — zaščitna korundna cev, F_c — vodniki (Mo žica), G — termoelement Pt-Rh 10% - Pt, H_a — adiabatna stena celice (Mo-pločevina), H_b — diferenčni termoelement, H_c — mikro pečica, H_d — grelni element mikro pečice s korundno izolacijo, I — krožni zasloni za zaščito pred toplotnim sevanjem, J — žica s korundno izolacijo.

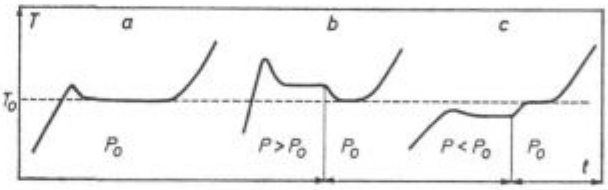
Fig. 7

Measuring cell of the adiabatic calorimeter.
E — specimen, F_a — heating wire (tungsten), F_b — protecting sheath (alumina), F_c — electric wires (molybdenum), G — thermo-couple (Pt-Rh 10 % - Pt), H_a — adiabatic wall of the cell (molybdenum sheets), H_b — thermo-couples (in opposition), H_c — micro-furnace, H_d — heating element of the micro-furnace, in alumina beads, I — circular shields, J — sustaining wire, in alumina beads.

Potem smo začeli s preiskavami kristalnih premen $\alpha \rightarrow \gamma$ in $\gamma \rightarrow \alpha$ v čistem železu. Premeni sta non-variantni, tako kot taljenje. Zato bi lahko

A number of measurements have been performed in order to test and to calibrate the device. When studying silver it was incidentally observed that the melting temperature is not affected if the heat input is changed, that is if the melting rate varies. In other words, if we consider the interface between melted and solid silver, the temperature at the interface always equals the equilibrium temperature between liquid and solid metal. On melting, the temperature at the interface does not at all depend on the speed of the interface moving across the specimen.

Then, the $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformations of pure iron were investigated. Like the melting process, such transformations are invariant ones. Therefore, we would expect the transformation temperature to be independent of the transformation rate. Figure 8 shows that the experimental results did not sustain this expectation. On the left, we see the temperature change of the specimen when the heat input has a constant value P_o: there is a well defined transformation temperature. Now, increasing the heat input, the middle curve shows that the transformation temperature is higher. Then, turning back to the lower initial heat input, one gets the same previous transformation temperature. The right shows the corresponding phenomenon if the initial heat input is

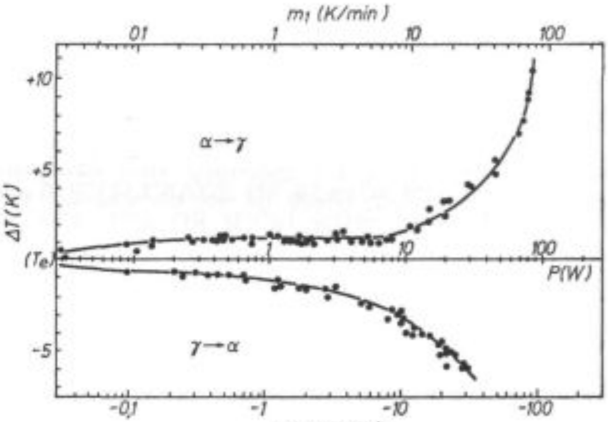


Slika 8

Vpliv P na temperaturo premene $\alpha \rightleftarrows \gamma$

Fig. 8

Influence of P on the transformation temperature.



Slika 9

Vpliv hitrosti premene na temperaturo premene $\alpha \rightleftarrows \gamma$ čistega železa.

Fig. 9

Influence of the transformation rate on the $\alpha \rightleftarrows \gamma$ transformation temperature of pure iron.

pričakovali, da bo temperatura premene neodvisna od hitrosti transformacije. Eksperimentalni rezultati, ki jih navajamo na sl. 8, se ne skladajo s tem pričakovanjem. Krivulja a na levi strani slike 8 kaže, kako se spreminja temperatura preizkušanca pri konstantnem dotoku toplote P_o. Temperatura transformacije je povsem jasna. Pri večjem dotoku toplote ($P > P_o$) dobimo večjo temperaturo premene, kot vidimo na krivulji b. Če med poskusom spremenimo dotok toplote na prvotno vrednost ($P = P_o$), znova dobimo prvotno temperaturo premene. Podobno kaže krivulja c, da se temperatura premene zniža, če je dotok toplote manjši, tj. če je $P < P_o$. Lahko torej zaključimo, da je temperatura medfazne površine α/γ odvisna od njene hitrosti gibanja vzdolž preizkušanca.

