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THE QUALITY OF SUPER-CLEAN STEELS PRODUCED AT ŽĎAS, inc.

KAKOVOST SUPERČISTIH JEKEL, IZDELANIH V PODJETJU ŽĎAS, inc.

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The production of Super-Clean Steels for the rotor forgings of compressors and generators for gas-turbine units started at ZDAS with the use of secondary metallurgy processes, a ladle furnace and vacuum degassing. The development and optimization of Super-Clean Steel production technology enables effective molten metal manufacture, conforming to the requirements for chemical composition and micro-cleanness. According to the results of the current production, the effective production of rotor forgings requires new technological steps in ingot casting.

Keywords: super-clean steel, steelmaking, secondary metallurgy, ingot casting

Proizvodnja superčistih jekel za odkovke rotorjev kompresorjev in generatorjev za plinske turbine se je začela z začetkom uporabe procesov sekundarne metalurgije, s ponovčno pečjo in z vakuumsko degazacijo. Razvoj in optimizacija tehnologije superčistih jekel omogočata učinkovito izdelavo taline z upoštevanjem kemične sestave in mikročistosti. Glede na rezultate sedanje proizvodnje so za učinkovito izdelavo rotorjev potrebne tehnološke izboljšave litja ingotov.

Ključne besede: superčisto jeklo, izdelava jekla, sekundarna metalurgija, litje ingotov

1 INTRODUCTION

The production of rotors at ZDAS consists of medium-weight forgings for equipment to generate electric power, gas turbines of the type GT – 009 with a maximum output of 11.7 MW and a gas temperature at the outlet up to 580 °C.[1]

In the frame of the production of a trial series of forgings for compressor and generator rotors in ZDAS, samples of steel were taken during the forging of ingots 8K10.0 and 8K13.0 from the steel grade 26NiCrMoV115.

The analyses of the chemical composition and the evaluations of the results from the viewpoint of the achieved parameters of chemical cleanliness, as well as from the viewpoint of the influence of casting and solidification on the differences between the chemical composition of the melt and the forging, make it possible to interpret the stability of the production process. The analyses of forging defects provided sufficient information about the possible causes of defects.

2 CHEMICAL COMPOSITION OF A FORGING MADE OF SUPER-CLEAN STEELS

Table 1 summarises the requirements for the chemical composition of super-clean steel (SCS) for

Table 1: Chemical composition of steel 26NiCrMoV115 in mass fractions, *w*/%
Tabela 1: Kemična sestava jekla 26NiCrMoV115 v masnih deležih, *w*/%

A	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	As	Sn	Sb
	(*w*/%)											(μg/g)		
min.	0.26	max.	max.	max.	max.	1.40	2.80	0.30	max.	max.	max.	max.	max.	max.
max.	0.32	0.30	0.07	0.007	0.005	1.70	3.00	0.45	0.15	0.010	0.12	100	100	50

Table 2: Chemical composition of steel 26NiCrMoV145 in mass fractions, *w*/%
Tabela 2: Kemična sestava jekla 26NiCrMoV145 v masnih deležih, *w*/%

B	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	As	Sn	Sb	X factor
	(*w*/%)											(μg/g)			
min.	0.26	max.	max.	max.	max.	1.60	3.50	0.30	max.	max.	max.	max.	max.	max.	max.
max	0.32	0.04	0.04	0.004	0.004	1.90	3.80	0.45	0.15	0.015	0.12	80	50	20	7.0

Table 3: Average content of elements in the heats of steel grade 26NiCrMoV115 in mass fractions, *w*/%
Tabela 3: Povprečna vsebnost elementov v talinah jekla 26NiCrMoV115 v masnih deležih, *w*/%

A	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	As	Sn	Sb
	(*w*/%)											(μg/g)		
AVG	0.295	0.210	0.023	0.0043	0.0028	1.588	2.913	0.390	0.106	0.0063	0.080	49.4	58.5	29.3
s	0.011	0.031	0.017	0.0008	0.0014	0.035	0.033	0.013	0.009	0.0020	0.024	7.7	15.1	2.5

Table 4: Average content of elements in the heats of steel grade 26NiCrMoV145 in mass fractions, *w*/%
Tabela 4: Povprečna vsebnost elementov v talinah jekla 26NiCrMoV145 v masnih deležih, *w*/%

