

## **Obdelava jekla s streljanjem oplaščene žice v štorski in ravenski jeklarni**

### **Treatment of Steel in Štore and Ravne Steelworks by Injection of Cored Wire**

V. Prešern\*, D. Kmetič\*, A. Rozman\*\*, P. Bračun\*\*\*

UDK: 669.18:669.891  
ASM/SLA: D9r, ADr, EGI41, EGr

Postopek streljanja oplaščene žice, polnjene s CaSi, borom, titanom, žveplom, ogljikom itd. predstavlja nov način izredno natančnega dolegiranja in obdelave jekla s kalcijem v ponovci. Novo tehnologijo smo v začetku 1988 pričeli uvajati v štorsko in ravensko jeklarno, danes pa že predstavlja standardno praks obdelave jekla v ponvi. Prikazali smo rezultate uvajanja tega postopka v pogledu vsebnosti žvepla, kisika in kalcija, sestave žlindre, čistosti jekla, modifikacije in livnosti.

#### **1. UVOD**

V slovenskih železarnah imamo že večletne izkušnje pri obdelavi jekla v ponvi z vpihovanjem CaSi. Z uvedbo tega postopka v redno proizvodnjo smo dobili čistejše jeklo z modificiranimi vključki, kar omogoča odливanje jekla tudi z več kot 0,025 % aluminija na kontinuirni livni napravi za gredice manjših presekov. Pomemben učinek vpihovanja CaSi je tudi odlično razžveplanje, kajti brez posebnih težav dosegamo vsebnosti žvepla, manjše od 0,010 %.

Najvažnejši razlogi in glavne prednosti uvedbe postopka vpihovanja CaSi so bili<sup>1,2,3</sup>:

— Obdelava jekla s CaSi omogoča kompletno modifikacijo aluminatnih vključkov v z aluminijem pomirjenih jeklih. S tem je odstranjena nevarnost mašenja izlivkov med litjem na kontinuirnih livnih napravah za gredice z majhnimi preseki.

— Kot posledico odličnega razžveplanja, dodatne dezoksidacije, modifikacije vključkov in močnega premešavanja jekla v ponvi, dobimo čistejše jeklo z dobro površino gredic.

— Nekatere mehanske lastnosti, kot n. pr. žilavost v prečni in vzdolžni smeri, trdnost in elongacija, se lahko povečajo do 30 %.

Ker pa ima postopek vpihovanja CaSi poleg naštetih prednosti tudi nekatere pomanjkljivosti, so v svetu v zadnjih nekaj letih razvili in zelo hitro uvedli v redno proizvodnjo obdelavo jekla s streljanjem CaSi v obliki polnjene žice.

*Injection of cored wire with CaSi, boron, titanium, sulphur, carbon, . . . is a new method of a very accurate additional alloying and of treatment of steel in ladle with calcium. The new technology was introduced in Štore and Ravne Steelworks in the beginning of 1988, and today it is the standard practice of steel treatment in ladle. The results of the introduction period from the point of sulphur, oxygen, and calcium contents, of slag composition, of steel purity, of modification, and of castability are presented.*

#### **1. INTRODUCTION**

*Slovene Ironworks have a many-year experience with steel treatment in ladle by injection of CaSi. Introduction of this method into regular manufacturing enabled to obtain purer steel with modified inclusions, thus steel with even more than 0.025 % aluminium could be continuously cast into billets of smaller cross sections. Essential effect of CaSi injection is also excellent desulphurisation since sulphur contents below 0.010 % are achieved without special difficulties.*

*The most important reasons and the basic advantages for the introduction of CaSi injection were<sup>1,2,3</sup>:*

— *Treatment of steel with CaSi enables practically complete modification of aluminate inclusions in aluminum-killed steel. Thus the danger of stoppage of nozzles in the continuous casting equipment for billets of smaller cross sections was removed.*

— *Purer steel with good surface of billets is obtained due to excellent desulphurisation, additional deoxidation, modification of inclusions, and good stirring of melt in the ladle.*

— *Some mechanical properties, e. g. toughness in lateral and transversal direction, strength, and elongation can be increased up to 30 %.*

*Since the CaSi injection method has also some disadvantages beside the mentioned advantages, the treatment of steel by the injection of CaSi in form of cored wire was developed in recent years in the world, and it was very rapidly introduced in standard steelmaking.*

*The main reasons for introduction of this method in our steelworks were:*

— *Treatment by the injection of cored wire is a simple method, and it demands no additional technical knowledge.*

\* doc. dr. Vasilij Prešern, mag. dipl. ing. met., SŽ Metalurški inštitut Ljubljana,

Dimitrij Kmetič, dipl. ing. met., SŽ Metalurški inštitut Ljubljana,

\*\* Alojz Rozman, mag. dipl. ing. met., SŽ Železarna Ravne,

\*\*\* Peter Bračun, dipl. ing. met., SŽ Železarna Štore

\*\* Originalno objavljeno: ZZB 22 (1988) 4.

\*\*\* Rokopis prejet: avgust 1988

Glavni razlogi za uvedbo tega postopka v naše jeklarne so bili:

— obdelava s streljanjem žice je enostaven postopek in ne zahteva skoraj nobenega dodatnega tehničnega znanja;

— velike količine argona (več kot 1000 l/min), ki jih potrebujemo pri vpihanju CaSi pogosto povzročijo, da se žlindra odpre, kar povzroča reoksidacijo taline in povečanje vsebnosti dušika;

— postopek vpihanja CaSi je občasno povzročil, da ni bilo mogoče pravilno zadeti vsebnosti aluminija, imeli smo težave s kontrolo temperature, prihajalo pa je tudi do prekinitev procesa vpihanja zaradi mašenja kopja za vpihanje;

— postopek obdelave jekla s streljanjem oplaščenih žic je mnogo bolj fleksibilen in omogoča tudi zelo natančno dolegiranje oz. dodajanje elementov, kot titan, bora, ogljika, žvepla.

## 2. OPIS POSKUSOV

Tako v Štorah kot na Ravnah so nabavili dvožilno napravo za streljanje oplaščene žice.

Polnjena žica je v obliki samonavajalnih kolutov. Preizkusili smo s CaSi polnjeno žico, premera 13 mm in 9 mm. Vsebnost kalcija v CaSi je vedno 30 %.

Žico s premerom 9 mm smo streljali v ponev s hitrostjo ca 150 m/min, 13 mm žico pa s hitrostjo ca 75 m/min.

V ravenski jeklarni smo postopek streljanja uveli pri VAD tehnologiji, ki zagotavlja vsaj 20-minutno premešavanje z argonom po zadnjem dodatku aluminija.

V štorski jeklarni pa smo istočasno s procesom streljanja žice uveli tudi premešavanje z argonom skozi kamnem na dnu ponve, kar nam bo omogočilo zadostno premešavanje.

