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MODIFICATION OF NON-METALLIC INCLUSIONS IN STEELS WITH ENHANCED MACHINABILITY

MODYFIKACJA WTRĄCEŃ NIEMETALICZNYCH W STALACH O POLEPSZONEJ SKRAWALNOŚCI

The objective of this paper is to identify non-metallic inclusions occurring in aluminium-killed steel with regulated sulphur content and modified with calcium, explain the reaction between calcium and non-metallic inclusions and identify secondary metallurgy parameters, which condition obtaining such forms of inclusions to be favourable to improvement in steel machinability.

Computer-aided thermodynamic calculations and production experiments were carried out. They enabled to determine technological parameters of treatment in liquid steel ladle deoxidised with silicon and aluminium, with low (0.01%) and increased (up to 0.03%) sulphur content.

By comparison of the computer-aided simulations and production experiment results it was found that calcium in the steel both modifies the aluminium oxide inclusions and reacts with sulphur, whereas deep desulphurisation (below 0.01%) is favourable to oxide modification. Non-metallic inclusions of calcium aluminates, which affect positively the machinability of steel, appear in liquid state in the steel bath.

During conventional casting and cooling down large ingots of steel with increased sulphur content, aluminates are significantly depleted in calcium as a result of reaction between calcium and sulphur dissolved in these aluminates and steel matrix. To obtain aluminates and (Ca,Mn)S sulphides rich in calcium in finished products accelerated steel cooling is to be applied, which takes place during continuous steel casting.

In steels modified with calcium, there is higher homogeneity of distribution and sizes of inclusions on finished products' cross-section and higher globularisation of these inclusions in comparison to non-modified steels. Improved steel machining properties in these steels and improved isotropy of mechanical properties in bars made from it were found.

Celem pracy była identyfikacja wtrąceń niemetalicznych powstających w uspokojonej glinem stali z regulowaną zawartością siarki i modyfikowanej za pomocą wapnia, wyjaśnienie przebiegu reakcji wapnia z wtrąceniami niemetalicznymi oraz określenie parametrów obróbki pozapiecowej, warunkujących uzyskanie postaci wtrąceń sprzyjających poprawie skrawalności stali.

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Wykonano komputerowe obliczenia termodynamiczne i eksperymenty przemysłowe, które pozwoliły określić parametry technologiczne obróbki w kadzi ciekłej stali, odtlenionej krzemem i glinem, z niską (0,01%) i podwyższoną (do 0,03%) zawartością siarki.

W wyniku skonfrontowania symulacji komputerowych z wynikami eksperymentów przemysłowych stwierdzono, że wapń w kąpieli stalowej modyfikuje wtrącenia tlenku glinu i reaguje z siarką, przy czym głębokie odsiarczenie (poniżej 0,01%) sprzyja modyfikacji tlenków. Wtrącenia niemetaliczne glinianów wapnia, które pozytywnie oddziałują na skrawalność stali, w kąpieli stalowej występują w stanie ciekłym.

Podczas klasycznego odlewania i studzenia dużych wlewków stali z podwyższoną zawartością siarki, następuje znaczne zubożenie glinianów w wapń w wyniku jego reakcji z siarką rozpuszczoną w tych glinianach i w osnowie stali. Uzyskanie bogatych w wapń glinianów i siarczków (Ca,Mn)S w gotowych wyrobach wymaga zastosowania przyspieszonego chłodzenia stali, co ma miejsce podczas ciągłego odlewania wlewków.

W stalach modyfikowanych wapniem w porównaniu z niemodyfikowanymi uzyskuje się większe ujednorodnienie rozmieszczenia i wielkości wtrąceń na przekroju wyrobów gotowych oraz większą globularyzację tych wtrąceń. Stwierdzono poprawę skrawalności tych stali oraz poprawę izotropii własności mechanicznych wykonanych z niej prętów.

1. Introduction

Development of steels with enhanced machinability has been going on incessantly from the beginning of the 1970s, as the share of machining costs in machine part manufacturing technology is still high and constitutes approx. 50% of their price [1,2].

In countries with highly developed technology, three basic generations of steel with enhanced machinability in relation to the base grade have been developed and introduced into production as a result of long-term research and experiments:

- *The first-generation steels,* good machining properties of which are the predominant feature of requirements in the field of mechanical properties. Machining properties of these steels are usually regulated by increasing their sulphur contents; the lead additives are used rather seldom. Control of sulphide inclusions is limited to adjusting the manganese content and oxygen level in steel, whereas control of oxide inclusions involves elimination of macro-inclusions.
- *Second-generation steels,* the improvement in machinability of which does not significantly deteriorate usable properties of products. The sulphur additive, used to improve the machinability, does not usually exceed 0.1% and is accompanied with modification of sulphide inclusions. Oxide inclusions are controlled by reducing their contents.
- *Third-generation steels,* which are required to demonstrate simultaneously good mechanical properties and good machinability. They are characterised by modified oxide inclusions at regulated sulphur content or modified sulphide and oxide inclusions at increased sulphur content.

The first- and second-generation steels are characterised by good machinability at low and medium cutting speeds, whereas the third-generation steels have good machinability at high cutting speeds. Production of higher-generation steels with enhanced machinability requires that the content, amount, chemical and phase composition of non-metallic inclusions be controlled. The discipline that handles these issues is named *inclusion engineering*.

This paper presents the results of doctoral dissertation [3], which objective was to examine and explain the processes of formation and modification of non-metallic inclusions in steels with enhanced machinability intended for forgings, produced with secondary metallurgy and modified with calcium. This paper compares results of thermodynamic equilibrium simulation in metal bath to results of microscopic examination of non-metallic inclusions in research production melts.

2. Enhanced machinability steel production

Factors affecting steel machinability

Any machining process depends on many factors related to the material being machined, cutting tool and machining conditions (type and parameters of the machining operation) [4].

In practice, good machinability can be associated with the following:

- low tool wear,
- high machining efficiency,
- low energy consumption, and
- good quality of machined surface.

The most essential machinability factor is a tool wear, which, apart from the material costs, determines the labour costs, by frequency of stoppages to sharpen, adjust and replace tools, and the number of machines operated by one operator. The wear of a cutting tool is a result of an overlap and interaction between a few basic processes, i.e. adhesion, abrasion, oxidation, element diffusion and mechanical fatigue [5, 6].

Machinability of steel is directly affected by its mechanical properties and plasticity related to the matrix structure and occurrence of abrasive and lubricating non-metallic inclusions [5]. At *low and medium cutting speeds* predominating is the abrasive wear on the flank face of the cutting tools. This is caused by hard particles of non-metallic inclusions, which are the result of steel deoxidation [6, 7]. At *high cutting speeds* the predominating mechanism of tool wear is diffusion of elements and depletion of the cutting blade's chemical composition.

The following is applied to improve and stabilise the steel machining properties:

- increase in content and uniform distribution of inclusions favourable from the point of view of machinability,
- elimination or advantageous modification of hard abrasive inclusions,
- limit of element microsegregation and steel structure anisotropy in product volume, as well as in batch of products.

Conventional additives to improve steel machinability are sulphur and lead, as well as bismuth, selenium and tellurium, whereas due to its toxicity, lead will be successively taken out of use.

The wear of cutting tool is, especially at high cutting speeds, reduced by protective layers, which are formed on the tool-work material interface.

The cutting tool surface examination showed that as the machining speed increases, the diffusion barriers are formed successively by: MnS sulphides, calcium and aluminium silicates, (Ca, Mn)S sulphides [8] and other sulphide and oxide phases at even higher machining temperatures [9].