B	C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	As*	Sn*	Sb*	X factor
	(*w*/%)											(μg/g)			
AVG	0.293	0.032	0.012	0.0032	0.0044	1.809	3.714	0.395	0.108	0.008	0.014	31.1	32.1	<20	5.81
s	0.012	0.010	0.004	0.0006	0.0039	0.046	0.040	0.0011	0.008	0.003	0.008	18.6	17.6	–	1.10

* Concentration of elements below the detection limits

Table 5: Correlation coefficients of elements (sample of the melt / forging)
Tabela 5: Korelacija kemične sestave talin in odkovkov

Elements	Ni	Cu	Mn	Si	Cr	V	S	Ca	Al	C	Mo	P	N	O
X (*w*/%) forging	0,99	0,99	0,99	0,98	0,97	0,92	0,89	0,85	0,78	0,78	0,75	0,60	0,46	0,05

compressor and generator rotors and **Table 2** for the discs of turbine and generator wheels.

The average contents of the alloying and tramp elements of 87 heats of steel grade 26NiCrMoV115 (A) and 19 heats of steel grade 26NiCrMoV145 (B) are given in **Tables 3** and **4**.

On the basis of the ordinary production of forgings a complete chemical composition was determined for 44 samples of steel from the forgings, i.e., for 44 ingots from various heats of the steel grade 26NiCrMoV115. **Figures 1** to **4** show the distribution of the content of the elements P, S, O and N.

For the monitored 44 heats the average content of phosphorus is 37.1 μg/g and the standard deviation is 7.65 μg/g. The contents vary in the range from 20 μg/g to 60 μg/g.

The average content of sulphur was of 29.3 μg/g, with the variation in the range from 10 μg/g to 50 μg/g and a standard deviation of 12.08 μg/g.

The distribution of oxygen content is shown in **Figure 3**. The average content of oxygen was 20.6 μg/g