Na sl. 9, kjer je T_e ravnotežna temperatura, tj. 1184 K, prikazujemo spremembo temperature premene (ΔT) v odvisnosti od dotoka toplote. V tem primeru dotok toplote 1 W ustreza hitrosti 0,5 mm/min gibanja medfazne površine. Meritve pri zelo šibkih dotokih toplote so pokazale, da ΔT naglo narašča od 0 do približno 1,25 K, ko dotok toplote raste od 0 do 0,25 W. Pri večji intenziteti ogrevanja preizkušanca je rast ΔT vse do 10 W veliko počasnejša, kot vidimo iz slike 9. Pri ohlajanju imamo ustrezen padec temperature premene.

Pri analizi teh rezultatov se je pojavilo vprašanje, ali nekatere nečistoče, npr. ogljik, vplivajo na temperaturo premene. Dejstvo je, da imamo med premeno $\alpha \rightarrow \gamma$ in $\gamma \rightarrow \alpha$ stalno prerazdelitev ogljika med α in γ fazo, kar vpliva na temperaturo medfazne površine. Tej možnosti smo namenili posebno pozornost. Glede na to, da ima ΔT pri danem toplotnem dotoku P ves čas poskusa konstantno vrednost, domnevamo, da difuzija nima opaznega vpliva na rezultate meritev, tj. prerazdelitev oligoelementov med premeno nima pomembnejše vloge.

Enake poskuse smo izvedli na zlitinah sistema železo-selen. Preizkušance lahko razdelimo po vsebnosti selena v skupini s 175 ppm in 550 ppm selena. V takih zlitinah imamo non-variantno premeno $\alpha \rightleftarrows \gamma$, ki poteka pri 913 °C (slika 10). Kot v primeru železa, je temperatura potujoče medfazne površine odvisna od hitrosti premene, kar vidimo na sl. 11. Primerjava s prej omenjenimi rezultati kaže, da majhne količine selena močno povečajo ta pojav pri ogrevanju. V primeru, ko je bila vsebnost selena v območju med 200 in 500 ppm, je bila razlika ΔT v temperaturi premene povečana za faktor 5. Presenetljivo je, da je ta vpliv selena veliko manjši pri ohlajanju.

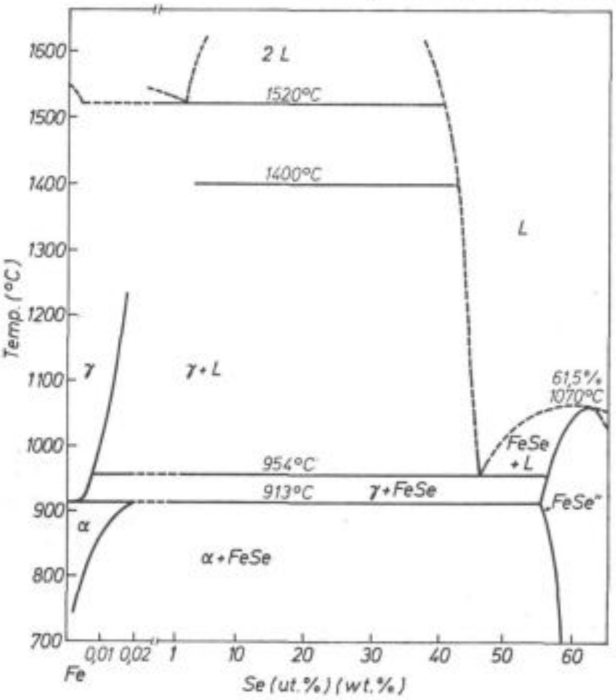
Pri teh zlitinah prerazdelitev selena med α in γ fazo zanesljivo vpliva na temperaturo medfazne površine, vendar je koeficient difuzije selena tako majhen, da ta efekt verjetno lahko zanemarimo. Premena poteka tako, da pri masivni transformaciji hitrost premene, pa tudi prisotnost nečistoč vplivata na temperaturo potujoče medfazne površine.

lower than P_o. Consequently, it turns out that the temperature at the moving interface depends on the speed of the interface.