Secondary metallurgy of steel with enhanced machinability

Production of steels with enhanced machinability comprises the following processes, which remain in close connection with one another:

- steel deoxidation,
- sulphur content adjustment,
- content control and modification of chemical composition of inclusions, and
- steel solidification.

Steel machinability is particularly affected by non-metallic inclusions, which occur as a result of deoxidisation and modification of steel, as well as inclusion of elements that are purposefully added to steel [9]. The following inclusion parameters affect steel machinability: shape, hardness, melting temperature, chemical composition and their distribution within a product. Relationships between the above-mentioned parameters and machinability are of a qualitative character and change at different combinations of machined material and cutting tool and at various machining parameters. The most numerous group of steels with enhanced machinability are sulphurised steels and steels modified with calcium, the machinability improvement of which is obtained as a result of modifications of both oxide and sulphide inclusions.

The objective of *modification of oxide inclusions* in steels with enhanced machinability is to adjust their chemical composition so that they can become softened and do not affect the cutting tool in terms of abrasion or, alternatively, form a renewable protective layer on its surface at the machining temperature. The contents of hard oxides (Al_2O_3 and SiO_2) are reduced by their transformation into softener aluminates or calcium aluminium silicates in the envelope of complex (Mn,Ca)S sulphides. For steels with enhanced machinability that are deoxidised with silicon and aluminium it is tried to obtain inclusions of anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and/or gelenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), for steels that are deoxidised with silicon and manganese – inclusions of spessartite $3MnO \cdot Al_2O_3 \cdot 3SiO_2$ [10], whereas for aluminium-killed steels – inclusions of complex calcium aluminates in the envelopes of calcium and manganese (Mn,Ca)S sulphide.

Modification of sulphide inclusions is to change their composition so that their solidification temperature can be increased and deformability during hot working can be reduced. By using calcium additives in place of MnS manganese sulphides, complex (Mn,Ca)S sulphides are obtained. Tellurium and selenium are used to form complex sulphide and telluride or selenide inclusions. Modified sulphides are more regularly distributed within a product, which is advantageous very much from the point of view of machinability, as well as other technological and usable properties of steel products.

Modification of oxides with calcium in the presence of sulphur constitutes a significant problem when producing steels with enhanced machinability, as, in the light of some papers, the transformation of oxide inclusions into calcium aluminates is conditioned by low activity of oxygen and sulphur [11–15]. However, there is no commonly recognised model of a process of modification of non-metallic inclusions in liquid steel. So far a few such models have been developed. Most often they adopt one of the two basic assumptions:

- calcium reacts, first of all, with solid aluminium oxide inclusions to form liquid aluminates that are rich in calcium, which sulphur dissolved in liquid metal reacts with [16],
- calcium reacts simultaneously with solid aluminium oxide inclusions to form liquid calcium aluminates and with sulphur to form sulphide inclusions [17].

Production of higher-generation steels with enhanced machinability requires a precise control of secondary metallurgy processes on the basis of measurements of oxygen activity, content of sulphur, aluminium and calcium in steel bath and the knowledge of required relationships among these elements' contents defined with computer-aided thermodynamic simulations.

3. Objective, material and range of own research

The objective of curried out work was to identify non-metallic inclusions occurring in aluminium-killed steel with regulated sulphur content and modified with calcium, explain the reactions between calcium and non-metallic inclusions and identify secondary metallurgy parameters, which condition obtaining such forms of inclusions to be conductive to improvement in steel machinability.

The production experiments curried out were preceded by computer-aided thermodynamic calculations, which were to provide preliminary information on formation of non-metallic inclusions, depending on the level of calcium, sulphur, oxygen, aluminium and silicon in steel bath and its temperature, and in consequence to define parameters of the treatment in a ladle with liquid steel deoxidised with silicon and aluminium, with low (0.01%) and increased (up to 0.03%) contents of sulphur, in order to obtain non-metallic inclusions that provide good machinability.

Production tests were carried out on unalloyed and low-alloy steels with low and medium contents of carbon, made in two domestic quality steel plants as intended for forgings (table 1). The range of the materials testing included:

- determinations of chemical composition of steel samples taken with lollipop-type immersed samplers during the secondary metallurgy,
- measurements of oxygen activity with Celox activity meter and hydrogen contents with Hydris analyser,
- determinations of chemical composition of slag,
- assessment of mechanical properties of forged and rolled bars intended for forgings,
- quantitative analysis of non-metallic inclusions with IBAS television image analyser,
- analysis of structure and distribution of inclusions with scanning electronic Philips XL30 microscope,

- identification of non-metallic inclusions with *X*-ray local microanalysis and *X*-ray phase analysis on the basis of isolate.

4. Thermodynamic calculations

Thermodynamic calculations were carried out with Thermo-Calc system that was developed in the Royal Technological Institute in Stockholm. To perform the calculations

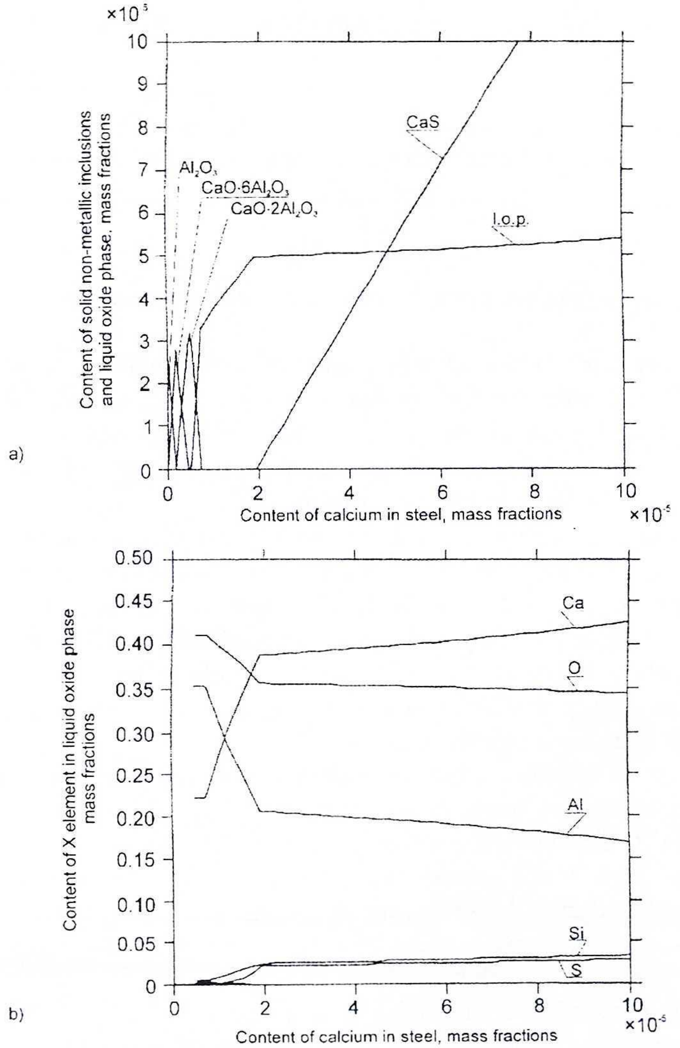

Fig. 1. Influence of calcium content in steel with the following chemical composition: 0.2% C, 0.8% Mn, 0.25% Si, 0.02% Al, 0.01% S, 0.002% O_T, on non-metallic inclusion precipitation process in steel bath at 1873K: a) type and content of non-metallic inclusions (l.o.p. – liquid oxide phase), b) chemical composition of liquid oxide phase

a database named SLAG, developed by IRSID, was used. This database comprises parameters of liquid solutions iron and multicomponent slag basis.