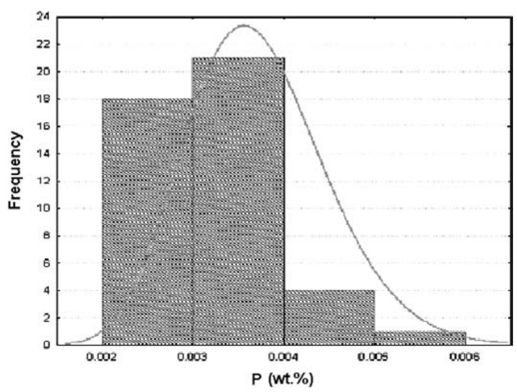

Figure 1: Phosphorus content – forging
Slika 1: Vsebnost fosforja v odkovkih

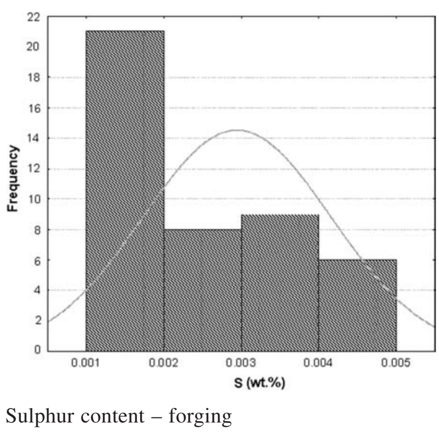

Figure 2: Sulphur content – forging
Slika 2: Vsebnost žvepla v odkovkih

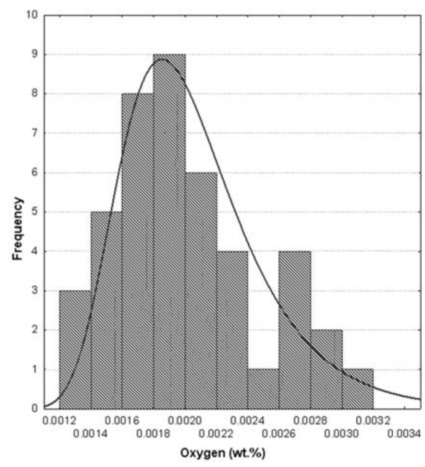

Figure 3: Oxygen content – forging
Slika 3: Vsebnost kisika v odkovkih

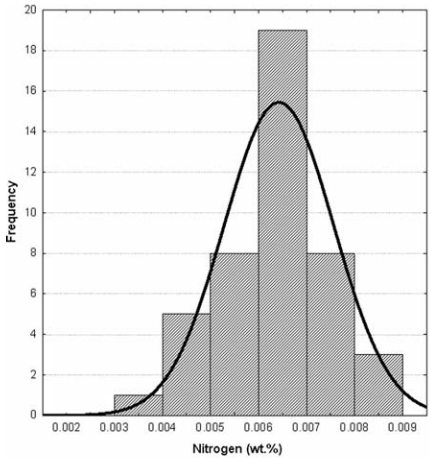

Figure 4: Nitrogen content – forging
Slika 4: Vsebnost dušika v odkovkih

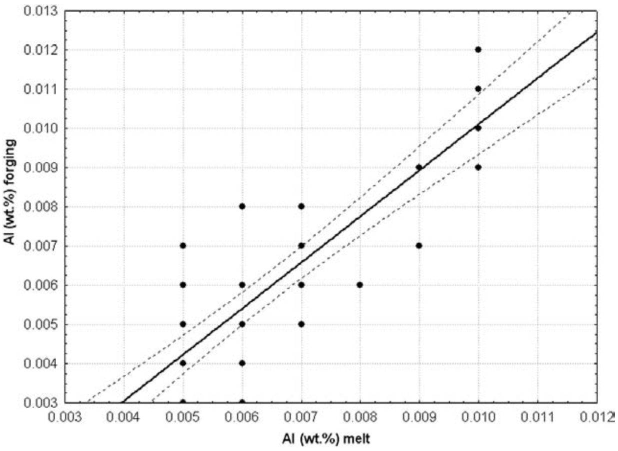

Figure 6: Aluminium content – melt / forging
Slika 6: Vsebnost aluminija – talina/odkovek

and the standard deviation was 4.56 μg/g. The oxygen content in the forgings varied in the range from 12 μg/g to 32 μg/g. The average content of nitrogen in **Figure 4** was 64.0 μg/g and the standard deviation was 11.36 μg/g. The nitrogen content in the forgings varied in the range from 34 μg/g to 84 μg/g.

3 AGREEMENT OF THE CHEMICAL ANALYSIS OF THE MELT WITH THE ANALYSIS OF THE FORGING

The results of the chemical composition of the samples of steel forgings were compared with the results of the chemical analysis of the melt to verify the agreement of both chemical analyses. The correlation coefficients of the individual elements in descending agreement are shown in **Table 5**.

The results in **Table 5** suggest that the agreement of the chemical composition of the forgings and the melts depends on the place in the sample ingot where the measurement was made. If we consider the position of the analysed sample is below the ingot head, which is the place of its biggest cross-section, and simultaneously the latest solidification part of the ingot body, it may be expected that due to segregations, the concentrations of some elements may be influenced during the ingot's solidification.

This assumption is confirmed by the order of the correlation coefficients of chromium, vanadium and molybdenum, i.e., elements that form carbides. Phosphorus and sulphur show a high degree of segregation and the low correlation coefficient suggests the segregation of nitrogen and aluminium, which have a great mutual affinity.

The lowest correlation coefficients according to **Table 5** were calculated for the gases, oxygen and nitrogen, while the correlation coefficient for the oxygen concentrations is negligible. In **Figures 5** to **8** the dependence of selected elements, i.e., calcium, aluminium, nitrogen and oxygen, is shown.

The disagreement in the oxygen and nitrogen contents is apparently related to the casting process and the sampling of metal for the analysis of both elements

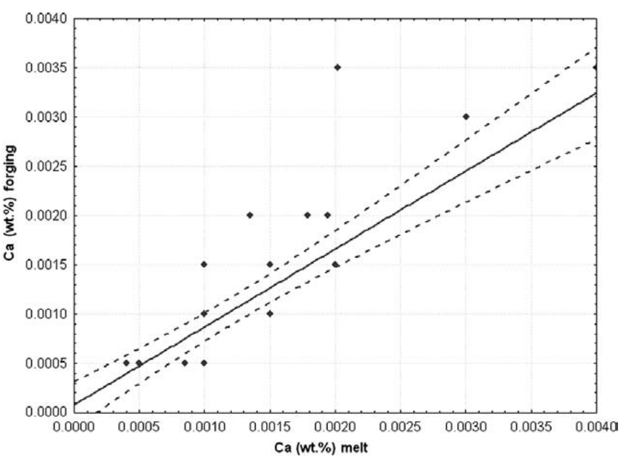

Figure 5: Calcium content – melt / forging
Slika 5: Vsebnost kalcija – talina/odkovek