V naši standardni tehnološki praksi bi morali za uspešen potek postopka obdelave jekla s streljanjem oplaščene žice v ponvi zagotoviti naslednje pogoje<sup>4</sup>:

— dolomitno bazično oblogo,

— uspešno dezoksidacijo z aluminijem,

— dobro dezoksidirano, bazično, dobro tekočo žlindro z majhno vsebnostjo FeO + MnO (tipične analize žlinder pred streljanjem in po njem so prikazane v tabeli 1).

— zadostno količino žlindre v ponvi (v svetu uporabljajo med 6 in 12 kg žlindre na tono jekla).

Vsekakor pa je potrebno zagotoviti pravilno sestavo in količino žlindre v ponvi tudi zaradi naslednjih razlogov<sup>5,6</sup>.

— Great amount of argon (over 1000 l/min) needed in injection of CaSi powder often causes the slag "opening", and thus the melt is reoxidized and nitrogen content is increased.

— Injection of CaSi powder sometimes caused that the correct aluminium content could not be achieved, there were difficulties in temperature control, and the injection was periodically interrupted due to stoppage of the injection lance.

— Steel treatment by injection of cored wire is much more flexible process which also enables a very accurate additional alloying or adding titanium, boron, carbon, sulphur.

## 2. DESCRIPTION OF EXPERIMENTS

In Štore and in Ravne steelworks twin-wire feeder was purchased.

The cored wire is in form of self-winding coils, and CaSi cored wire, 9 and 13 mm in diameter, was tested. Calcium content in CaSi was always 30 %.

9 mm thick wire was injected into ladle with around 150 m/min, and 13 mm wire with around 75 m/min.

In Ravne steelworks the injection process was introduced in the VAD technology which enables at least a 20 minute stirring with argon after final addition of aluminium.

In Štore steelworks the cored wire injection was introduced together with the argon stirring through a porous plate on bottom of ladle which will enable sufficient stirring.

In our standard technological practice the following conditions must be achieved for a successful treatment of steel with the injection of cored wire into ladle<sup>1</sup>:

— dolomitic basic lining,

— successful deoxidation by aluminium,

— well deoxidized, basic, easily flowable slag with low FeO-MnO contents (typical slag analyses before and after the injection are given in Table 1),

— sufficient amount of slag in ladle (6 to 12 kg slag per ton steel are applied in the world).

Anyhow, the correct composition and the amount of slag in ladle must be achieved also due to the following reasons<sup>5,6</sup>:

— to create the possibility of binding the products of deoxidation and desulphurisation reactions,

— to avoid the reoxidation of steel with atmosphere air,

— to avoid uncontrolled reactions between slag and steel.

Tabela 1: Tipična sestava žlinder pred in po streljanju oplaščene žice s CaSi

|                   |      | CaO % | MgO % | SiO <sub>2</sub> % | Al <sub>2</sub> O <sub>3</sub> % | FeO % | MnO % | CaF <sub>2</sub> % |
|-------------------|------|-------|-------|--------------------|----------------------------------|-------|-------|--------------------|
| Jeklarna<br>Štore | pred | 46    | 16    | 16                 | 12                               | 2     | 1     | 7                  |
|                   | po   | 50    | 16    | 15                 | 12,5                             | 1     | 0,5   | 5                  |
| Jeklarna<br>Ravne | pred | 52,5  | 10    | 15                 | 12                               | 1,5   | 1     | 8                  |
|                   | po   | 53    | 10    | 14,5               | 13                               | 1     | 0,5   | 8                  |

Table 1: Typical composition of slags before and after the injection of CaSi cored wire

|                     |        | CaO % | MgO % | SiO <sub>2</sub> % | Al <sub>2</sub> O <sub>3</sub> % | FeO % | MnO % | CaF <sub>2</sub> % |
|---------------------|--------|-------|-------|--------------------|----------------------------------|-------|-------|--------------------|
| Štore<br>Steelworks | Before | 46    | 16    | 16                 | 12                               | 2     | 1     | 7                  |
|                     | After  | 50    | 16    | 15                 | 12,5                             | 1     | 0,5   | 5                  |
| Ravne<br>Steelworks | Before | 52,5  | 10    | 15                 | 12                               | 1,5   | 1     | 8                  |
|                     | After  | 53    | 10    | 14,5               | 13                               | 1     | 0,5   | 8                  |

- da ustvarimo možnost vezave produktov reakcij dezoksidacije in razšveplanja,
- da preprečimo reoksidacijo jekla iz atmosfere,
- da preprečimo nekontrolirane reakcije med žlindro in jeklom.

### 3. METALURŠKI REZULTATI

#### 3.1. Kalcij

Osnovna naloga kalcija pri obdelavi jekel, pomirjenih z aluminijem, je modifikacija čistih trdnih aluminatnih vključkov v tekoče kompleksne vključke, vrste  $\text{CaO}-\text{Al}_2\text{O}_3$ .

Vsebnost kalcija v jeklu mora biti tolikšna, da je razmerje kalcij:aluminij večje kot  $0.14^{7,8}$ , ko pride do modifikacije v željeno obliko kompleksnih vključkov s tališčem pod temperaturami litja jekel.

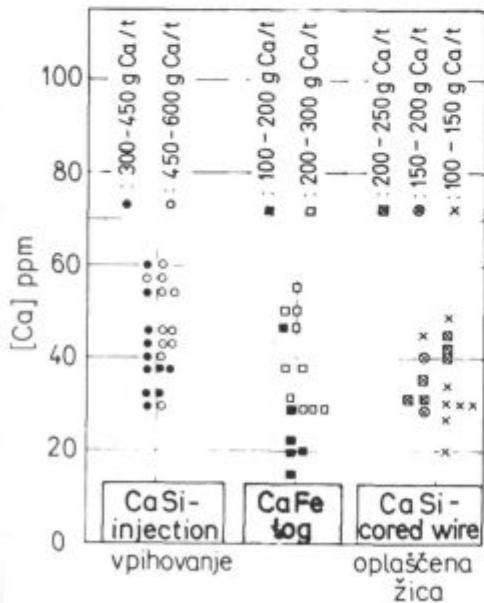
Da pa v glavnem dobimo takšno razmerje, je potrebno poznati izkoristek kalcija pri strejanju oplaščene žice. Ugotovili smo, da je bil izkoristek pri opazovanih talinah med 15 in 25 % in je večji in v ozjih mejah trosenja, kot je pri obdelavi jekla z vpihovanjem drobnozrnatega CaSi. Primerjava izkoristkov kalcija pri treh različnih metodah, ki smo jih uporabili v slovenskih železarnah, je razvidna s **sliko 1**; razmerje med kalcijem in aluminijem pri opazovanih talinah pa prikazuje **slika 2**.