These calculations related to determination of the following aspects in function of Ca, S, O_T, Al, Si contents and liquid steel temperature:

- type of non-metallic phases precipitated,
- chemical composition of liquid oxide phases, and
- activity of calcium dissolved in liquid steel.

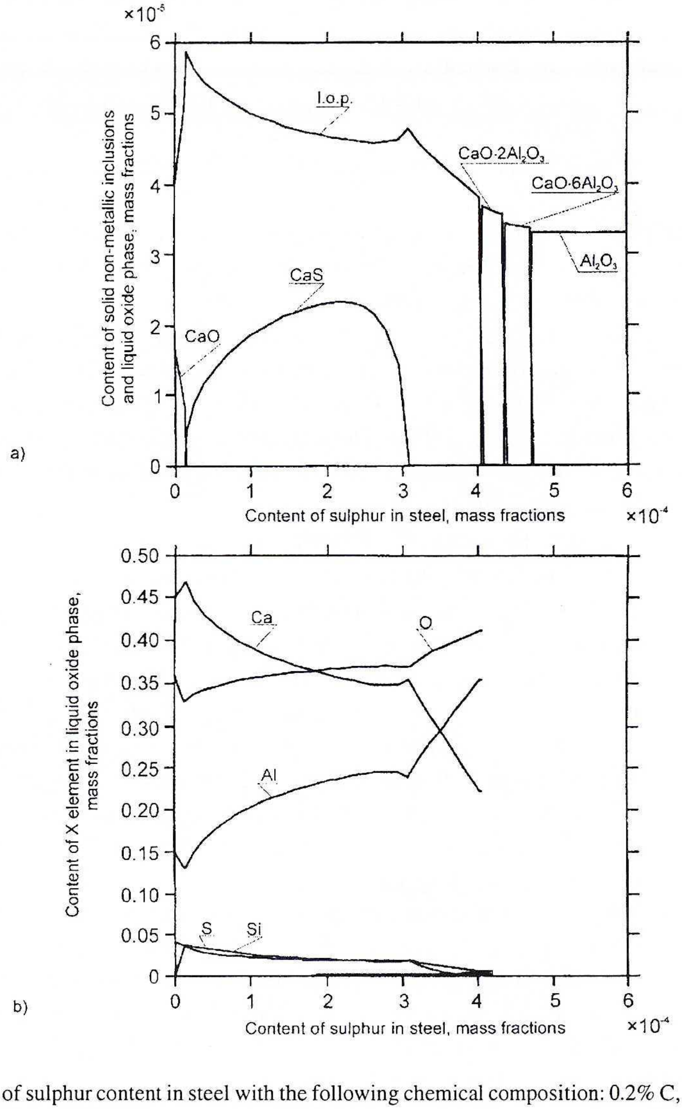

Fig. 2. Influence of sulphur content in steel with the following chemical composition: 0.2% C, 0.8% Mn, 0.25% Si, 0.02% Al, 0.002% O_T, 0.003% Ca on non-metallic inclusion precipitation process in steel bath at 1873K: a) type and content of non-metallic inclusions (l.o.p. – liquid oxide phase), b) chemical composition of liquid oxide phase

As a result of these calculations it was stated that obtaining of advantageous, from the point of view of machinability, low-melting calcium aluminates that are liquid at 1873K, is to a crucial extent affected by the contents of calcium (Fig. 1), sulphur (Fig. 2) and oxygen (Fig. 3), and to a lesser extent by the content of aluminium (Fig. 4) and silicon.

Level of calcium significantly affects the type of non-metallic inclusions occurring in thermodynamic equilibrium with liquid steel (Fig. 1a). As the calcium content increases within the range of 0 to 0.002%, these inclusions in a steel containing 0.002% of total oxygen are the following oxides successively: Al_2O_3, $CaO \cdot 6Al_2O_3$, $CaO \cdot 2Al_2O_3$ and liquid oxide phase, whereas its composition shows it is enriched in calcium at the expense of aluminium, in proportion corresponding to transformation of $CaO \cdot Al_2O_3$ into $3CaO \cdot Al_2O_3$ (Fig. 1b). The more than 0.002% growth in calcium content in steel is the reason of significant growth in CaS calcium sulphide content and successive enrichment of liquid aluminates in Ca. It is also worth noticing that liquid aluminates may include up to approx. 3% of sulphur and silicon.

Level of sulphur in steel strongly affects the type and content of non-metallic inclusions (Fig. 2a). With the sulphur content of up to approx. 0.03%, calcium in the amount of 0.003% forms liquid calcium aluminates and solid CaS sulphides in the steel. However, as the sulphur content increases the calcium activity in metal bath strongly decreases, which manifests itself in the rise in content of the element in unbounded state at the expense of its content in aluminates and the content of CaS sulphide that is not formed if the sulphur content in steel is somewhat above 0.03%. Depletion of liquid oxide phase in calcium and its enrichment in aluminium corresponds to transformation of $3CaO \cdot Al_2O_3$-type aluminates into $CaO \cdot Al_2O_3$-type aluminates (Fig. 2b).

Level of total oxygen in liquid steel determines the total contents and type of non-metallic inclusions, including the contents and chemical composition of liquid aluminates. As the level of oxygen in steel increases, the content of oxides grows and the content of calcium sulphide inclusions drops, whereas the latter ones are not formed in steel bath with assumed chemical composition at the content of total oxygen exceeding 30 ppm (Fig. 3a). The growing level of oxygen in steel reduces the activity of calcium in steel bath and its content in oxygen inclusions, including liquid oxide phase (Fig. 3b). Depletion of liquid oxide phase in calcium and its enrichment in aluminium corresponds to transformation of $3CaO \cdot Al_2O_3$- type aluminates into $CaO \cdot Al_2O_3$- type aluminates. The amount of calcium additive required to obtain liquid oxide phases that affect advantageously the machining properties grows in slightly deoxidised steels.

More than 0.005% growth in **aluminium content** in steel transforms $2CaO \cdot SiO_2$- type silicates into liquid oxide phase, which content is maintained on a rather stable level, whereas the content of CaS phase increases (Fig. 4a). As the aluminium content in steel grows up to approx. 0.06%, its fraction in liquid calcium aluminates increases at the expense of calcium, which corresponds to transformation of $3CaO \cdot Al_2O_3$-type aluminates into $12CaO \cdot 7Al_2O_3$-type aluminates (Fig. 4b).

Growth in **silicon content** within the range of 0 to 0.8% in analysed steel does not affect significantly the content of non-metallic inclusions. It makes a slight depletion of aluminates in aluminium and appropriate growth in silicon and calcium content. At the same time, the content of CaS decreases slightly, which is connected with reduction in calcium activity in metal bath.