Figure 9 shows the numerical results. The value T_e being the equilibrium temperature, that is 1184 K, the increase in the transformation temperature, ΔT, has been plotted as a function of the heat input. In the present case, 1 W corresponds approximately to 0.5 mm/min. in the speed of the moving interface. Measurements with very low heat inputs have shown that ΔT rapidly increases from 0 to about 1.25 K when the heat input varies from 0 to 0.25 W. Then, as shown in figure 9 the increase in ΔT is much slower, up to a heat input of 10 W.

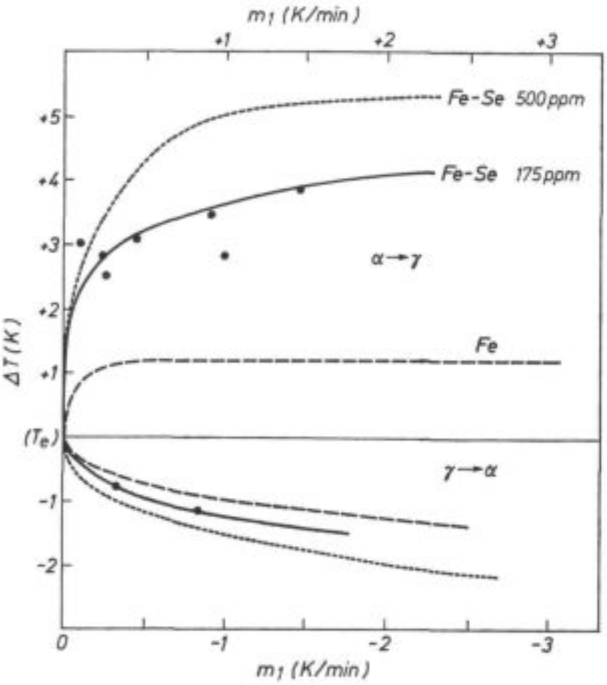
On cooling, there is a corresponding decrease in the transformation temperature.

Concerning these results, the question has been raised as to whether the transformation temperature may be influenced by some impurity like carbon. As a matter of fact, during the $\alpha \rightleftarrows \gamma$ transformations, there is a permanent redistribution of carbon between the two phases which effectively affects the temperature at the interface. This point has been carefully discussed. During an experiment with a given value of the heat input, ΔT has a constant value. Mainly because ΔT does not change during the experiment, it is felt that diffusion processes do not materially affect the results: the redistribution of residual elements should not play a significant role during the transformation.



Slika 10
Ravnotežni diagram Fe-Se

Fig. 10
Fe-Se equilibrium diagram.



Slika 11

Vpliv selena na temperaturo premene α ⇄ γ

Fig. 11

Influence of Se on the α ⇄ γ transformation temperature.

D. VPLIV OLIGOELEMENTOV NA NASTANEK KOROZIJSKIH JAMIC NA POVRŠINI AVSTENITNIH NERJAVNIH JEKEL[13, 14]

Kljub našemu zanimanju za temeljne raziskave je proizvodnja čistih kovin v našem laboratoriju prvenstveno povezana s prakso, tj. z uporabnimi lastnostmi jekel. V zvezi z mehanskimi lastnostmi smo že omenili raziskave krhkosti[1, 2, 3] železa in jekla. Sedaj bomo obravnavali nekatere pojave korozije pri nerjavnih jeklih.

Izmed večjih problemov v zvezi z uporabo avstenitnih nerjavnih jekel je nastanek korozijskih jamic na površini, t. im. pitting korozija, eden najpomembnejših. Pri tej posebni vrsti korozije je nastanek korozijskih jamic na površini bistvena faza korozijskega procesa. Ko že nastane majhna površinska jamica, ta nadalje neizogibno raste in se razvija. Sedaj je že na splošno sprejeto, da nekovinski vključki inicirajo nastanek korozijskih površinskih jamic. Verjetnost nastanka jamice je odvisna od vrste vključka. S praktičnega stališča je torej pomembno, da poznamo obnašanje različnih vrst vključkov, ki lahko nastopajo v nerjavnih jeklih. To lahko spoznamo s korozijskimi poizkusi, pri katerih preštejemo jamice, nastale na površini preizkušanca, ki je bil izpostavljen določenemu korozijskemu vplivu v skrbno kontroliranih pogojih. Lahko pa dobimo enakovredne, če ne boljše podatke in v veliko krajšem času s pomočjo t. im.

