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EVALUATION
OF SUPER CLEAN STEELS ACCORDING TO CHEMICAL COMPOSITION

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Realization of products in power engineering represents the verification and optimization of steel making technology of 2,8NiCrMoV and 3,5NiCrMoV types intended for forgings of the gas turbine shaft and compressor disk. The minimum content of tramp and trace elements is requested, especially phosphorus, sulphur, copper, antimony, arsenic and tin. Silicon, manganese and aluminium are considered as undesirable elements.

Key words: *super clean steel, trace elements, chemical cleanness*

Vrednovanje superčistiih čelika prema kemijskom sastavu. Realizacija proizvoda u energetskom inženjerstvu predstavlja optimalizaciju tehnologije proizvodnje čelika tipa 2,8NiCrMoV i 3,5NiCrMoV namijenjenim kovanju osovine plinske turbine i diska kompresora. Zahtijeva se minimalni sadržaj pratećih elemenata i oligoelemenata, naročito fosfora, sumpora, bakra, antimona, arsena i kositra. Silicij, magnezij i aluminij se smatraju nepoželjnim elementima.

Ključne riječi: *superčisti čelik, prateći elementi, kemijska čistoća*

INTRODUCTION

Customersˇ demands on high quality of the product in the light of internal quality as well as chemical purity of steel constitute a new qualitative limit for ŽĎAS, a. s.' meta-allurgical plant.

Equipment of ŽĎAS, a. s. electric steel plant enables to make commercial high-grade steels with guaranteed high internal purity. Making of super clean steels means essential enhancement in qualitative requirements that requests new technological elements as well as operative management of steel making and treatment process.

In order to verify the possibility to make these steels under ŽĎAS, a.s. conditions, three test melts of grades acc. to the Table 1. were made. Two melts of 2,8NiCrMoV grade and one melt of 3,5NiCrMoV grade.

According to provision of EPRI, steel chemical purity is evaluated by Bruscat factor. Ni-Cr-Mo-V based super clean steel is characterized by attaining B factor value < 8. [2] Mechanical properties are shown in Table 2.

Table 1. **Specification of optimized chemical composition within Technical and Delivery Prescriptions**
Tablica 1. **Specifikacija optimalnog kemijskog sastava s tehničkim propisima i propisima o isporuci**

Steel grade	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	As	Sn	Sb	Bfactor
	wt. / %														
2,8NiCrMoV	0,26	max.	max.	max.	max.	1,40	2,80	0,30	max.	max.	max.	max.	max.	max.	-
	0,32	0,40	0,07	0,007	0,005	1,70	3,00	0,45	0,15	0,010	0,12	0,0100	0,0100	0,0050	-
3,5NiCrMoV	0,26	max.	max.	max.	max.	1,60	3,50	0,30	max.	max.	max.	max.	max.	max.	max.
	0,32	0,40	0,04	0,004	0,004	1,90	3,80	0,45	0,15	0,015	0,12	0,0080	0,0050	0,0020	7,0
B factor = (10 · wt. % P + 5 · wt. % Sb + 4 · wt. % Sn + wt. % As) · 100															

SELECTION
AND OPTIMIZATION OF THE CHARGE

Selection of metallic charge for making super clean steels is characterized by considerable demands on chemical purity of the steel made. On elimination of elements eliminable from the steel making and treatment process, demand on very low contents of trace elements, copper, arsenic, tin and antimony remains. Consequently, preparation of the charge to get a melt of given chemical composition requests to use super clean raw materials.

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Table 2. **Mechanical properties of steel grades**
Tablica 2. **Tehnička svojstva kvalitetnih čelika**

Steel grade	Mechanical properties in longitudinal direction at 20°C					
	Yield strength at 0,2 % / Nmm^{-2}	Tensile strength / Nmm^{-2}	Elongation / %	Contraction / %	Impact energy / J	Ductile fracture / %
2,8NiCrMoV	700 - 800	≤ 960	≥ 15	≥ 50	≥ 90	100
3,5NiCrMoV	800 - 900	≤ 1080	≥ 14	≥ 45	≥ 100	100

Steel scrap

Steel scrap is still basic metallic raw material for making steel in the electric arc furnace. Growing share of purchased scrap in the charge results in rise of concentration of undesirable elements in steel. Values obtained from monitoring of undesirable elements content in purchased steel scrap at ŽĎAS, a. s. in 2002 considerably exceed limit contents for 2,8NiCrMoV and 3,5NiCrMoV steels. See Figure 1. (Cu, Sn, As and Sb content during 1.-5. 2004).