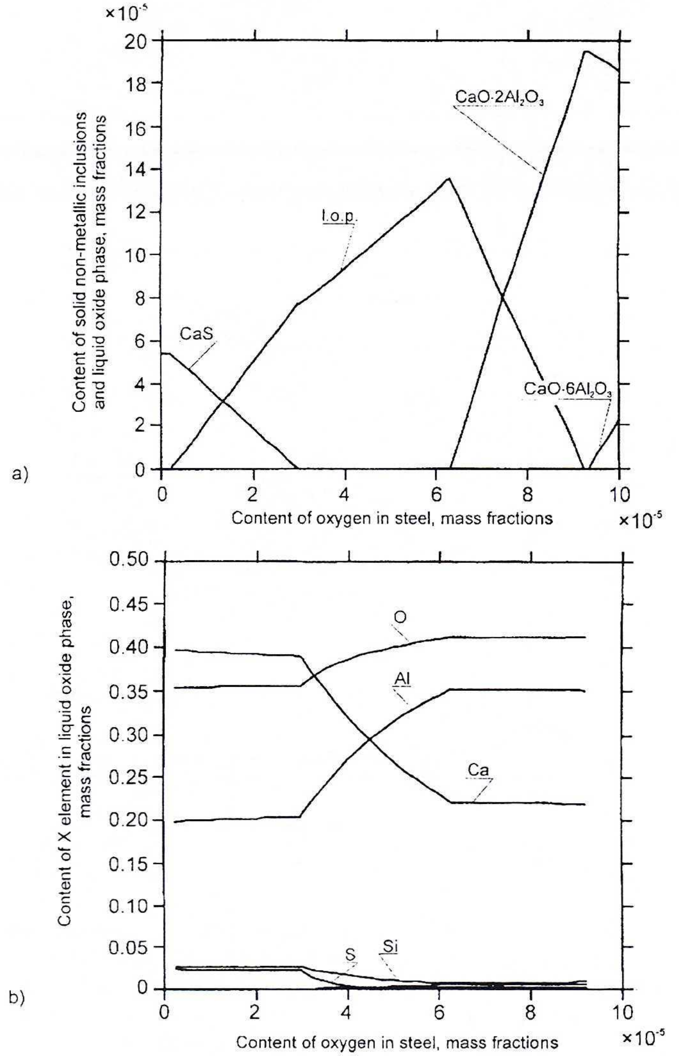

Fig. 3. Influence of total oxygen content in steel with the following chemical composition: 0.2% C, 0.8% Mn, 0.25% Si, 0.02% Al, 0.01% S, 0.003% Ca on non-metallic inclusion precipitation process in steel bath at 1873 K: a) type and content of non-metallic inclusions (l.o.p. – liquid oxide phase), b) chemical composition of liquid oxide phase

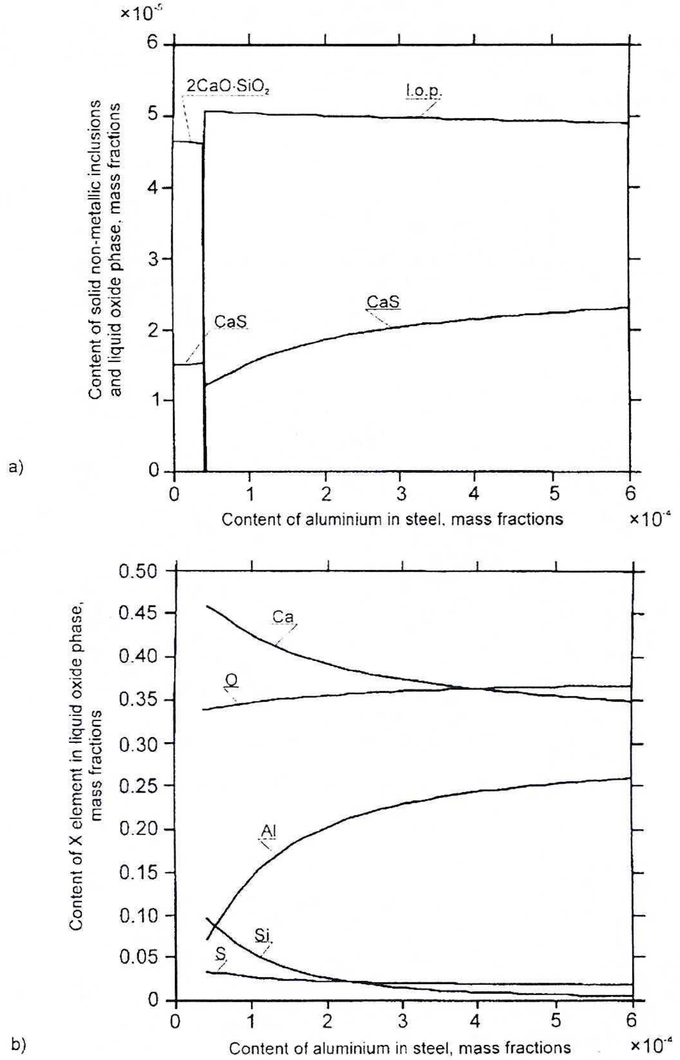

Fig. 4. Influence of aluminium content in steel with the following chemical composition: 0.2% C, 0.8% Mn, 0.25% Si, 0.01% S, 0.002% O_T, 0.003% Ca on non-metallic inclusion precipitation process in steel bath at 1873 K: a) type and content of non-metallic inclusions (l.o.p. – liquid oxide phase), b) chemical composition of liquid oxide phase

Reduction in steel bath **temperature** within the range of 2000 to 1600 K makes the type and equilibrium contents of aluminates change and CaS content grow (Fig. 5a). Precipitation of CaS sulphides reduces calcium content in aluminates, which corresponds to transformation of $3CaO \cdot Al_2O_3$-type liquid aluminates into $12CaO \cdot 7Al_2O_3$-type aluminates (Fig. 5b) and then into $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$.

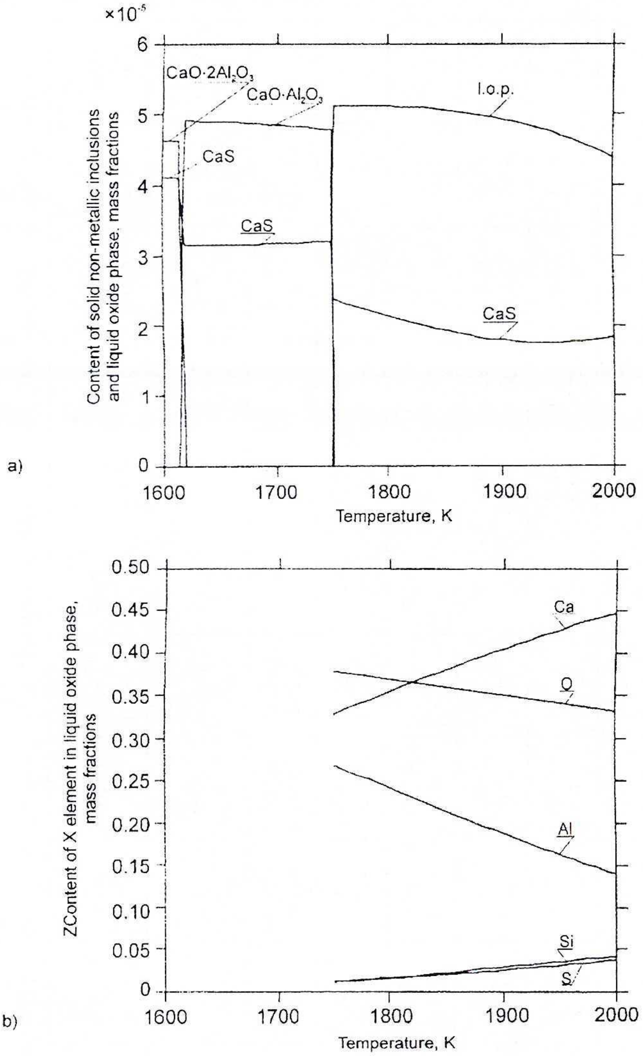

Fig. 5. Influence of temperature of steel bath with the following chemical composition: 0.2% C, 0.8% Mn, 0.25% Si, 0.02% Al, 0.01% S, 0.002% O_T, 0.003% Ca on non-metallic inclusion precipitation process: a) type and content of non-metallic inclusions (l.o.p. – liquid oxide phase), b) chemical composition of liquid oxide phase

5. Industrial tests

The production technology of manufacturing steels with enhanced machinability comprises the following processes:

- melting in electric arc furnace,

TABLE 1

Grades of steels with regulated and increased sulphur content involved in tests

Item	Grade Standard	Chemical composition, %										
		C	Mn	Si	P	S	Cr	Ni	Mo	Al_T	Cu	Others
1	708M40* BS 970	0.38–0.45	0.70–0.90	0.17–0.37	max. 0.020	0.020–0.030	0.90–1.10	max. 0.30	0.25–0.35	min. 0.03	max. 0.18	
2	709M40* BS 970	0.38–0.44	0.70–0.80	0.17–0.35	max. 0.020	0.020–0.030	0.90–1.10	max. 0.30	0.25–0.35	min. 0.03	max. 0.18	
3	871M40* BS 970	0.36–0.44	0.45–0.70	0.10–0.40	max. 0.035	max. 0.040	1.00–1.40	1.30–1.70	0.20–0.35	0.015–0.030	max. 0.18	
4	080M40* BS 970	0.38–0.42	0.60–0.80	0.17–0.35	max. 0.020	max. 0.015	max. 0.25	max. 0.25		0.015–0.035	max. 0.18	
5	080M42* BS 970	0.40–0.42	0.70–0.90	0.15–0.35	max. 0.020	0.010–0.030	max. 0.25	max. 0.20		0.015–0.030	max. 0.18	
6	070M20* BS 970	0.18–0.23	0.50–0.70	0.15–0.35	max. 0.020	0.015–0.025		max. 0.30		0.015–0.035	max. 0.18	
7	22HNMhD (TWT-HW-ZBR-2/90)	0.19–0.25	0.60–0.95	0.20–0.30	max. 0.035	0.030–0.040	0.35–0.65	0.35–0.75	0.15–0.25	0.02–0.06**	max. 0.25	B 0.003–0.006
8	17NiCrMo7G (WT-FIAT)	0.15–0.20	0.45–0.65	0.15–0.35	max. 0.020	0.020–0.040	0.040–0.60	1.65–2.00	0.20–0.30	0.020–0.050	max. 0.18	W max. 0.20

*) – chemical compositions are presented as abbreviated in accordance with orders and internal recommendations of steel plants as regards the ranges covered by the standard

**) – metallic aluminium (dissolved)

- refining treatment in ladle furnace,
- vacuum treatment,
- modification of inclusions and final regulation of steel chemical composition in the ladle,
- argon bubbling,
- bottom casting into ingot moulds with argon shrouding.

Two types of melts modified with calcium were made: with low sulphur content 0.008–0.014% and with increased sulphur content 0.02–0.04%. Melts with low sulphur content were made by adding calcium and sulphur into degassed bath in the following variants: in one batch, in a few batches or sequentially according to the following scheme: Ca-S-Ca-S.

Processing of melts with increased sulphur content included the following:

- sulphurising of degassed steel to obtain 0.025% S content,
- adding calcium to obtain 0.0025% Ca content,
- adding sulphur to obtain its content on the level of 0.03–0.04%.

Calcium, sulphur and regulative Al additives were added by means of cored wires. During the secondary metallurgy a rich sampling program to analyse the chemical composition of metal and slag and to take the measurements of oxygen activity was completed.

In some heats, the fine-grained FeSi was added on top slag surface to control its basicity index (%CaO/%SiO_2) below 1.5.

6. Materials testing results

Mechanical and technological properties of steel with calcium additive

Products made from steels subjected to treatment with calcium complied with mechanical properties required in the standard (table 2). The calcium treatment improved the isotropy of impact resistance while this influence was strongest for melts with the highest calcium content.

The machining tests of forgings from these steels were successful and these forgings were classified as a charge for details produced with high input of machining. In addition, the steel machinability was tested under laboratory conditions on the basis of measurements of wear of turning tool made from high-speed steel. These measurements were curried out on bars forged from 7 melts of steel with different calcium and sulphur contents and with different hardness level. The variable parameters here were cutting speed and machining time. The measurements were taken at four different machining speeds between 43 and 110 m/min. The tool wear was measured after 2, 5 and 10 minutes. The results of Z wear measurements were correlated with the sulphur and calcium contents in the steel and with machining parameters. The following dependence was obtained:

TABLE 2

Heat-treated forged bar mechanical property measurement results

Heat no Steel grade (Remarks)	Yield point R_e [MPa]	Tensile strength R_m [MPa]	Elongation A_5 [%]	Reduction of area Z [%]	Direction of impact sample	Impact strength KCV [J/cm^2]
29495 080M40 (modified, 25 ppm Ca, 0.009% S)	432 (280)*	664 (550)	29 (16)	58	L	45 (16)
					T	37
29590 080M40 (modified, 11 ppm Ca, 0.01% S)	424 (280)	652 (550)	28 (16)	57	L	43 (16)
					T	36
20977 708M40 (modified, 3 ppm Ca, 0.029% S)	597 (525)	789 (700–850)	20,5 (17)	61	L	99 (50)
					T	26
21327 070M20 (modified, 13 ppm Ca, 0.020% S)	282 (215)	437 (430)	39 (21)	70	L	204
					T	78
21342 709M40 (modified, 7 ppm Ca, 0.014% S)	611 (585)	818 (775–925)	20,9 (15)	65	L	148 (50)
					T	36
21399 080A42 (modified, 24 ppm Ca, 0.015% S)	418 (280)	651 (550)	28,7 (16)	52	L	40 (16)
					T	35
21654 709M40 (non-modified, 1 ppm Ca, 0.019% S)	605 (585)	809 (775–925)	20,4 (15)	63,7	L	159 (50)
					T	33
78504 22HNMh (modified, 10 ppm Ca, 0.040% S)	786	994	17,2	44,7	L	KCU 66,6
78713 17NiCrMo7G (modified, 14 ppm Ca, 0.02% S)	1330 (980)	1425 (1230–1520)	13,2 (8,0)	47,3	L	KU [J] 36,6 (30)

( )* – required minimum values or range of values specified by relevant standards (BS 970, WT-FIAT) are given in the brackets

L – samples taken along with bar axis, T – samples taken perpendicularly to bar axis

$$Z = -0.141 - 2.781\ S - 19.35\ Ca + 7.2 \cdot 10^{-4}\ h + 3.41 \cdot 10^{-3}\ v + 1.69 \cdot 10^{-2}\ t,$$

where: Z – wear (mm),
S, Ca – sulphur and calcium contents in steel (%),
h – sample hardness (HB),
v – machining speed (m/min),
t – machining time (minutes).

This dependence shows that as sulphur and calcium contents increase in steel, the tool wear becomes reduced, which means the machinability of the modified steel improves.

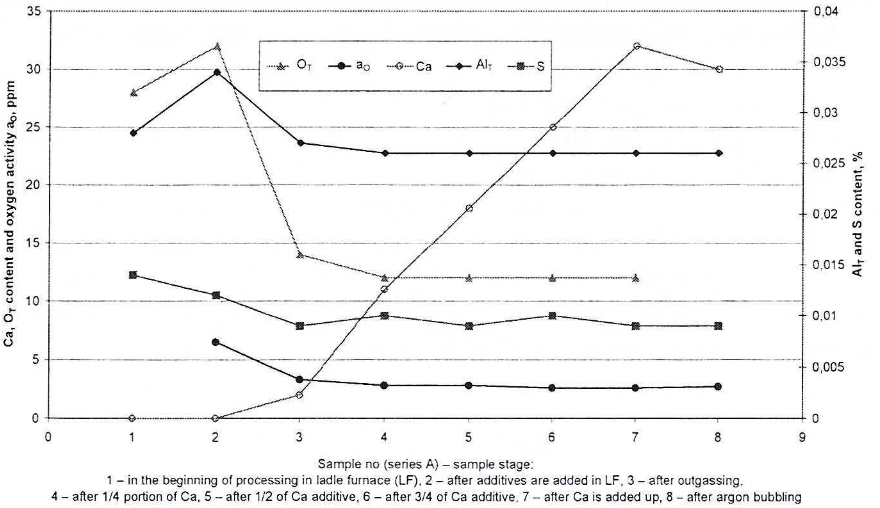

Fig. 6. Changes in chemical composition of steel bath during ladle processing of 080M40 steel, heat 29495

Changes in chemical composition of steel bath during secondary metallurgy

Fig. 6 presents the changes in the contents of selected elements in steel bath characteristic for applied secondary metallurgy, whereas the differences in curve functions for individual melts were mainly the result of the way of adding calcium and sulphur.