The same experiments have been performed with iron-selenium alloys. Two kinds of specimen have been used with low selenium contents of 175 and 500 ppm respectively. In such alloys, there is an invariant α ⇄ γ transformation at 913 °C (Fig. 10). As in the case of iron, the temperature at the moving interface depends on the transformation rate. This is shown in figure 11. Now, the comparison with the foregoing results shows that small contents of selenium considerably enhance the phenomenon on heating. In the present case, with selenium contents in the range of some 200 to 500 ppm, the difference in the transformation temperature is approximately multiplied by a factor of 5.

On cooling, the influence of selenium is surprisingly much more limited.

In these alloys, the temperature at the interface is certainly affected by the redistribution of selenium between the α and γ phase. However, the diffusion coefficient of selenium is so low that this effect is likely to be negligible. The transformation proceeds in such a way that α and γ phase have practically the same composition on either side of the interface: this situation is characteristic of a so called »massive transformation«.

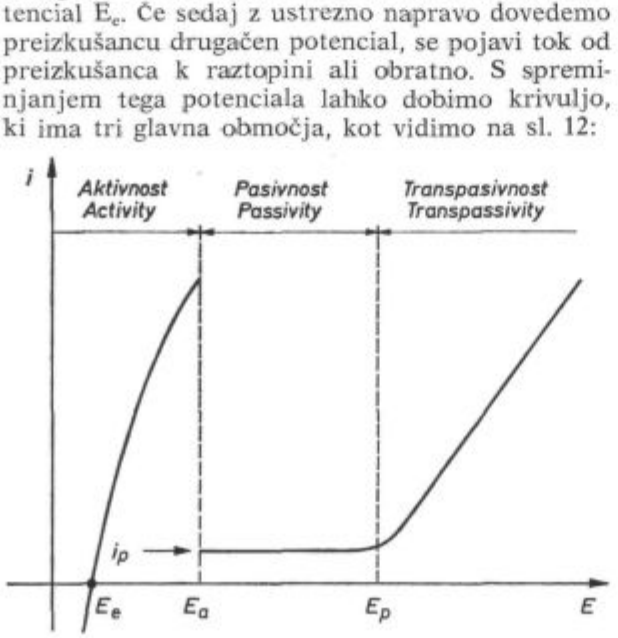
From a fundamental point of view, these results show how the temperature at the moving interface during a massive transformation is influenced both by the transformation rate and by the presence of trace elements in the metal.

D. INFLUENCE OF RESIDUALS (AS SOLUTES OR INCLUSIONS) ON THE PITTING INITIATION IN AUSTENITIC STAINLESS STEELS[13, 14]

In spite of the interest of fundamental investigations, it has already been pointed out, that the preparation of pure metals in our laboratory is primarily concerned with practical properties of steels. Regarding mechanical properties, research works about the brittleness of iron and steel have been mentioned[1, 2, 3]. Some corrosion phenomena in stainless steels will be discussed now.

Among difficult problems concerning austenitic stainless steels, pitting is one of the most important. In that particular kind of corrosion the initiation of pits is the essential step because once a small corrosion hole has been formed on the surface, it will inevitably develop. Then, it is now generally agreed that corrosion pits initiate on non-metallic inclusions. However, depending on the nature of the inclusion this phenomenon is more or less likely to happen. From a practical point of view, it is therefore important to know the behaviour of the various kinds of inclusions which can be present in a stainless steel. This can be done by corrosion tests, counting the number

»polarizacijskih krivulj«. Vzemimo primer preizkušanca, ki je potopljen v korozijsko raztopino. Če je električno izoliran, prevzame določen potencial glede na raztopino, to je t. im. ravnotežni potencial E_e. Če sedaj z ustrezno napravo dovedemo preizkušancu drugačen potencial, se pojavi tok od preizkušanca k raztopini ali obratno. S spreminjanjem tega potenciala lahko dobimo krivuljo, ki ima tri glavna območja, kot vidimo na sl. 12:



Slika 12

Tipična polarizacijska krivulja jekla

Fig. 12

Typical polarization curve of a steel.