Izkoristi kalcija se zelo dobro ujemajo tudi s podatki iz drugih jeklarn po svetu<sup>7,9,10,11</sup>.

Količina kalcija je v osnovi odvisna od količine doda ne žice in dokazali smo, da lahko na naših pogojih prika jemo optimalne rezultate pri naslednjih količinah dodane žice polnjene s CaSi:

- ogljik < 0,25 % : 0,7 do 0,9 kg CaSi/t
- 0,25 % < ogljik < 0,40 % : 0,7 kg CaSi/t
- ogljik > 0,40 % : 0,4 do 0,6 kg CaSi/t

Razdelitev vsebnosti aluminija in kalcija za nekatere poskusne taline prikazujeta **sliki 3 in 4**.



Slika 1

Primerjava izkoristkov kalcija pri vpihovanju CaSi, uporabi CaFe-logov in strejanju oplaščene žice s CaSi

**Fig. 1**  
Comparison of calcium yields in injection of powdered CaSi, in applying CaFe logs, and in injection of CaSi cored wire

### 3. METALLURGICAL RESULTS

#### 3.1. Calcium

Basic task of calcium in the treatment of aluminium-killed steel is the modification of pure solid aluminate inclusions into liquid complex inclusions of  $\text{CaO}-\text{Al}_2\text{O}_3$  type.

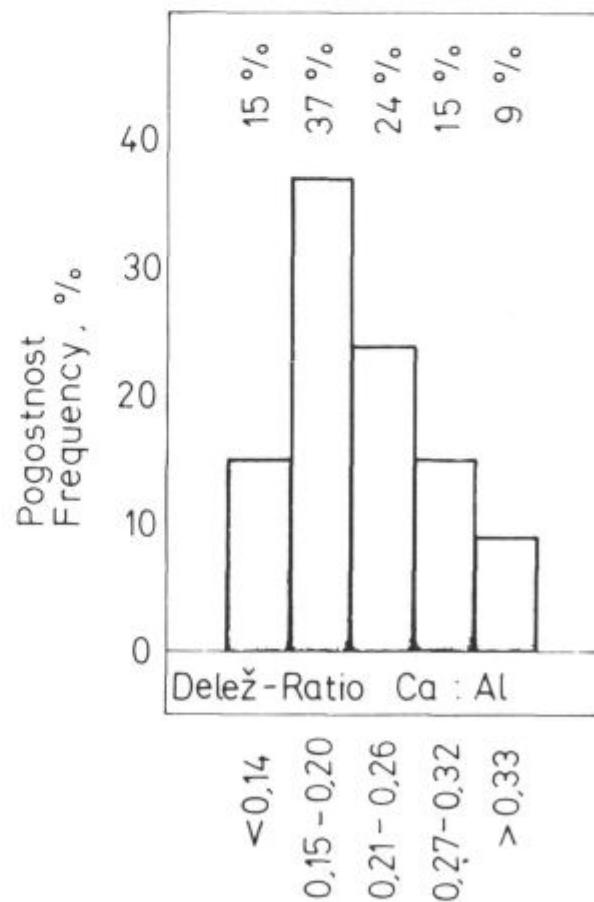
Calcium content in steel must be such that  $\text{Ca}/\text{Si}$  ratio is greater than  $0.14^{7,8}$  when modification into desired form of complex inclusions with melting points below the casting temperature of steel is achieved.

In order to achieve such a ratio, it is necessary to know the yield of calcium in the injection of cored wire. It was found that the yield in tested melts varied between 15 and 25 %, and it is higher and in narrower limits than in the treatment of steel by the injection of fine grained CaSi. Comparison of calcium yields by three different methods being applied in Slovene Ironworks is shown in Fig. 1, and  $\text{Ca}/\text{Si}$  ratio in the investigated melts in Fig. 2.

Calcium yields are in a very good agreement with the data of some other steel plants in the world<sup>7,9,10,11</sup>.

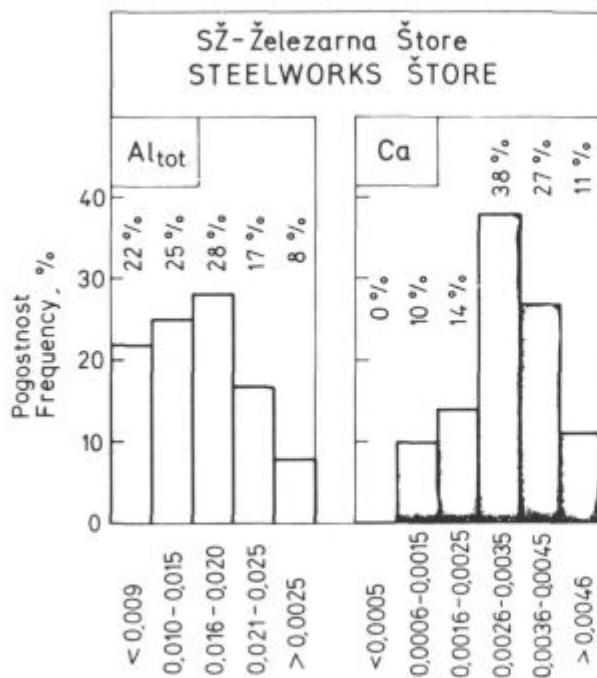
The amount of calcium itself depends on the amount of added wire, and it was proved that the optimal results can be expected for our conditions at the following amounts of added CaSi cored wire:

- carbon < 0,25 % : 0,7 to 0,9 kg CaSi/t
- 0,25 % < carbon < 0,40 % : 0,7 kg CaSi/t
- carbon > 0,40 % : 0,4 to 0,6 kg CaSi/t.



Slika 2  
Razmerje med kalcijem in aluminijem v poskusnih talinah

**Fig. 2**  
Calcium/aluminium ratio in tested melts



Slika 3:

Vsebnosti aluminija in kalcija v poskusnih talinah v štorski jeklarni

Fig. 3

Aluminium and calcium contents in tested melts in Štore steel-works

### 3.2 Kisik

Ker je končna vsebnost kisika v jeklu eden od najvažnejših kazalcev kvalitete jekla, smo analizirali spremenjanje vsebnosti kisika od streljanja žice s CaSi do končne vsebnosti v izvaljanem jeklu.

Že kar v uvodu lahko postavimo važno ugotovitev, da so rezultati poskusov jasno pokazali, da je bolj kot sam vpliv kalcija in aluminija za vsebnost kisika v jeklu odločilno premešavanje z argonom in sestava žlindre v ponovi. Taline, ki naj bi po termodinamičnih zakonitostih imele več kisika, pa so bile dovolj prepokane z argonom pod ustrezeno žlindro, so imele bistveno manjše končne vsebnosti kisika od neprepokane talin.