Pig iron

Pig iron is made mainly from primary ore sources. In terms of trace element contents, high metallurgical purity is its basic characteristics.

Processing of pig iron, when making steel in the electric arc furnace, is limited by several factors. Above all, high purchase price compared with steel scrap economically excludes common use of pig iron for electric steel making.

Technically, chemical composition is disputable. Pig iron having high carbon and silicon contents in the charge constitutes some reduction in charge melting time, however extension of melt oxidizing period, increased also consumption of addition agents and accompanying economic losses. In spite of mentioned negatives, pig iron is used for EAF in special cases to a limited extent. With respect to conventional blast-furnace production, pig iron is readily available in the territory of the Czech Republic. Guaranteed chemical composition including trace element contents of the superior-quality delivery is shown in the Table 3.

Table 3. **Chemical composition of Pig Iron**
Tablica 3. **Kemijski sastav sirovog željeza**

	C	Mn	Si	P	S	Cr
Pig Iron	wt. / %					
	3,60	max.	0,50	max.	max.	max.
	4,60	0,07	1,00	0,070	0,020	0,03
	Ni	Cu	Mn	As	Sn	Sb
	wt. / %					
	max.	max.	max.	max.	max.	max.
	0,002	0,002	0,001	0,0001	0,0004	0,0011

As to demands on chemical composition of super clean steels, casting pig iron meets requirements for the basic metallic charge.

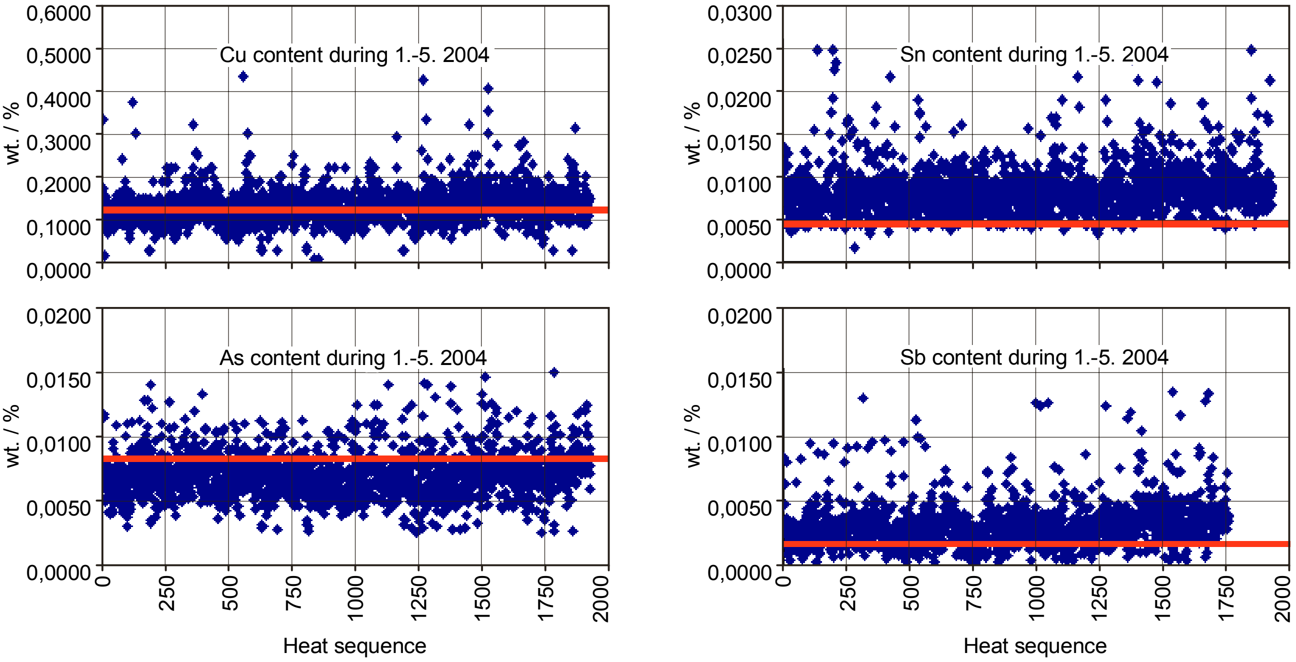

Figure 1. **Content cupper, tin, arsenic and stibium during the period from January to May 2004. year**
Slika 1. **Sadržaji bakra, kositra, arsena i antimona mjereni u vremenu od siječnja do svibnja 2004. godine**

Direct reduced iron

Nowadays, a product of the development of new metallurgical processes of iron ore processing are mainly direct reduced iron marked DRI (Direct Reduced Iron) and HBI (Hot Briquette Iron). DRI and HBI products of iron ore direct reduction replace purchased steel scrap and offer advantages associated with relatively easy manipulation, considerable saving of electric power and very low content of harmful and tramp elements [3].