1. aktivacijsko območje med ravnotežnim potencialom E_e in potencialom E_a, ki ga imenujemo »aktivacijski«, »pasivacijski« ali »Flade potencial«;

2. pasivacijsko območje, ki je na zgornji strani omejeno s »porušnim potencialom« E_p;

3. »transpasivacijsko« območje.

V pasivacijskem območju je kovina zaščitena s »pasivacijskim slojem«. Pasivacijski tok i_p je v splošnem tako majhen, da korozija skoraj ne poteka. Kolikor daljše je to območje, toliko večja je odpornost proti koroziji. Porušni potencial je opredeljen:

— s porušitvijo pasivacijskega sloja ali

— z začetnim pojavom korozije na nekem vključku.

Ta druga opredelitev pojasnjuje, zakaj porušni potencial pogosto imenujemo »pitting potencial«, tj. potencial, pri katerem nastajajo korozijske jamice na površini jekla. Lahko se zgodi, da je pitting potencial vključkov večji od porušnega potenciala, pri katerem se pretrga pasivacijski sloj, V tem primeru se pri vrednosti pitting potenciala pojavi porast korozijskega toka v transpasivacijskem območju.

Vključki so na splošno dobro opredeljeni s svojim pitting potencialom v določenem korozivnem okolju. Vključki so toliko bolj škodljivi, oz. nevarni, kolikor manjši je njihov pitting potencial.

of pits which are formed on a specimen under well defined conditions. However, it is possible to get a similar if not better information using a much less time consuming procedure by means of the so called »polarization curves«.

Let us consider a specimen which is dipped in a given corrosive medium. If it is electrically isolated it takes on a certain potential with respect to the solution: this is the equilibrium potential E_e. Now, if a different potential is applied to the specimen by means of a suitable device, a current will flow from the specimen into the solution or in the opposite direction. Changing the potential, one gets a complete curve which exhibits three main regions (Fig. 12):

1. the activity region, betwen E_e and E_a. The latter potential is called the »activation potential« or »passivation potential« or »Flade potential«.

2. the passivity region limited on the high side by the »breakdown potential« E_p.

3. the »transpassivity« region.

In the passivity range, the metal is protected by a »passive layer«. The passivation current i_p is generally so low that there is no significant corrosion of the metal. Generally speaking, the longer is this region, the better is the steel. Furthermore, the rupture potential is determined:

— either by the breakdown of the passive layer.

— or by the onset of corrosion on some inclusion.

The second mechanism explains why the breakdown potential is frequently called, in the case of stainless steels, the »pitting potential«. However, it can happen that the pitting potential of the inclusions is higher than the true rupture potential of the passive layer. In such a case, there will be an increase in the corrosion current at the value of the pitting potential, in the region of transpassivity.

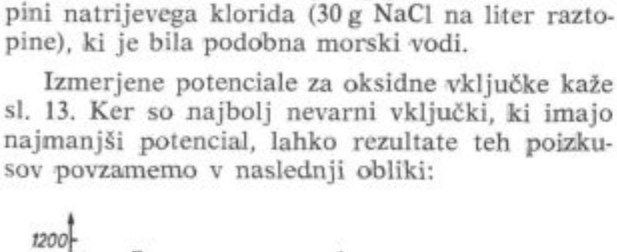
On the whole, in a given medium, the inclusions are characterized by their pitting potential. The lower it is, the worse are the inclusions. Therefore, it is obviously of interest to classify the inclusions with respect to their pitting potentials. It is hardly possible to achieve an accurate classification using industrial steels because there are in general several kinds of inclusions with a whole range of compositions. On the other hand, this can be done with high purity metals containing one well defined category of inclusions.

Such a research work has been performed in our laboratory. The base steel was of grade 18 to 10. Thanks to suitable doping, various kinds of inclusions have been produced: oxides, sulphides, selenides, tellurides. As a general rule, the specimens have been water-quenched at 1150 °C. However, some other treatments, including deformation at high or low temperature have also been used.

Zato je zanimiva razvrstitev vključkov po njihovem pitting potencialu. Seveda je nemogoča natančna klasifikacija vključkov v nerjavnem industrijskem jeklu, ker tehnična nerjavna jekla vsebujejo celo vrsto različnih vključkov s spremenljivo kemično sestavo, ki se lahko spreminja v določenem območju. Za tako klasifikacijo rabimo torej čiste materiale, ki vsebujejo le eno, dobro opredeljeno vrsto vključkov.