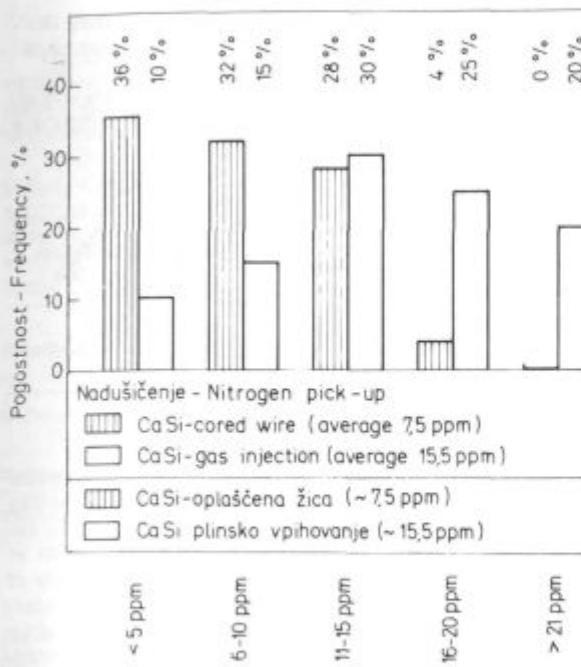
Razdelitev skupnega končnega kisika v poskusnih talinah prikazujemo v tabeli 2.

Tabela 2: Razdelitev skupnega končnega kisika v poskusnih talinah obdelanih s streljanjem oplaščene žice s CaSi

|                  | Otot, % | < 0.0030 | 0.0031 - 0.0050 | 0.0051 - 0.0070 | > 0.0071 |
|------------------|---------|----------|-----------------|-----------------|----------|
| Ravne (20 talin) | Delež   | 30       | 65              | 5               | 0        |
| Štore (50 talin) | Delež   | 10       | 46              | 40              | 4        |

Table 2: Distribution of total final oxygen in tested melts treated by the injection of CaSi cored wire

|                  | Otot, % | < 0.0030 | 0.0031 - 0.0050 | 0.0051 - 0.0070 | > 0.0071 |
|------------------|---------|----------|-----------------|-----------------|----------|
| Ravne (20 melts) | Portion | 30       | 65              | 5               | 0        |
| Štore (50 melts) | Portion | 10       | 46              | 40              | 4        |



Slika 5

Primerjava nadušičenja zaradi vpihanja CaSi in streljanja oplaščene žice s CaSi

Fig. 5

Comparison of nitrogen pick-up in injection of powdery CaSi and CaSi cored wire

Ustvarjanje pogojev za dovolj majhne končne vsebnosti kisika je nujna naloga, saj trdijo<sup>12,13</sup>, da lahko zastonno čistost jekla pričakujemo le, ko je skupna vsebnost kisika manjša od 0.0050 ali celo 0.0040 %.

### 3.3 Dušik

Povprečne vsebnosti dušika v jeklu iz naših elektroobločnih peči so 70 do 100 ppm. Pri obdelavi jekla v ponvi pa pride do povečanja vsebnosti dušika v jeklu. Z meritvami v različnih fazah tehnološkega postopka smo potrdili, da se vsebnosti dušika povečajo.

Izdelali smo primerjavo povečanja vsebnosti dušika med talinami, obdelanimi s streljanjem žice, polnjene s CaSi, in z vpihanjem CaSi, kar prikazuje slika 5.

Pri vpihanju CaSi pogosto prihaja do povečanja vsebnosti dušika za 20 in več ppm, povprečno povečanje večjega števila talin pa je bilo 15.5 ppm. Rezultati obdelave s streljanjem žice pa kažejo, da je povečanje vsebnosti dušika za polovico manjše.

Razlog je, da prihaja pri streljanju žice le poredko do odpiranja površine žlindre oz. jekla v ponvi, ker uporabljamo bistveno manjše količine argona kot pri vpihanju in je reakcija mnogo mirnejša.

### 3.4 Žveplo

Znano je, da postopek streljanja žice s CaSi ne uporabljamo za razvedljivanje. Pri poskusnih talinah z optimalnimi količinami uporabljene žice so bile stopnje razvedljavanja med streljanjem dejansko majhne (do 15 %).

Že v uvodu smo omenili, da lahko pride pri obdelavi jekla z večjo vsebnostjo žvepla (nad 0.020 %) do tvorbe čistih vključkov, vrste CaS, ki imajo visoko tališče in lahko povzročajo mašenje izlivkov, podobno kot čisti aluminati vključki. Eden od pogojev za uspešno obdelavo s

Distribution of total final oxygen in tested melts is shown in Table 2.

Creating the conditions to achieve sufficiently low final oxygen contents is an urgent task, since it is claimed<sup>12,13</sup> that a sufficient purity of steel can be expected when total oxygen content is below 0.0050 or even 0.0040 %.

### 3.3. Nitrogen

Average nitrogen contents in steel from our electric arc furnaces vary between 70 and 100 ppm. During steel treatment in ladle nitrogen content in steel is increased. Measurements of nitrogen content in various stages of technological process confirmed this.

A comparison of the increase of nitrogen content between the melts which were treated by the injection of CaSi core wire and by the injection of powdered CaSi was made, and it is presented in Fig. 5.

When powdery CaSi is injected the nitrogen contents often increase for 20 or more ppm. The mean value for a greater number of tested melts was 15.5 ppm. The results of treatment by the injection of cored wire show that the nitrogen content is increased for half of previous values.

The reason is that injection of wire only seldom causes "the opening" of slag layer in ladle since smaller amounts of argon are applied than in the injection of powder, and the reaction is much more smooth.

### 3.4. Sulphur

It is known that the injection of CaSi cored wire is not applied as a desulphurisation method. In tested melts with the optimal amounts of applied wire, the desulphurisation during injection was virtually low (up to 15 %).

It was mentioned already in the introduction that pure CaS inclusions with high melting point can be formed in treatment of steel with higher sulphur content (over 0.020 %), and they can cause stoppage of nozzles like pure aluminate inclusions. One of the conditions for successful treatment by the injection of cored wire is sufficient preceding desulphurisation.

Also steel with sulphur contents over 0.020 % was treated by the injection of CaSi cored wire, but accurate metallographic investigations did not reveal pure CaS inclusions. Thus we are of opinion that the obtained results confirm (also in agreement with some references<sup>7,18</sup>) that the permitted interval of sulphur content at a suitable amount of aluminium and calcium is wider than theoretically supposed<sup>9,20</sup>.

### 3.5. Yield of Elements in Cored Wire

The yield of calcium which was added in form of CaSi cored wire, and the yield in the injection of fine grained CaSi was already discussed. Thus some data on yields of boron and titanium which were added in form of cored wire in Štore and in Ravne Steelwork will be explained here.

FeTi and FeB cored wires were tested. FeTi wire had 13 mm diameter and it contained 72 % titanium and 4.5 % aluminium, while FeB wire had 9 mm diameter and it contained 12 % boron.