Table 4. shows basic technical characteristics of reduced iron.

Table 4. **DRI/HBI Technical Characteristics**
Tablica 4. **Tehnička svojstva izravno reduciranog željeza i željeza u vrućim briketima**

DRI/HBI	Fe total	Fe metallized	Level of metallization	C	SiO_2	CaO	S	Apparent density
	/ wt. %		/ %	/ wt. %				$t \cdot m^{-3}$
	min.	min.	min.	min.	max.	min.	max.	min.
	90,0	83,0	92	1,00	4,30	1,00	0,011	4,9

As to the chemical composition, the DRI/HBI meets requirements for the basic metallic charge for making 2,8NiCrMoV and 3,5NiCrMoV super-clean steels. Compared to the pig iron, fairly good price and low carbon content are of advantage.

Ferroalloys and clean metals

When making commercial-grade steels, ferroalloys of various purity grade are used for alloying. In addition to basic metal and iron, the ferroalloys contain number of other elements that usually occur in ores together with metal to be extracted (e.g. Fe, P, S, Cu, As, Sn, Sb) or pass to the metal from the ore processing and ferroalloy making (e.g. C, Si, Al).

Carbon is contained in the steel in the course of the whole process of molten metal making and treatment. Introduction of carbon into the melt is ensured by use of suitable metal charge and ferroalloys or direct carburisation with coke, carburisers and/or synthetic carbon. In addition to carbon, these additives, however, also introduce hydrogen, nitrogen, oxygen and sulphur into the steel.

Chrome and its ferroalloys contain a number of elements that constitute undesirable elements in making super-clean steels. In standard ferro-chrome, high concentration of silicon, phosphorus, arsenic, tin and antimony is undesirable. The demand on cut-off of these elements is met by technically pure chrome.

Nickel made electrolytically and delivered in the form of anode or cathode nickel meets requirements for trace element contents.

Molybdenum in the form of ferro-molybdenum does not meet the requirements for chemical composition, especially with high concentration of phosphorus, copper, arsenic, tin and antimony. When making molybdenum, it is possible to achieve reduction in undesirable element contents by clean metal metallurgy.

Vanadium in the form of ferroalloy constitutes acceptable contamination of the melt with undesirable elements when making these steels alloyed to 0,15 percentages by weight of vanadium.

Aluminium is a basic desoxidation element in steel making used in several quality modifications in the form of pigs or shots. Aluminium metal contains up to 14 percentages by weight of silicon and traces of some other elements, e. g. Fe, Mg, Ca, Sb. Superior aluminium having silicon content up to 4 percentages by weight constitutes, with respect to the amount of aluminium introduced into the metal in the course of steel making, acceptable contamination of the basic melt with silicon.

Oxidizing and flux materia

Conditions of metallurgical process of steel making and treatment are significantly influenced by amount and quality of oxidizing and flux materials. In terms of possible contamination of steel with undesirable elements, gaseous oxygen - O_2 and iron ore - Fe_xO_y rank among the pure oxidizing materials. Scale from hot steel forming constitutes a mix of oxides of a number of elements commonly occurring in the steel that can get reduced during the treatment and considerably influence chemical composition of the metal phase. Under the conditions created for steel dephosphorization, they enable to easily increase the share of FeO in the slag. During the whole process of making, atmospheric oxygen also acts indispensably. Mainly burnt lime and fluorite rank among flux material. To a limited extent, we can also consider limestone that, however, influences energy budget of the melt as well as processes taking place in the slag with its own thermo dissociation.

For the technologies of secondary metallurgy, ŽĎAS, a. s. successfully uses $CaO\text{-}Al_2O_3\text{-}SiO_2$ based synthetic slags. By adding the lime and aluminium skimmings, chemical composition of the slag is controlled and refining processes optimized.