As a result of the steel treatment in a ladle furnace followed by vacuum degassing, a strongly deoxidised bath was obtained with low **oxygen** activity level within the range between 3 and 8 ppm. The level of total oxygen after these secondary metallurgy processes was also low. It was between 10 and 20 ppm. As a result of adding calcium, further reduction in oxygen activity was obtained while total oxygen remained on practically constant level. The final stage of the ladle treatment, which involved steel bath argon bubbling before its casting to the ingot moulds, enhanced removal of non-metallic inclusions from the steel bath, due to which the total oxygen content was being reduced while the oxygen activity remained on practically constant level. The content of total oxygen in the steel melt depended on the number and method of chemical composition adjustments of the bath before casting, steel stream argon shroud efficiency during casting, quality of refractory materials used for ladle lining, trumpet and runner bricks used in uphill casting and quality of ingot mould powder. When steel was cast into the ingot moulds with insufficient stream protection, the bath was oxidised.

The content of **aluminium** in steel bath, added in order to deoxidise the steel and obtain fine grain after crystallisation, was being reduced during vacuum treatment. After steel bath vacuum degassing, supplementary Al additives were used, if necessary. The ratio of the content of aluminium dissolved in steel bath to its total content in steel (Al_d/Al_T) was approx. 0.9. The final level of total aluminium content in steel was affected by passing of solid and liquid inclusions containing Al_2O_3 into the top slag.

The content of **calcium** in the bath was growing as it was added. However, it was being reduced during the final argon bubbling and holding the bath before or during its casting. The final yield of Ca, compared to its content in a finished steel product, is reduced in function of the time between the modifier is added and casting.

The content of **sulphur** in steel bath was being reduced during vacuum treatment. When adding calcium and performing other technological operations that preceded the steel casting, the bath was desulphurised as well. The yield of sulphur added to steel in the ladle was low. It was maximum about fifty per-cent for heats during which sulphurising was carried out with no interference in sulphide capacity of the slag.

Non-metallic inclusions in steel bath

To determine changes in chemical composition, form and content of non-metallic inclusions during successive operations within the secondary metallurgy treatmant, the liquid steel samples were cooled down quickly. It allowed us to limit diffusion processes in solidifying metal and "freeze" the liquid non-metallic inclusions as unchanged.

The basic types of inclusions in steel samples taken before calcium was added were Al_2O_3 or Al_2O_3-MgO -type oxides and MnS sulphides. More complex oxide inclusions, MnO-SiO_2-Al_2O_3 or MgO-Al_2O_3-CaO, were noticed more rarely.

The steel modification with calcium additive increased the content of oxide inclusions containing calcium. Chemical constitution of these inclusions was diverse, whereas most often these were CaO-Al_2O_3-type aluminates with CaO : Al_2O_3 weight ratio of 1 : 1 to 3 : 1 (Fig. 7–10). Occurrence of stand-alone aluminates (Fig. 7), aluminates in sulphide envelope (Fig. 8), as well as complex oxide- sulphide conglomerates (Fig. 9 and 10) was noted. Constitution of the latter ones shows they arouse as a result of joining CaS particles with liquid aluminates or precipitation of CaS sulphides during solidification of aluminates containing sulphur. In addition to MnS inclusions, the group of sulphide inclusions also included CaS calcium sulphide inclusions and complex (Ca,Mn)S sulphides.

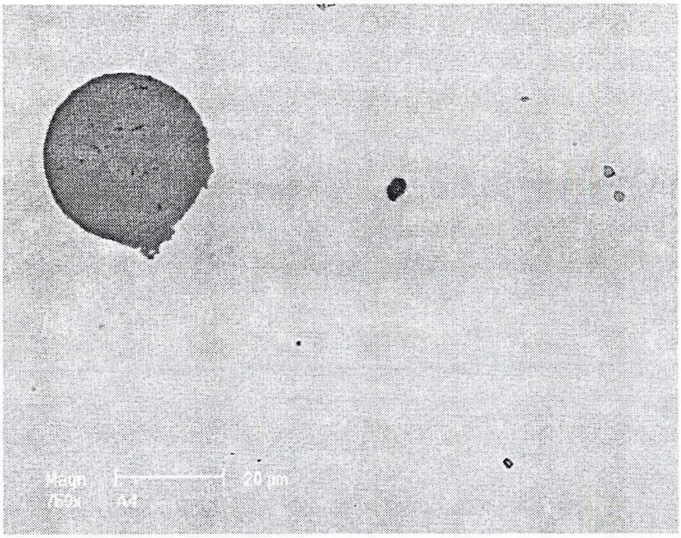

Fig. 7. Calcium aluminate of $2CaO \cdot Al_2O_3$-type in 080M40 steel, heat 29495, sample A4 taken after the first portion of calcium is added

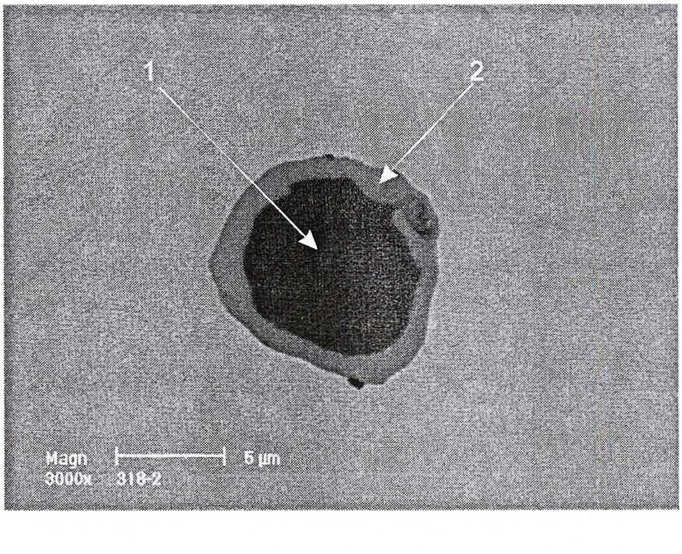

Fig. 8. Oxide-sulphide inclusion in 871M40 steel

1 – $CaO \cdot Al_2O_3$-type oxide with small MgO content and trace of SiO_2

2 – (Ca,Mn)S-type sulphide with about twice as big Ca content in comparison to Mn