Both wires were tested in combination with the injection of CaSi cored wire and just here the extraordinary flexibility and suitability of the injection equipment with two drives and guides was proved. As mentioned, the

streljanjem žice zato je, da zagotovimo zadostno predhodno razšveplanje.

S strelenjem oplaščene žice s CaSi smo obdelali tudi jekla z vsebnostmi žvepla nad 0,020 %, vendar kljub natančnim metalografskim preiskavam čistih CaS vključkov nismo zasledili. Zato menimo, da dobavljeni rezultati potrjujejo (tudi v soglasju z delom literature<sup>7, 18</sup>), da je dovoljeno vsebnosti žvepla pri primerni količini aluminija in kalcija širše, kot ga navajajo teoretične predpostavke<sup>9, 20</sup>.

### 3.5 Izkoristki elementov v oplaščeni žici

O izkoristku kalcija, dodanega v obliki CaSi v žici, in o primerjavi z izkoristkom pri vpihovanju drobnozrnatega CaSi smo že govorili, na tem mestu pa bomo podali nekatere podatke o izkoristkih bora in titana, ki smo ju v obliki polnjene žice preizkusili tako v štorski kot ravenski jeklarni.

Preizkusili smo s FeTi in FeB polnjene žice (FeTi z 72 % titana in 4,5 % aluminija ter premerom 13 mm, FeB z 12 % bora in premerom žice 9 mm).

Obe vrsti žice smo preizkušali v kombinaciji s strelenjem žice s CaSi in prav tu se je pokazala izredna fleksibilnost in pripravnost naprave za strelenje z dvema pogonoma in vodiloma. Kot že rečeno, je namen titana predvsem v vezavi dušika, bor v obliki karbida pa pomaga doseči željeno območje zanesljive prekajivosti.

Izračunani izkoristki tako titana kot bora so odlični in v zelo ozkih mejah trošenja in jih prikazujemo v tabeli 3.

Tabela 3: Izpleni elementov pri dodajanju v oplaščeni žici

| Element | Analitično območje določevanja, (%) | Poprečen izplen, (%) | $\delta$ | Dezoksidacijska praksa |
|---------|-------------------------------------|----------------------|----------|------------------------|
| titan   | 0,010 — 0,050                       | 90                   | 5        | Si + Al                |
| bor     | 0,0015 — 0,0030                     | 85                   | 5        | Si + Al + Ti           |
| kalcij  | 0,0010 — 0,0060                     | 15 — 25              |          | Si + Al                |

### 3.6 Livnost

Že dolgo vemo, da je livnost večine jekel, pomirjenih z aluminijem (posebno pri postopku kontinuirnega ulivanja gredic manjših dimenzij), največkrat močno zmanjšana zaradi trdnih aluminatnih vključkov, ki se nabirajo na izlivkih<sup>14</sup>. Do hitrega mašenja manjših izlivkov pride že pri vsebnosti aluminija nad 0,010 %. Velika notranja medfazna energija aluminatnih vključkov v jeklu je tista pogonska sila, da se aluminatni delci lepijo na stene iz ognjevarnega materiala in med seboj.

Takšne težave pri odlivanju jekel smo uspešno rešili z uvedbo postopka vpihovanja drobnozrnatega CaSi z argonom. Vendar pa je od časa do časa še prihajalo do težav pri odlivanju, predvsem zaradi večkrat nezanesljivega zadevanja vsebnosti aluminija in pa, kot že omenjeno, zaradi prekinitev postopka vpihovanja zaradi zamašitve kopja za vpihovanje.

Z uvedbo postopka strelenja oplaščene žice s CaSi smo gotovo naredili tehnički korak naprej. Ne samo, da pri vseh dosedanjih poskusih nismo imeli tehničnih problemov in smo dejansko vedno lahko v jeklo dodali željeno količino CaSi, mnogo lažji in enostavnejši ter veliko bolj kontroliran je celotni postopek. Poleg tega pa imamo še novo možnost izredno natančnega dodajanja poljubnih količin ostalih materialov.

aim of titanium addition is binding of nitrogen, while boron in form of carbide enables to achieve the desired region of hardenability band.

Calculated yields of titanium and of boron are excellent and in very narrow limits of dissipation, and they are shown in Table 3.

Table 3: Yield of elements added with cored wire

| Element  | Analytical region of determination (%) | Mean yield (%) | $\delta$ | Deoxidation practice |
|----------|--|----------------|----------|----------------------|
| Titanium | 0,010 — 0,050                          | 90             | 5        | Si + Al              |
| Boron    | 0,0015 — 0,0030                        | 85             | 5        | Si + Al + Ti         |
| Calcium  | 0,0010 — 0,0060                        | 15 — 25        |          | Si + Al              |

### 3.6 Castability

It is known for a long time that the castability of most aluminium killed steel (especially for continuous casting of billets with small cross section) is often highly reduced due to solid aluminate inclusions which pile in nozzles<sup>14</sup>. Smaller nozzles are rapidly stopped already at aluminium contents over 0,010 %. High internal interphase energy of aluminate inclusions in steel is the driving force for sticking of aluminate particles on the refractory walls and to each other.

Such problems in steel casting were successfully solved by the introduction of the injection of fine grained CaSi with argon. But difficulties in casting appear from time to time mainly due to uncertainty in achieving the aluminium content or, as also mentioned before, due to interruption of the process when the injection lance is stopped.

Introduction of the injection of CaSi cored wire means certainly a technological step forward. Not only that in all tests so far no technical problems appeared and that always the desired amount of CaSi could be added into steel, the overall method is much easier and more simple and much more easily controllable. Besides, there is still a new possibility for a very accurate adding of optional amount of other materials.

### 4. METALLOGRAPHIC INVESTIGATIONS

The basic finding of metallographic investigations of steel melts being treated by the injection of cored wire was that a suitable amount of wire assures the modification of aluminate inclusions and thus sufficiently pure steel.

Typical composition of an oxide inclusion can be represented by  $x\text{CaO}-y\text{Al}_2\text{O}_3-\text{CaS}$  and examples of such inclusions in some melts are given in Figs. 6 and 7. The inclusion contained 25 % calcium and 35 % aluminium. Steel purity determined by the K4 method is presented in Fig. 4. It is evident that suitable shape of inclusions<sup>5, 16, 17</sup> enabled to obtain purer steel.

Table 4: Steel purity determined by the K4 method

| Way of treatment                        | Portion of melts, % |          |          |
|---|---------------------|----------|----------|
|   | K 4 < 5             | K 4 < 15 | K 4 < 30 |
| Untreated                               | 0                   | 50       | 85       |
| Treated by injection of CaSi cored wire | 25                  | 70       | 100      |

At a certain aluminium content in steel, there exists theoretically a critical sulphur content above which for-

#### 4. METALOGRAFSKE PREISKAVE

Osnovna ugotovitev metalografskih raziskav jekel, obdelanih s streljanjem oplaščene žice, je, da smo s približno količino žice zagotovili modifikacijo aluminatnih vključkov in dovolj čisto jeklo.