STEEL MAKING IN ELECTRIC ARC FURNACE

Proposed technology of making was based on presumed guarantee of chemical composition of the primary melt, especially contents of Cu, As, Sn and Sb trace elements. Suitable conditions during the charge melting and oxidizing periods of the melt enable then to correct the Si, Mn and P content to requested level. Product of treatment of the metal phase in the electric arc furnace is non-deoxidized molten metal having satisfactory content of Si, Mn, P and trace elements, perfectly free from oxidation slag and poured into the refining ladle of secondary metallurgy.

Preparation of the charge and melting

Result of performed analysis of charging stock, mainly as regards the requirement for trace element contents, is the basic metal charge composed of pig iron and DRI/HBI direct reduced iron. Share of individual components of the charge respected technical/economical aspects of steel making in the electric arc furnace. In addition to chemical composition, recovery is essential feature of components of the metal charge. The Table 5. shows theoretically calculated metal recovery when processing pig iron. The Table 6. evaluates the theoretical metal recovery when using DRI/HBI reduced iron for creation of the basic charge.

Values of total melting loss in both tables feature considerable difference that is necessary to be taken into account when calculating the charge. High content of iron oxides in DRI/HBI increases the total melting loss of the elements and the share of oxides of acidic character especially SiO_2 requests correction of slag basicity by increased lime addition when treating in the EAF.

The calculation of the amount of flux materials for the charge was based on the need to verify the influence of slag chemical composition on the course of some chemical reactions especially reduction of manganese content.

Chemical composition of metal after the charge smelting is shown in the Table 7., chemical analyses of slags in the Table 8.

It is obvious from the Table 8. that the lime additive in amount of 26 kg·t^{-1} for the charge of the A melt ensures slag basicity $B_{EAF} > 1$.

Chemical composition of metal bath and slag after the smelting evidently does not depend on selected slag mode. Considerable influence, however, has the temperature in connection with the time from full melting-down of the metal charge till taking of sample for chemical analysis. The A melt at the moment of sampling at a temperature of 1450 °C presents considerably lower share of Fe_xO_y oxides in the slag compared to the slag of the B melt at a temperature of 1345 °C. Reduction of iron oxides in the slag takes place with concurrent oxidation of other elements. This is proved by lower contents of silicon and carbon in A and C melts. Gas content values interesting are, especially very low values of hydrogen and above all nitrogen.

Table 5. **Pig iron - metal recovery and calculated melting loss of the charge**
Tablica 5. **Sirovo željezo - oporavak metala i izračunati gubici pri taljenju šarže**

Pig Iron	Chemical composition												Total
	C	Mn	Si	Cr	Ni	Mo	V	P	As	Sn	Sb	Fe	
Analysis / wt. %	4,40	0,04	0,30	0,01	0,01	0,01	0,00	0,030	0,0001	0,0004	0,0011	95,20	100,0
Yield / wt. %	0,31	0,02	0,01	0,01	0,01	0,01	0,00	0,003	0,0001	0,0004	0,0011	85,68	86,0
Weight loss / %	93	50	98	0	0	0	50	90	0	0	0	10	14,0

Table 6. **DRI/HBI metal recovery and calculated melting loss of the charge**
Tablica 6. **Izravno reducirano željezo / željezo u vrućim briketima - oporavak metala i izračunati gubitak pri topljenju šarže**

DRI/HBI	Chemical composition									Total
	C	Fe_xO_y	SiO_2	CaO	S	As	Sn	Sb	Fe	
Analysis / wt. %	1,00	8,70	4,30	1,00	0,011	0,0005	0,0005	0,0010	85,00	100,0
Yield / wt. %	0,30	0,00	0,00	0,00	0,001	0,0005	0,0005	0,0010	76,50	76,8
Weight loss / %	70	100	100	100	90	0	0	0	10	23,2

Table 7. **Chemical composition of metal after the charge smelting - 1st test**
Tablica 7. **Kemijski sastav metala nakon topljenja šarže - 1. test**

Heat Sample	$t_{sampling}$ / °C	C	Mn	Si	P	S	Cr	Ni	Cu	Mo	V	Al	As	Sn	Sb	H	N	O
		wt. / %											/ ppm					
A - 1	1450	2,45	0,04	0,13	0,023	0,010	0,02	0,01	0,01	0,00	0,00	0,00	< 50	< 50	< 30	1,8	19	175
B - 1	1345	3,15	0,03	0,21	0,027	0,009	0,05	0,01	0,01	0,00	0,00	0,00	< 50	< 50	< 30	1,1	-	-
C - 1	1495	3,00	0,01	0,01	0,022	0,010	0,01	0,01	0,01	0,00	0,00	0,00	< 50	< 50	< 30	-	16	170