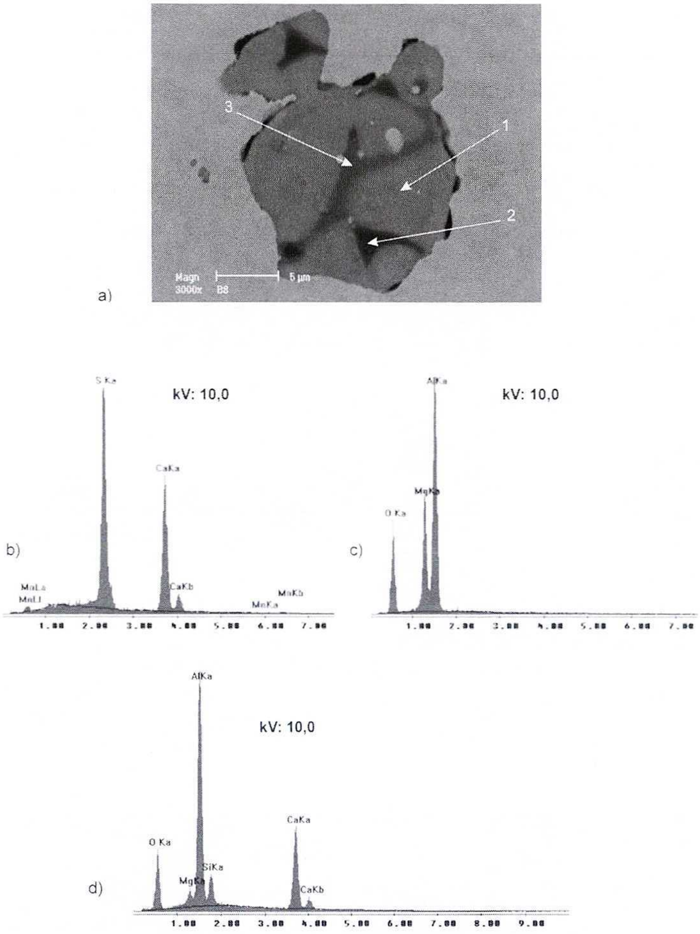

Fig. 9. Oxide-sulphide inclusion in 080M40 steel heat 29590, sample B8 taken after calcium is added: microscopic image (a) and results of chemical composition analysis in point:
1 – CaS sulphide with trace of Mn (b), 2 – $Al_2O_3 \cdot MgO$-type oxide (c), 3 – $3CaO \cdot Al_2O_3$-type calcium aluminate with SiO_2 and MgO input (d)

Argon bubbling after calcium and sulphur are added passes the inclusions, especially the largest oxide and sulphur conglomerates, into slag. It was confirmed by chemical analysis of the steel composition, which showed that the contents of calcium and total oxygen were reduced after argon bubbling while the oxygen activity itself remained on the same level. As a result of inert gas stirring, the average size of non-metallic inclusions – mainly the oxide ones – was reduced, which was caused by passing inclusions with larger sizes into the covering slag.

After the secondary metallurgy of the steels under investigation has been completed, the average size of multi-phase (oxide-sulphide) inclusions did not exceed 6 µm or, in case of single oxides and sulphides, 3 µm.

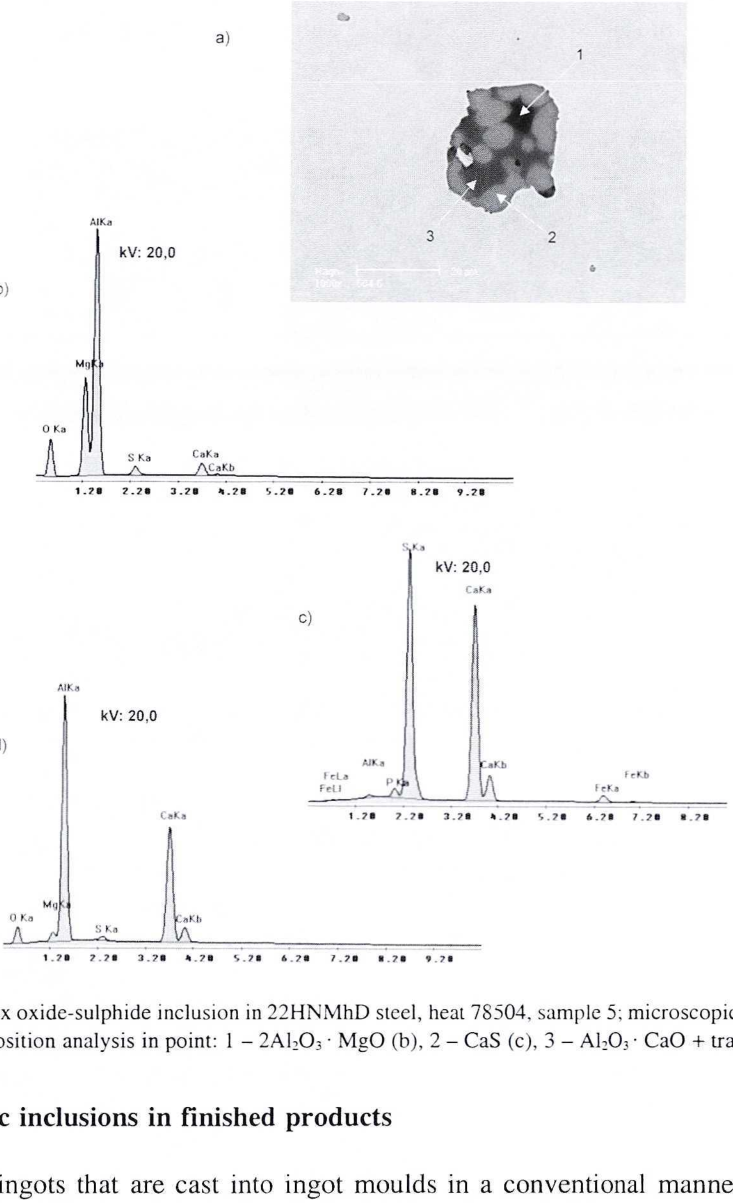

Fig. 10. Complex oxide-sulphide inclusion in 22HNMhD steel, heat 78504, sample 5; microscopic image (a) and chemical composition analysis in point: 1 – $2Al_2O_3 \cdot MgO$ (b), 2 – CaS (c), 3 – $Al_2O_3 \cdot CaO$ + trace of MgO (d)

Non-metallic inclusions in finished products

Forging ingots that are cast into ingot moulds in a conventional manner, solidified slowly, which significantly extended times of non-metallic phase precipitation and solidification processes. The content, size, shape and chemical composition of non-metallic inclusions in finished steel products were different in comparison to their state in frozen samples of liquid steel. High content of (Ca,Mn)S and MnS-type sulphides was found in finished forgings, whereas in the steel bath, CaS calcium sulphides were predominating.

The content of stand-alone calcium aluminates was reduced significantly. They observed to be replaced by multi-phase oxide-sulphide inclusions with higher fraction of (Mn,Ca)S-type sulphide phases, in relation to oxide phases, that contained aluminium, calcium, magnesium and silicon (Fig. 11 and 12). In addition, a large content of stand-alone manganese sulphides was found.

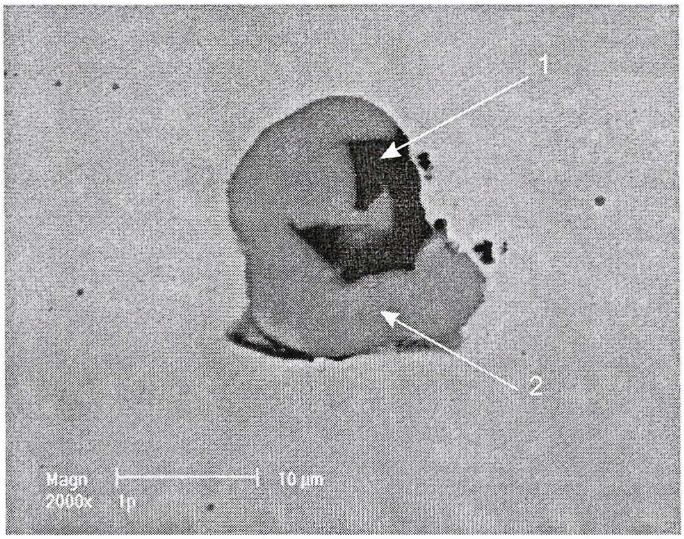

Fig. 11. Oxide-sulphide inclusion in 22HNMhD steel, heat 78504, sample "1p" from hot rolled bar; 1 – $CaO \cdot 6Al_2O_3$-type calcium aluminate, 2 – (Mn,Ca)S sulphide with small Ca content

The analysis of non-metallic inclusions in bars made from steels with and without calcium additives showed the following dependencies:

- in case of steels modified with calcium, it was found greater homogeneity of inclusion distribution on bar cross-section than in non-modified steels in which the content of inclusions in the bar axis is higher than in the outer zone,
- in case of steels modified with calcium, it was found greater homogeneity of sizes of inclusions on bar cross-section than in non-modified steels in which larger inclusions occur in the bar axis,
- the shape of non-metallic inclusions in modified steels is much globular than in non-modified steels.