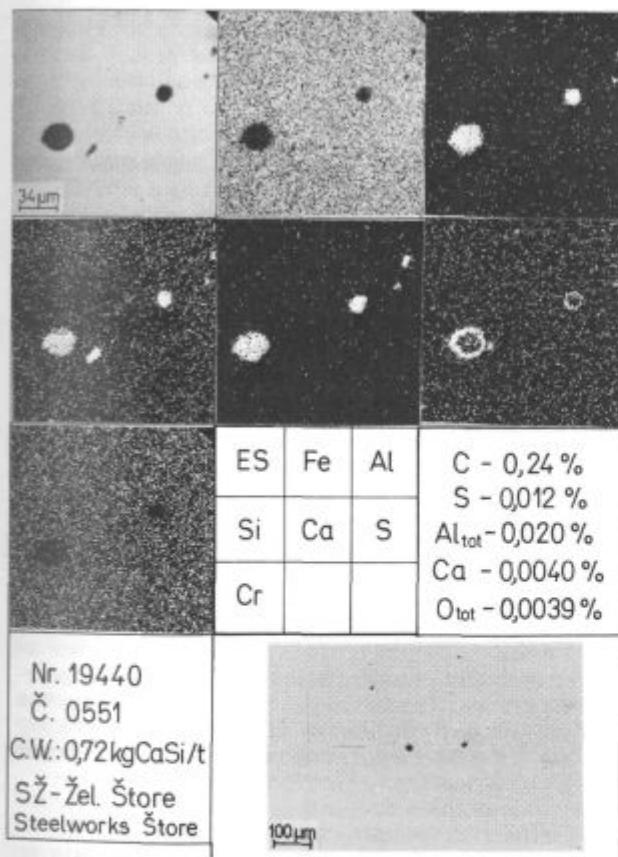
Tipična sestava oksidnega vključka je  $x\text{CaO} \cdot \text{Al}_2\text{O}_5 \cdot \text{CaS}$  in primeri takih vključkov v nekaterih talinah so prikazani na slikah 6, 7 a in 7 b, kjer smo v vključku določili 25 % kalcija in 35 % aluminija. Čistost jekla po metodi K4 prikazujemo v tabeli 4. Ravidno je, da smo dobili čistejše jeklo s primerno obliko vključkov<sup>15, 16, 17</sup>.

Tabela 4: Čistost jekla po metodi K 4

| Način obdelave         | Delež talin, % |          |          |
|------------------------|----------------|----------|----------|
|                        | K 4 < 5        | K 4 < 15 | K 4 < 30 |
| Neobdelane             | 0              | 50       | 85       |
| Streljanje žice s CaSi | 25             | 70       | 100      |

Pri določeni vsebnosti aluminija v jeklu obstaja teoretično neka kritična vsebnost žvepla, nad katero lahko pričakujemo tvorbo CaS. Istočasno pa je v jeklu potrebna določena količina kalcija za zagotovitev popolne modifikacije čistih trdnih aluminatnih vključkov.

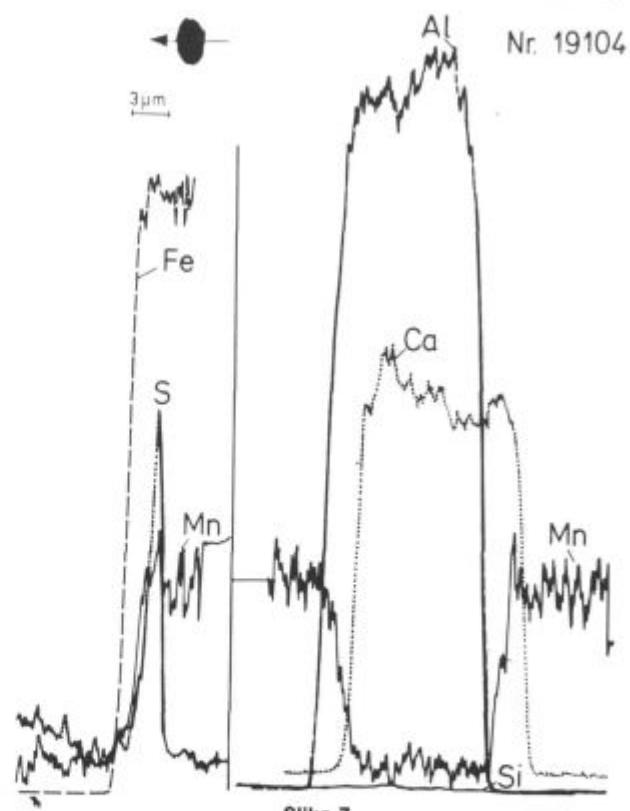
Kot pa že rečeno, so naše raziskave potrdile, da gre za širše dovoljeno območje vsebnosti aluminija, žvepla in kalcija. Čistih vključkov vrste CaS nismo zasledili, do-



Slika 6  
Tipičen izgled in sestava modifikiranega vključka

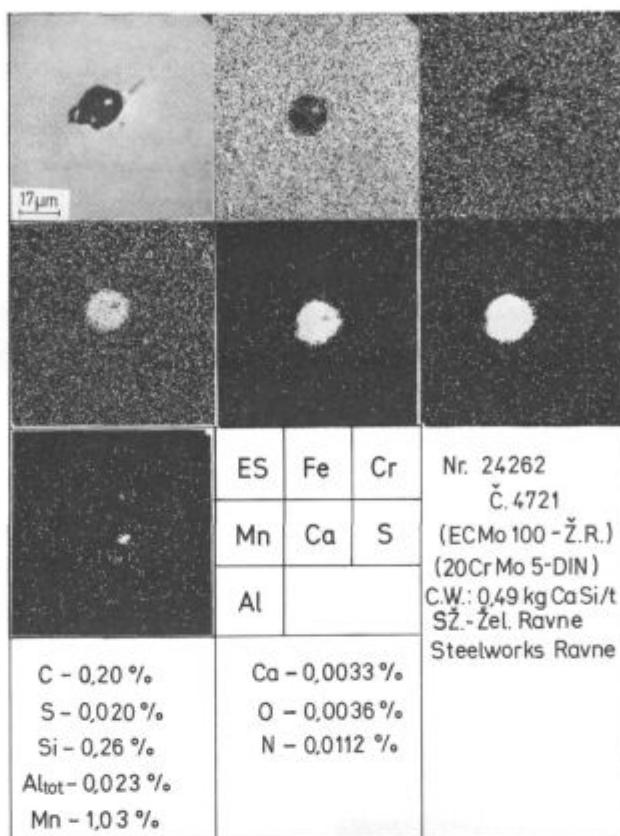
Fig. 6  
Typical appearance and composition of modified inclusion

|   | 3 μm |  |   |    |
|---|------|--|---|----|
|   |      | ES   | Fe  | Al |
|   | Mn   | Ca   | S   |    |
|   | Si   |  |   |    |
| Nr. 19104<br>Č. 1431<br>oplaščeno žico:<br>cored-wire:<br>1,00kgCaSi/t<br>SŽ-Žel. Štore<br>Steelworks Štore |      | C - 0,34 %<br>Si - 0,19 %<br>Al <sub>tot</sub> - 0,022 %<br>S - 0,016 %<br>Mn - 0,70 % | Ca - 0,0019 %<br>O <sub>2</sub> - 0,0051 %<br>N <sub>2</sub> - 0,0110 % |    |