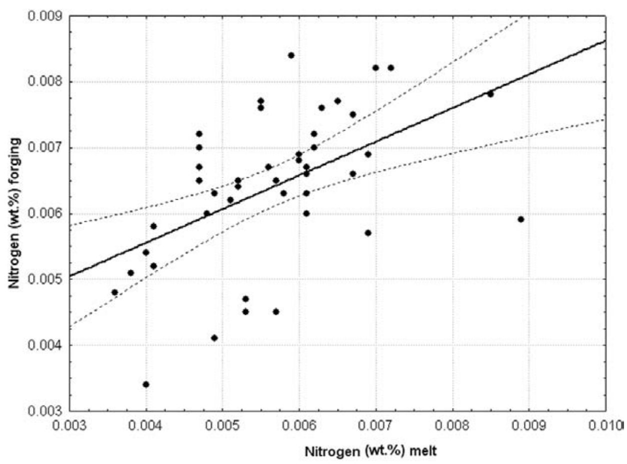

Figure 7: Nitrogen content – melt / forging
Slika 7: Vsebnost dušika – talina/odkovek

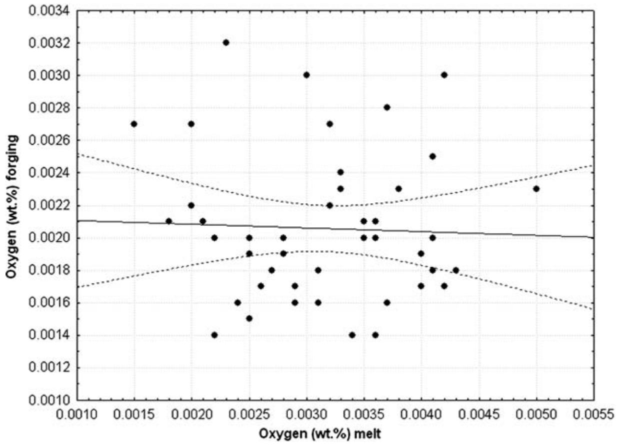

Figure 8: Oxygen content – melt / forging
Slika 8: Vsebnost kisika – talina/odkovek

from the melt. The sampling occurs by taking a small amount of melt from the flow of metal under the slide gate into the steel ladle, from which the metal is afterwards poured again into the ingot mould. This process occurs with considerable contact of the melt with surrounding atmosphere, which creates good conditions for the saturation of the degassed melt with oxygen and nitrogen.

For the oxygen content, we consider the concentration determined by the chemical analysis of the sample taken from the forging to be realistic one. On the basis of the results of the analyses it is possible to discuss the potential control of the steel's chemical composition, as well as possibility of verifying the obtained individual elements concentrations already during hot-metal production. Namely, the prediction of oxygen and nitrogen contents in the production of hot metal appears to be rather problematic with respect to the final forging contents. This suggest that the existing methodology for taking samples of melts by pouring for a determination of the gas contents in steel of the type 26NiCrMoV115 and 26NiCrMoV145 is unsatisfactory.

The solution to this issue may be the realisation of equipment that can take samples with the elimination of the earlier mentioned influence of the atmosphere, i.e., preferably by sampling directly from the ladle at the end of the treatment by the VD or VCD process and from the ingot, either already during pouring or after its completion.

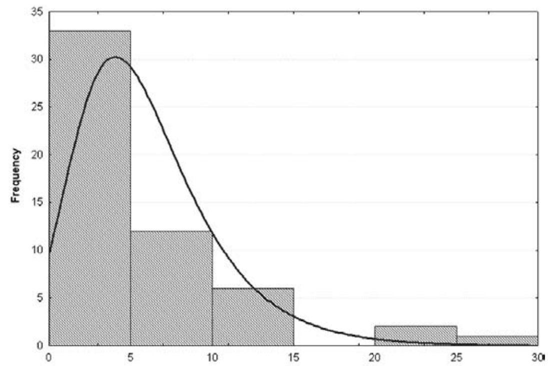

Figure 9: Micro-cleanness DIN50602, method K_4
Slika 9: Mikročistost po DIN50602, metoda K_4

4 METALLOGRAPHIC CLEANLINESS OF SUPER-CLEAN STEEL FORGINGS

The metallographic cleanliness of steel in conformity with the standard DIN 50602 was determined according the method K4 for 44 heats from identical samples, as for previous examinations, and for an additional 10 heats using samples taken in a similar manner. Thus there was a total of 54 heats.