Mechanism of non-metallic inclusion modification in steels with calcium content

The production experiments and tests of samples taken from successive stages of the secondary metallurgy and finished forgings incline us to formulate the following hypothesis on rebuilding of non-metallic inclusions under the influence of calcium.

In deeply deoxidised steels with regulated sulphur content below 0.03% and at growing calcium content in metal bath, this element reacts with Al_2O_3 inclusions first of all. As Ca atoms diffuse, they become liquid whereas the composition of liquid oxide phase transforms from $CaO \cdot Al_2O_3$ into $3CaO \cdot Al_2O_3$. At the same time, sulphur diffuses to it until the solubility limit of approx. 3% is obtained. If the amount of calcium dissolved in steel exceeds the level required to modify the oxides, at the same time solid CaS sulphide inclusions are formed.

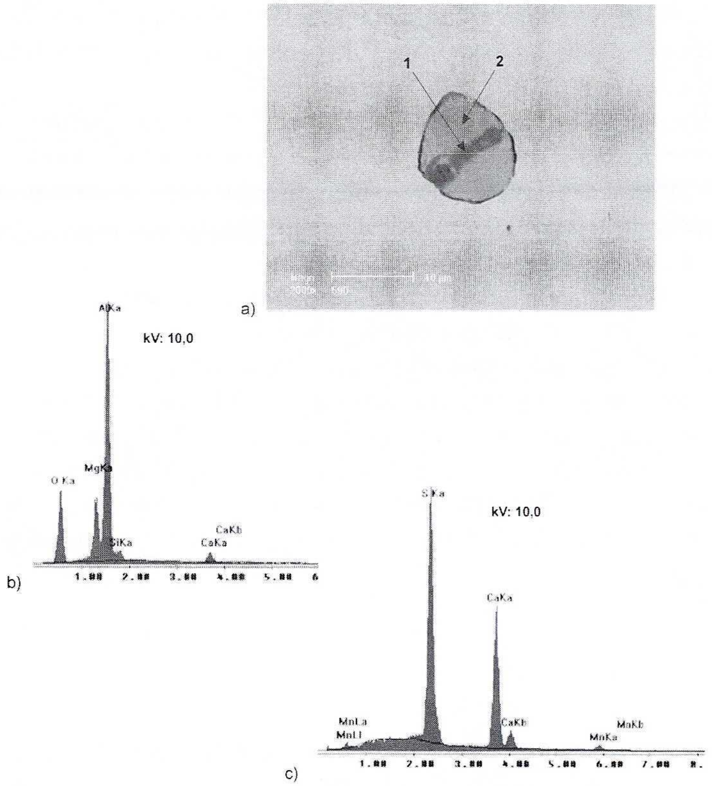

Fig. 12. Sulphide-oxide inclusion in 080M40 steel, heat 29590, sample from forging: microscopic image (a) and chemical composition analysis in point: 1 – complex $2Al_2O_3 \cdot MgO$-type oxide with small CaO and SiO_2 content, 2 – (Ca,Mn)S sulphide with small Mn content (c)

When the steel is cooled down slowly, calcium reacts with sulphur dissolved in liquid, and then solidified aluminates. As a result they become transformed according to the following scheme:

$$3CaO \cdot Al_2O_3 \Rightarrow 12CaO \cdot 7Al_2O_3 \Rightarrow CaO \cdot Al_2O_3 \Rightarrow CaO \cdot 2Al_2O_3 \Rightarrow CaO \cdot 6Al_2O_3.$$

CaS-phase inclusions form inside these aluminates and on their surface. At lower temperatures, they are nuclei for manganese sulphide as a result of which sulphides become transformed into (Mn,Ca)S.

Depending on how advanced the diffusion processes and reaction between calcium and sulphur are, there are depleted calcium aluminates or even simple Al_2O_3 and MgO oxides with (Mn,Ca)S sulphides envelopes and stand-alone (Mn,Ca)S sulphides with various calcium contents in finished products.

In continuous casting of steel with small ingot cross-section, cooling and solidification of steel proceeds much faster than in casting large conventional ingots. As a result, calcium aluminates richer in calcium are obtained, which composition is more similar to the one observed in the metal bath.

The characteristic feature of calcium aluminates and sulphides, which showed large calcium content in the steel bath, is that they have a spherical-like form.

In less deoxidised steels (total oxygen content over 30 ppm), as well as in steels with increased sulphur content (over 0.035%), if calcium is added to obtain the content of above 30 ppm, no solid CaS sulphides are formed as calcium aluminates are reconstructed and liquefied. They are precipitated at lower temperatures when steel bath is being cooled down. The precipitation proceeds in a similar way.

The materials testing results obtained are consistent with results of thermodynamical calculations, which enable to understand and explain the course of inclusion modification during secondary processing and steel solidification. The mechanism of shaping non-metallic inclusions described above is not in contradiction to detailed models presented in various publications. No evidence was found to support the theory of layer solidification of aluminates with formation of separate phases with varying calcium contents.

Technological recommendations

The production trials and materials testing on steel with increased sulphur content and calcium modification allowed to formulate the following technological recommendations:

- the amount of calcium added to liquid steel in order to modify inclusions must be determined on the basis of liquid steel parameters: the level of O_T, Al, S and the temperature and knowledge of Ca yield under specific steel-making equipment conditions,
- temperature of liquid steel should be selected so that it is not necessary to heat it up to the casting temperature after the modification process has been completed,
- Al content in liquid steel before Ca is added should be selected in such a way so that it is possible to obtain the content of this element in finished steel on a level close to the lower limit defined in the standard without necessity to use a correction additive after the modification has been completed,
- modification of non-metallic inclusions in strongly deoxidised sulphurised steel requires that the covering slag should be controlled as it should neither oxidise nor desulphurise the metal bath,
- effective protection of liquid steel before re-oxidisation is required.

7. Conclusions

As a result of comparison of computer-aided simulations to the results of production experiments, the following conclusions concerning behaviours of non-metallic inclusions in liquid steel and their occurrence in finished product were formulated:

1. Calcium in steel bath modifies alumina inclusions and reacts with sulphur, whereas deep desulphurisation (below 0.01%) is favourable to oxide modification. Non-metallic inclusions of calcium aluminates, which affect positively the machining properties of steel, appear in liquid state in the steel bath.
2. During conventional casting and cooling down large ingots of steel with increased sulphur content, aluminates are significantly depleted in calcium as a result of reaction between calcium and sulphur dissolved in these aluminates and steel matrix. To obtain aluminates and (Ca,Mn)S sulphides rich in calcium in finished products, accelerated steel cooling is to be applied, which takes place during continuous casting of steel.
3. In steels modified with calcium, there is higher homogeneity of distribution and sizes of inclusions on finished products' cross-section and higher globularisation of these inclusions in comparison to non-modified steels. Improved steel machinability and improved isotropy of mechanical properties were found.

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