Table 8. **Chemical composition of slag after the charge smelting - 1st test**
Tablica 8. **Kemijski sastav troske nakon topljenja šarže - 1. test**

Heat Sample	C	S	FeO	Fe_2O_3	MnO	Cr_2O_3	V_2O_5	TiO_2	CaO	P_2O_5	SiO_2	Al_2O_3	MgO	CaF_2	B_{EAF}
	wt. / %														
A - 1	0,07	0,03	2,81	0,32	0,39	0,03	0,04	0,59	42,77	0,02	38,96	6,63	5,03	0,76	1,1
B - 1	0,10	0,01	16,96	1,11	0,81	0,40	0,06	0,86	14,48	0,02	48,62	8,76	5,72	0,36	0,3

Oxidation and tapping

During melting, reactions among Fe_xO_y oxides and other elements contained in the basic charge take place and under concurrent gaseous oxygen blowing partial or full oxidation of some elements also takes place.

Unless the expected full oxidation of silicon and manganese was achieved in the melting phase, oxygen blowing was performed and using primary slag properties, the content of silicon and above all manganese was reduced to the values requested by the specification. Prior to oxygen blowing, chemical composition of the slag was modified by its partial removal and adding lime. Attained speed of melt decarburization of 0,04 to 0,05 percentages by weight of $C\cdot min^{-1}$ corresponded to common conditions.

The steel dephosporization process requested different conditions, namely especially high basicity and low viscosity of the slag, share of 10 to 15 percentages by weight of FeO in the slag, temperature of steel ranging from 1520 to 1570 °C and carbon content ranging from 0,70 to 0,10 percentages by weight of C, are important in light of provision of optimum course of carbon reaction. Parameters of the slag were modified by adding lime, fluorite and Fe_xO_y iron oxides in the form of hammer-scale. Dephosphorization was realized by variation of the slag in 3 to 5 cycles. When phosphorus content of less than 0,004 percentages by weight of P had been reached, the oxidation slag was skimmed thoroughly and prior to subsequent heating-up to a temperature of 1670 to 1690 °C, new slag was charged on the steel surface consisting of lime. The only purpose was to cover the metal surface and to protect the electric arcs. When the tapping temperature had been reached, the covering slag was skimmed perfectly and tapping was performed. Output parameters of the metal bath before being tapped from the electrical arc furnace into the refining ladle are shown in the Table 8. When tapping, coke and partially deoxidation aluminium are batched into the ladle for preliminary alloying.

STEEL REFINING ON SECONDARY METALLURGY EQUIPMENT

On the secondary metallurgy equipment, steel refining takes place to ensure precision alloying, deep steel deoxidation and desulphurization, thermal and chemical homogenizing, modification of inclusions and high purity of the metal bath.

Alloying and refining in LF furnace

After the melt had been heated up to a temperature of approx. 1630 °C, all slag was removed from the metal surface in the ladle for the melt C (3,5NiCrMoV). For the melts A and B, the slag was kept. Very strict limitation of manganese and phosphorus content in steel is the reason for skimming residues of the furnace slag from the refining ladle.

Measured content of total oxygen in the steel after having reached the LF considerably exceeded values of 50 ppm. Therefore preliminary aluminium deoxidation was performed by adding aluminium pigs on the steel surface. Carbon content correction was performed by adding coke and chemical composition of the slag was modified by adding LDSF synthetic slag. Before steel alloying, the melt was heated up to specified temperature of 1620 to 1630 °C. The alloying itself was performed by means of clean metals and ferroalloys: Cr metal, Ni metal, Mo metal and FeV. Then the slag mode was modified by adding lime and Al skimmings (STERAL 100). Continuously, the slag was deoxidized by aluminium shots.

Sampling was performed after the steel temperature had attained 1600 to 1640 °C. Based on the test results, precision alloying and aluminium content correction were performed. Since no slag analyzing equipment is available at ŽĎAS, a. s., aluminium was orientation-alloyed to a content of 0,060 to 0,080 percentages by weight of Al before VD. Steel temperature before VD was controlled within the range of 1670 to 1680 °C. Oxygen activity of individual melts ranged from 10 to 20 ppm.

VD process

At ŽĎAS, a. s., deep vacuum is reached automatically and so are controlled working pressures of the VD process. Deep vacuum – pressure < 200 Pa, constitutes conditions, under which intense steel degassing, especially hydrogen and nitrogen content elimination, takes place.