Slika 7  
a) Izgled modifikiranega vključka  
b) Kvantitativna analiza tega vključka

Fig. 7  
a) Appearance of modified inclusion  
b) Quantitative analysis of this inclusion



Slika 8

Izgled in sestava modificiranega vključka vrste CaO-CaS-MnS

Fig. 8

Appearance and composition of CaO-CaS-MnS modified inclusion

kazali pa smo prisotnost kompleksnih vključkov vrste CaS-MnS (slika 8), ki pa verjetno ne povzročajo težav pri litju.

## 5. OCENA STROŠKOV

Za ocenitev tehnologije streljanja oplaščene žice je potrebna tudi groba ocenitev stroškov takega postopka in primerjava postopka streljanja oplaščene žice s postopki vpihovanja drobozrnatega CaSi.

Moderna naprava za vpihovanje stane danes približno 10-krat toliko kot naprava za streljanje žice z dvema žilama.

Seštevek in pregled nekaterih najpomembnejših operativnih stroškov in primerjavo teh stroškov med obema postopkom dodajanja CaSi podajamo v tabeli 5.

Podatke v razpredelnici smo dobili na osnovi naslednjih ocen stroškov:

- CaSi prah za vpihovanje : ca 3 DEM/tono
- CaSi v oplaščeni žici : ca 9 DEM/tono
- Električna energija : 0,08 DEM/kWh
- Argon : 4 DEM/m<sup>3</sup>

Računali smo, da je povprečna poraba CaSi pri oplaščeni žici 0,7 kg/tono, pri vpihovanju CaSi pa 2,0 kg/tono.

Ocenjeni stroški pri uporabi CaSi v obliki polnjene žice so 10,4 DEM/tono in 15,0 DEM/tono pri vpihovanju CaSi. Ugotovimo lahko, da je minimalno zmanjšanje stroškov pri prehodu na obdelavo jekla s streljanjem oplaščene žice 4,6 DEM/tono jekla, kar se dobro ujema tudi s podatki iz tujih jeklarn<sup>7,21</sup>.

mation of CaS can be expected. Simultaneously steel must contain a certain amount of calcium in order to achieve complete modification of pure solid aluminate inclusions.

As already mentioned, our investigations confirmed that permitted intervals of aluminium, sulphur, and calcium contents are wider. Pure CaS inclusions were not found, but presence of complex CaS-MnS inclusions (Fig. 8) was confirmed, though they probably do not cause difficulties in casting.

## 5. ESTIMATION OF COSTS

In order to evaluate completely the technology of injection of cored wire, also a rough estimate of costs of such a method and a comparison of costs between the injection of cored wire and the injection of fine grained CaSi are needed.

Modern injection equipment for gas injection costs ten times more than a twin-wire feeder equipment for cored wire.

The sum and review of some most important operational costs and comparison of these costs for the two methods are given in Table 5.

Data in the table were obtained from the estimates of the following costs:

- CaSi powder for injection : around 3 DEM/t
- CaSi in cored wire : around 9 DEM/t
- electric power : 0,08 DEM/kWh
- argon : 4 DEM/m<sup>3</sup>

We have assumed that mean CaSi consumption for cored wire is 0,7 kg/t steel while in injection of powdery CaSi it is 2,0 kg/t.

**Tabela 5: Primerjava stroškov med vpihovanjem CaSi in streljanjem oplaščene žice s CaSi**  
 (Ocenjeni stroški v aprilu 1988 v DM na tono jekla pri letni obdelavi 50.000 ton jekla s CaSi)

| Vrsta stroška                    | Vpihovanje<br>CaSi | Oplaščena<br>žica      |
|----------------------------------|--------------------|------------------------|
| Investicija v opremo             | 2                  | 0.2                    |
| Vzdrževanje                      | 1.5                | 0.5                    |
| Ognjevzdržna obzidava            | 3                  | 3                      |
| Kopje (monolitno)                | 2                  | 0                      |
| Argon                            | 0.1<br>(500 l/min) | 0                      |
| Energija za topotne izgube       | 0.4<br>(+ 10 K)    | (prihranek<br>5 kWh/t) |
| Delo                             | 0.4                | 0.4                    |
| CaSi potreben za obdelavo (kg/t) | (2.0)              | (0.7)                  |
| Cena CaSi                        | 5.6                | 6.3                    |
| Skupno                           | 15.0               | 10.4                   |
| Obdelava z oplaščeno žico        | 10.4 DM/t          |                        |
| Obdelava z vpihovanjem           | 15.0 DM/t          |                        |

Estimated costs in applying CaSi in form of cored wire are 10.4 DEM/t, while in injection of powdery CaSi they are 15.0 DEM/t. It can be stated that minimal reduction of costs is 4.6 DEM/t steel if injection of cored wire is applied, which is in a good agreement with the data of foreign steel plants<sup>7,21</sup>.

**Table 5: Comparison of costs between the injection of powdered CaSi and the injection of CaSi cored wire**  
 (Estimated costs in April 1988 in DEM/ton steel for annual treatment of 50,000 t steel with CaSi)

| Cost                       | Powdered CaSi   | Cored wire           |
|----------------------------|-----------------|----------------------|
| Investment into equipment  | 2               | 0.2                  |
| Maintenance                | 1.5             | 0.5                  |
| Refractory lining          | 3               | 3                    |
| Lance (monolithic)         | 2               | 0                    |
| Argon                      | 0.1(500 l/min)  | 0                    |
| Energy for heat losses     | 0.4<br>(+ 10 K) | (Savings<br>5 kWh/t) |
| Labour                     | 0.4             | 0.4                  |
| CaSi for treatment (kg/t)  | (2.0)           | (0.7)                |
| Cost of powder             | 5.6             | 6.3                  |
| Total                      | 15.0            | 10.4                 |
| Treatment with cored wire  |                 | 10.4 DM/t            |
| Treatment by powdered CaSi |                 | 15.0 DM/t            |

## 6. ZAKLJUČKI

Po nekajmesečnem delovanju novega postopka streljanja oplaščene žice s CaSi (pa tudi borom, titanom) v štorski in ravenski jeklarni lahko ugotovimo, da s tem postopkom uspešno nadomestimo postopek vpihovanja drobnozrnatega CaSi pri izdelavi in odilovanju z aluminijem pomirjenih jekel.