The distribution of micro-cleanness determined according the standard DIN 50602 method K4 is shown in **Figure 9** interlaid with the curve of the normal distribution with the exclusion of the extreme values of $K_4 > 20$. The average micro-cleanness $K_4 = 6.3$ with a standard deviation of 5.61 was calculated for 54 heats. The values of K_4 were in the range from 0 to 29.

From the viewpoint of the current requirements for the cleanliness of steel the values $K_4 > 10$ can be considered as deteriorated and $K_4 > 20$ as unsatisfactory. However, the limits stipulated in this manner are relative and they are based on the assumption that the deteriorated micro-cleanness will considerably influence the mechanical properties, particularly the strength characteristics and the transition temperature or the creep resistance of the forgings.

In accordance with the defined measures, very good micro-cleanness was found for 45 heats (83.3 %) out of the 54 examined heats, while 6 heats (11.1 %) had worse micro-cleanness, and an unsatisfactory micro-cleanness was found for 3 heats, i.e., in 5.6 % of production.

In spite of the deteriorated parameters of the metallographic purity of the steels for some heats, the forgings passed the required tests of mechanical properties, even without special measures concerning their heat treatment. It is therefore possible to consider the achieved metallographic cleanliness of super-clean steels is acceptable. However, the objective should be to achieve the value of $K_4 < 10$.

The measures aimed at ensuring the required cleanliness may be the optimisation of slag mode or its possible modification. Due to the occurrence of exogenous inclusions it is not possible to also exclude the casting technology, including issues related to the ceramics used for pouring.[2]

5 ANALYSIS OF THE DEFECTS IN SUPER-CLEAN STEEL FORGINGS

Altogether, 122 shafts were produced until 2006, out of which 18 shafts were classified as unsatisfactory due to the occurrence of undesirable ultrasonic defects. A

Figure 10: Defective generator rotor shaft – forging No. 447 660
Slika 10: Defektna gred rotorja generatorja – odkovek št. 447 660

Figure 11: Detail of extent and location of the defect on the generator rotor shaft – forging No. 447 660
Slika 11: Velikost in mesto napake na gredi rotorja generatorja – odkovek št. 447 660

total of 14.8 % of the total number of produced shafts was rejected. Altogether, 63 pieces of shafts were made from the ingots 8K10,0 and 59 shafts from the ingots 8K13,0, while 10 pieces of rejected shafts were made from the ingots 8K10,0 and another 8 pieces of rejected shafts were made from the ingots 8K13,0 [3].

Figure 12: Forging No. 447 660. Macro-shape of the sample at the place of defect location.
Slika 12: Odkovek št. 447 660. Vzorec z mestom napake.

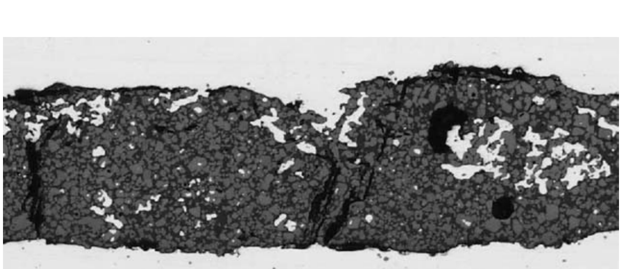

Figure 13: Micro-shape of the large part of inclusion (500-times)
Slika 13: Mikrooblika večjega dela vključka (povečava 500-kratna)

Defective forgings were submitted to a metallographic investigation and in the following review documents the results of the analysis of the forging No. 447 660 of the generator rotor shaft are presented. The shaft with a diameter of 270 mm ingot heel in **Figures 10** and **11** did not pass the ultrasonic test performed on the roughed piece prior to drilling of straight-through hole with a diameter of 95 mm. It was expected that with drilling of the hole the defects will be removed. After drilling and heat treatment an areal defect KSR 1 to 4 mm was detected at a depth of 60 mm to 75 mm in the central part of the piece.

A sample was taken from the forging in the transversal direction and the exact position of the defect was localised by repeated ultrasonic testing. A sample for metallographic analysis was taken from the place of the defect and after completion of the section at the location of the defect longitudinally with respect to the axis of the original forging continuous non-metallic inclusions was discovered on the full length of the sample (24 mm) of width of 1 mm. The macro-shape of the inclusion is shown in **Figure 12** and its micro-shape in **Figures 13** and **14**. The steel microstructure consisted predominantly of sorbite and bainite.