All three test melts were made by duplex vacuum degassing technology aimed at reaching the maximum degree of deoxidation of both mentioned steel grades. In the first vacuum degassing cycle, steel and slag deoxidation took place insufficiently. This was evident even from high oxygen activity and low degree of desulphurization. On one occasion, partial carbon deoxidation even took place.

Table 9. **Output parameters of metal before being tapped from EAF**
Tablica 9. **Izlazni parametri metala prije probijanja ELP**

Heat	t / °C	C	Mn	Si	P	S	Cr	Ni	Cu	Mo	V	Al	As	Sn	Sb	H	N	O
		wt. / %											/ ppm					
A	1659	0,18	0,04	0,01	0,003	0,008	0,07	0,04	0,01	0,00	0,00	0,00	< 50	< 50	< 30	-	34	700
B	1626	0,13	0,03	0,01	0,005	0,007	0,22	0,06	0,01	0,00	0,00	0,00	< 50	< 50	< 30	-	-	-
C	1660	0,06	0,04	0,01	0,004	0,010	0,09	0,03	0,01	0,01	0,00	0,00	< 50	< 50	< 30	-	-	-

Table 10. **Final chemical composition of the melts**
Tablica 10. **Konačni kemijski sastav taline**

Heat Sample	C	Mn	Si	P	S	Cr	Ni	Cu	Mo	V	Al	As	Sn	Sb	H	N	O	Ca	Bfactor
	wt. / %											/ ppm							
A_{final}	0,28	0,04	0,05	0,003	0,001	1,58	3,00	0,02	0,33	0,10	0,010	20	20	10	1,4	56	32	10	4,5
B_{final}	0,30	0,05	0,03	0,004	0,004	1,56	2,86	0,03	0,36	0,11	0,005	20	20	10	1,6	35	24	10	5,5
C_{final}	0,30	0,04	0,01	0,004	0,005	1,82	3,67	0,01	0,40	0,10	0,017	20	20	10	1,5	54	30	10	5,5

B factor = (10 · wt. % P + 5 · wt. % Sb + 4 · wt. % Sn + wt. % As) · 100

Therefore, it was necessary to do the second vacuum degassing after the heating on LF.

Steel samples for final chemical analysis are taken during ingot casting. The Table 9. shows final chemical composition of the melts.

Ingot casting

At ŽĎAS, a. s., steel is cast in moulds at atmospheric pressure by a technology of bottom casting via the gating system. When casting the steel, molten steel gets into contact with surrounding atmosphere. With respect to oxygen and nitrogen content disequilibrium, intensive secondary steel oxidation and nitrification take place. Oxides and nitrides of reactive elements, arisen during the casting, rank among exogenous inclusions that significantly reduce static and especially dynamic strength properties of steel [4]. Especially the steels treated by the vacuum technology are to be cast in inert atmosphere (Ar).

The gating system consists of sprues made of fire clay based ceramics. Erosive effect induced by metal flow is eliminated by increasing the Al_2O_3 share in basic fire-clay mould to 62 %.

In case of ingot bottom casting, molten metal is protected with casting powder being dosed on the steel surface in the mould. For casting low- and medium-alloyed steels to big ingots, casting powder of ALSICAL company is used.

Ingot tops are treated with heat-insulation lining located along the perimeter of the sink head, exothermic powder applied on the metal surface at the moment of completion of ingot casting and after the elapse of reaction time – exothermic mixture combustion time, all ingot top surface is thoroughly powdered with insulating compound.

The ingots are cooled in moulds in the cooling area down to an ambient temperature. After the mould stripping and visual check of ingot surface quality, the ingots are dispatched to ŽĎAS, a. s. forge shop.

CONCLUSION

Production of super-clean steels intended to make forgings of rotary parts of the gas-turbine unit constitute significant enhancement of qualitative level of production of ŽĎAS, a. s.' electric steel plant. Execution of experimental melts confirmed a wide range of problems in making super-clean steels. Molten metal treatment enabled the requested metallurgical reactions and ensured high quality of steel confirmed by material test results.

Knowledge and experience gained during making three test melts indicate other directions of the development in solving the problems of technology of making super-clean steels type 2.8NiCrMoV and 3.5NiCrMoV. Just now, they are, for example, optimization of the charge composition, modification of the slag mode, reduction of the total melting time or optimization of the ingot casting speed and verification of influence of the casting ceramics on resulting quality of the forgings.

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