S primerno tehnologijo lahko izdelamo in na kontinuirni napravi za gredice manjših dimenzijs odlijemo dovolj čisto jeklo z majhno vsebnostjo kisika in primerno sestavo ter obliko nekovinskih vključkov.

Najvažnejše in najbolj pomembne prednosti postopka streljanja oplaščene žice s CaSi in prednosti tega postopka v primerjavi z vpihovanjem CaSi so:

- zaradi mnogo mirnejše reakcije je manjše povečanje vsebnosti dušika, vodika in tudi kisika, mnogo manjša je emisija plinov med reakcijo;

- izkoristek kalcija je pri streljanju žice bistveno boljši in v primerjavi z vpihovanjem je poraba CaSi skoraj 3-krat manjša;

- v primerjavi s klasično tehnologijo je neprimerno boljši in v ožjih mejah trosenja tudi izkoristek ostalih elementov, ki jih dodajamo v polnjeni žici;

- manjše so topotne izgube: običajno pada temperatura jekla med obdelavo s streljanjem žice le ca 10 K, kar je bistveno manj od skoraj 30 K pri postopku vpihovanja;

- dana je možnost skoraj idealnega dolegiranja oz. natančnega zadevanja vsebnosti nekaterih elementov, kot n. pr. aluminija, bora, titana, ogljika, žvepla, ...;

- z upoštevanjem optimalne tehnologije dosežemo kompletno modifikacijo aluminatnih vključkov v okrogle, kompleksne vključke z nizkimi temperaturami tališč, ki ne povzročajo težav pri odilovanju z aluminijem pomirjenih jekel;

- investicijski in operativni stroški so pri postopku streljanja oplaščene žice manjši v primerjavi s postopkom vpihovanja.

## 6. CONCLUSIONS

A few-months operation of the injection of CaSi (and also boron, and titanium) cored wire in Štore and Ravne Steelworks confirmed that his method can successfully substitute the injection of fine grained CaSi in manufacturing and casting aluminium killed steel.

Applying a suitable technology enables to make and continuously cast into billets of smaller cross section a sufficiently pure steel with low oxygen content, and suitable composition and shape of non-metallic inclusions.

The most important advantages of the injection of CaSi cored wire, also in comparison with the injection of powdered CaSi are:

- due to much smoother reaction the increase of nitrogen, hydrogen, and also oxygen contents is smaller, and much smaller is also the emission of gases during the reaction;

- calcium yield is in injection of cored wire essentially better, and compared with the injection of powdered CaSi the CaSi consumption is nearly 3 times lower;

- compared with the standard technology this method is essentially better since yield of other elements added with cored wire is in narrower limits of dissipation;

- heat losses are lower: usually temperature drop of steel melt in treatment by the injection of cored wire is only about 10 K, which is essentially less than 30 K in the injection of powdered CaSi;

- the possibility of nearly ideal additional alloying or achieving accurate contents of some elements as aluminium, boron, titanium, carbon, sulphur, etc. is given,

- applying the optimal technology gives the complete modification of aluminat inclusions into spheroidal, complex inclusions with low melting points which do not cause difficulties in casting aluminium killed steel;

- investment and operational costs for the injection of cored wire are lower than those for the injection of powdered CaSi.

## LITERATURA/REFERENCES

1. Prešern V., P. Bračun: Continuous Casting '85, London, 22—24 May 1985, Paper 6.
2. Prešern V., J. Arh, P. Bračun, S. Paridaens, P. Verschueren: SCANINJECT IV, Lulea, Sweden, June 11—13, 1986, P3.
3. Prešern V., J. Arh, P. Bračun, A. Rozman: Inter. Conf. Secondary Metallurgy, Aachen, (W. Germany), September 21—23, 1987, p. 350—359.
4. Guessier A. L., V. Vachiery, J. L. Tranchant, R. Szezesny: Iron and Steel Ingineer, Oct. 1983.
5. Holappa L. E.: SCANINJECT II, Lulea, Sweden, June 1980.
6. Carlsson G., T. Lehner: Radex-Rundschau, 1981, 1/2, 374—379.
7. Turkdogan E. T.: INTERNATIONAL CALCIUM TREATMENT SYMPOSIUM, 30 June 1988, University of Strathclyde, Glasgow, Paper 2.
8. Faries F., P. C. Gibbins, C. Graham: Ironmaking and Steelmaking, 13, 1986, 13, 1, 26—31.
9. Faulring G. M., J. W. Farrell, D. C. Hilti: Ironmaker and Steelmaker, 7.
10. Guessier A., P. Boussard, F. Pellicani, A. Thomas: Revue de Métallurgie-CIT, 1984, 8—9, 641—649.
11. Tolnay L., S. Varga: 2nd European Electric Steel Conference, Florence, September 29—October 1, 1986.
12. Robinson J. W.: SCANINJECT IV, June 11—13, 1986, Lulea, Sweden.
13. Utaise K., Y. Muraishi, K. Shigematsu: INTERNATIONAL CALCIUM TREATMENT SYMPOSIUM, 30 June 1988, University of Strathclyde, Glasgow, Paper 13.
14. Jeanneau M., M. Poupon: Revue de Métallurgie, 1981, 6, 517—524.
15. Tähtinen M.: Modern Developments in Steelmaking, Paper 7, February 16—18, 1981, Jamshedpur, India.
16. Saxena S. K., H. Sandberg, T. Weldenstrom, A. Persson, S. Steensen: Scandinavian Journal of Metallurgy, 7, 1978, 3, 126—133.
17. Pellicani F., F. Villette, J. Dubois: SCANINJECT IV, Paper 29, June 11—13, 1986, Lulea, Sweden.
18. Bourguignon J. R., J. M. Dixmier, J. M. Henry: Continuous Casting '85, Paper 7, London, May 22—24, 1985.
19. Riboud P., C. Gatellier: Secondary Steelmaking Conference, London, October 1984, p. 7, 1—7, 8.
20. Leroy F.: Revue de Métallurgie-CIT, 1985, 12, 887—897.
21. Jung H. P., Kremer K. J., Spitzer H., Vöge H., Henrich R.: Stahl und Eisen 104, 1984, 4, 197—204.
22. Fliege L., Gorges H.: Techn. Mitt. Krupp Werksberichte, 43, 1985, 2, 57—66.
23. Guessier A.: AFFIVAL cored wire brochure No. 2830, October 1982.