V našem laboratoriju smo zato izvedli ustrezne raziskave na čistem jeklu 18—10, v katerem smo s skrbnim dodajanjem zelo majhnih količin določenih nečistoč proizvedli točno določene vrste vključkov: okside, sulfide, selenide in teluride. Vsi preizkušanci so bili gašeni v vodi s 1150 °C. Uporabljali smo tudi druge vrste obdelave, oz. predelave, vključno z deformacijo pri višji ali nižji temperaturi. Pitting potenciale smo določali na preizkušancih, ki so bili potopljeni v vodni raztopini natrijevega klorida (30 g NaCl na liter raztopine), ki je bila podobna morski vodi.

Izmerjene potenciale za oksidne vključke kaže sl. 13. Ker so najbolj nevarni vključki, ki imajo najmanjši potencial, lahko rezultate teh poizkusov povzamemo v naslednji obliki:



Slika 13

Pitting potenciali različnih oksidnih vključkov: mV/ECS — elektrodni potencial kovine merjen z nasičeno kalomel referenčno elektrodo, HT — toplotno obdelano (kaljeno v vodi pri 1150 °C), H — homogenizirano (žarjeno pri 1250 °C), D — žarjeno pri 800 °C za odpravo napetosti.

Fig. 13

Pitting potentials of oxide inclusions: mV/ECS — electrode potential of the metal, measured with a saturated calomel reference electrode, HT — heat treated (water quenched at 1150 °C), H — homogenized (annealed at 1250 °C), D — stress relieved (at 800 °C).

1. Najmanj nevarni so TiO_2 vključki, ki imajo potencial približno 800 mV.

2. Najbolj nevarni so MgO vključki, ki imajo potencial približno 400 mV.

3. Različni načini obdelave in predelave skoraj ne vplivajo na potencial in s tem na škodljivost MgO vključkov.

The pitting potentials have been determined in an aqueous solution of sodium chloride similar to sea water, that is with 30 g of sodium chloride per litre of solution.

Figure 13 shows the results for oxide inclusions. Remembering that the most dangerous inclusions correspond to the lowest pitting potentials, this figure can be commented as follows:

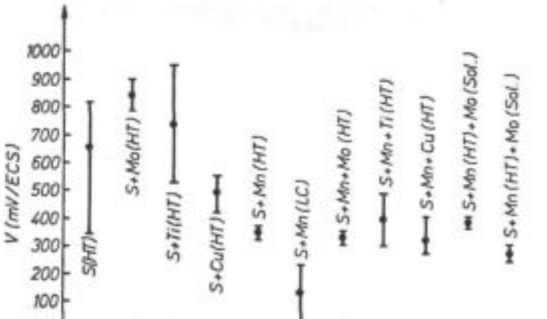
1. TiO_2, with a pitting potential of about 800 mV is the least dangerous inclusion.

2. MgO, with a pitting potential of about 400 mV is the most dangerous one.

3. Considering the MgO inclusions, it is apparent that different treatments do not materially change their pitting potential.

4. Introducing copper or molybdenum into the metal changes te pitting potential of chromite inclusions, although the composition of the inclusions themselves remains unaltered. This shows that the pitting potential of the inclusions depends on the behaviour of the passive layer. For instance, molybdenum significantly improves the resistance to pitting, a fact that has long been known in practice.

Figure 14 shows the results for sulphides. On the whole, the pitting potentials are much lower than in the case of oxides. Manganese sulphides are especially dangerous. As in the former case, molybdenum has a favourable influence. Considering the inclusions of titanium sulphide, the presence of manganese in the matrix seems to have an adverse effect, contrary to molybdenum.



Slika 14

Pitting potenciali sulfidnih vključkov: mV/ECS in HT kot na sl. 13. Sol — raztopljeno v osnovi, LC — vroče valjano.

Fig. 14

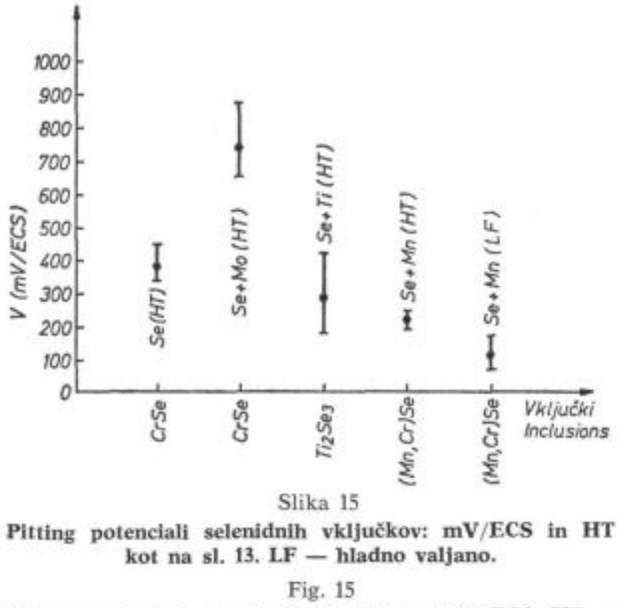
Pitting potentials of sulphide inclusions: mV/ECS, HT — — see Fig. 13. Sol — element dissolved in the matrix, LC — hot rolled

Figures 15 and 16 show the results concerning respectively inclusions of selenides and tellurides. Similar comments as in the former two cases could be made.

4. Baker ali molibden v jeklu spreminjata pitting potencial kromitnih vključkov, čeprav njihova kemična sestava ostane nespremenjena. To kaže, da je pitting potencial vključkov odvisen od obnašanja pasivacijskega sloja. Tako je npr. iz prakse že dolgo znano, da molibden bistveno zvišuje odpornost proti pitting koroziji.

Na sl. 14 prikazujemo rezultate za sulfidne vključke. Njihovi potenciali so na splošno veliko nižji kot pri oksidnih vključkih. Posebno nevaren je MnS. Dodatek molibdena ima ugoden učinek, kot pri oksidnih vključkih. V primeru titanovega sulfida ima prisotnost mangana v osnovni masi nasproten učinek kot molibden.

Sliki 15 in 16 kažeta rezultate za selenidne, oz. teluridne vključke. Analiza rezultatov nas privede do podobnih ugotovitev, kot v primeru oksidnih in sulfidnih vključkov.



Slika 15

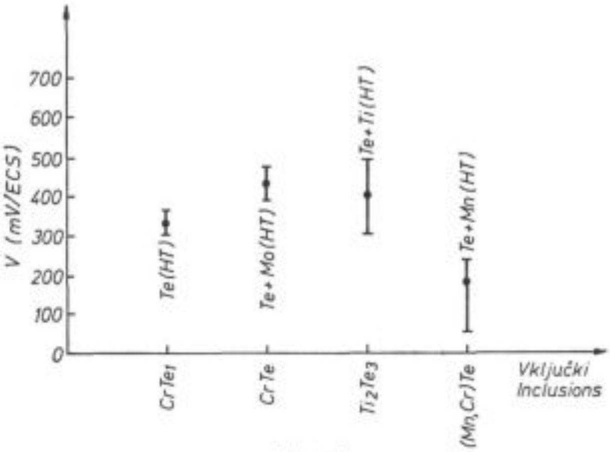
Pitting potenciali selenidnih vključkov: mV/ECS in HT kot na sl. 13. LF — hladno valjano.

Fig. 15

Pitting potentials of selenide inclusions: mV/ECS, HT — — see Fig. 13, LF — Cold rolled

E. ZAKLJUČKI

V rezimeju lahko zaključimo, da uporaba osnovnih kovin, izdelanih iz zelo čistih materialov, omogoča natančnejšo opredelitev vloge posamezne primesi. Zaradi kompleksne interakcije med posameznimi elementi primesi, kot tudi med določenimi primesmi in glavnimi komponentami kovine, bodo za rešitev vsakega specifičnega problema pogosto potrebni številni poskusi na celi vrsti zlitin istega osnovnega tipa. Ko pa je eksperimentalna tehnika raziskav zagotovo in trdno opredeljena, potem to ne predstavlja nepremostljivih težav.



Slika 16

Pitting potenciali teluridnih vključkov: mV/ECS in HT kot na sl. 13.

Fig. 16

Pitting potentials of telluride inclusions: mV/ECS, HT — — see Fig. 13.

D. CONCLUSION

Summing up, it can be said that using base metals prepared with high purity materials, it is possible to characterize more accurately the role of the individual constituents. Because of complex interactions of trace elements with each others or with the main constituents of the metal, any particular problem will often require many experiments with a number of alloys. But once the general working techniques are firmly established, this does not represent tremendous difficulties.

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