More analyses were performed in collaboration with the Institute of Metals and Technology Ljubljana. An identical sample was analysed by emission electron microscope JEOL JSM 6500F and an energy-dispersive spectroscope – EDS INSA CRYSTAL 300. In **Figure 15** the points of the analyses and in **Table 6** the results of the analyses are shown.

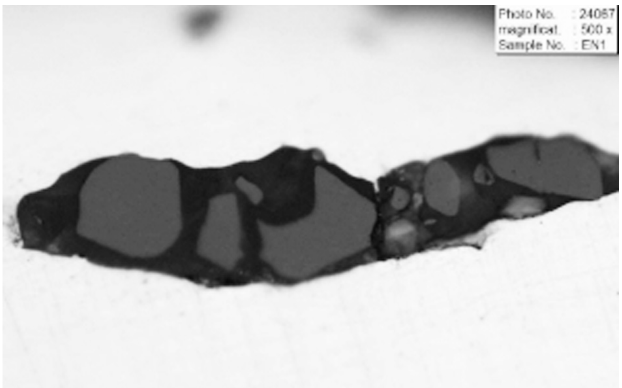

Figure 14: Shorter rows of oxides were near the large inclusion (500-times)
Slika 14: Krajši oksidni vključek blizu večjega (povečava 500-kratna)

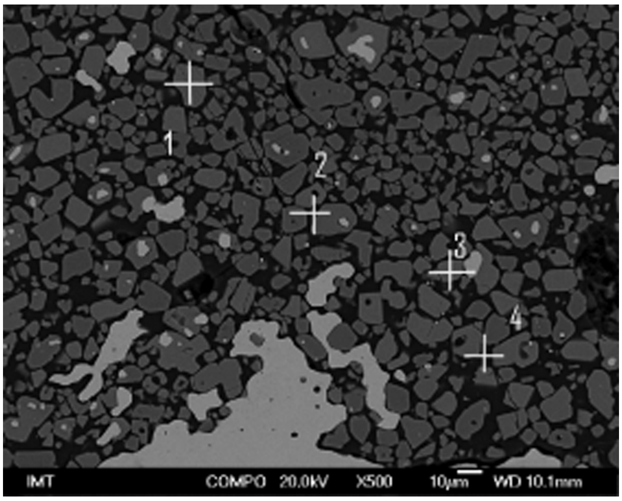

Figure 15: Points of analysis of inclusion
Slika 15: Mesta analize vključka

The chemical composition of the non-metallic–ceramic materials used during the production of steel was made for a comparison with the results of the analysis of the chemical composition of the inclusions – see **Table 7**.

On the basis of a comparison of the results of the analysis in **Tables 6** and **7** and the content of the basic elements Si, Na and K it is possible to consider the analyses on points 2 and 4 as inclusions based on the casting powder PC20. Spectre 1 and 3 correspond to the slide gate sand fill Chromix 8/5. Similar conclusions were drawn also in the other 6 cases of unsatisfactory shafts. From the description and the set of data for the chemical composition of the impurities found in the forgings for the shafts of steel 26NiCrMoV115, as determined by emission electron microscope JEOL JSM 6500F and by energy dispersive spectroscope EDS INSA CRYSTAL 300, it was determined that the main cause of the unacceptable defects of the forgings was the occurrence of non-metallic particles with a chemical composition corresponding to the casting powder PC 20 and to the slide gate fill sand Chromix 8/5. The determination of the real causes of the occurrence of this combination of non-metallic materials in ingots and forging is the subject of further tests and investigations.

6 CONCLUSIONS

In this work the production of super-clean steels at ZDAS from the perspective of chemical composition is evaluated. The chemical analyses of the melts steel were compared with the chemical composition of the forgings.

Table 6: Chemical composition in the analysed points shown in **Figure 15**
Tabela 6: Kemična sestava v točkah, označenih na **sliki 15**

Spectre	O	Al	Si	K	Mg	Na	Ca	Cr	Ti	V	Mn	Fe	Total
	(*w*/%)												
1	32.78	8.16	0.32	–	6.78	–	–	32.02	–	–	–	19.93	100
2	44.93	9.00	24.85	0.73	3.61	2.77	1.26	0.56	0.57	–	11.72	–	100
3	29.87	10.20	0.47	–	5.79	–	–	33.77	0.57	2.26	13.49	3.56	100
4	37.17	11.24	31.08	1.09	1.65	2.57	2.23	–	–	–	11.56	1.40	100

Spectre 1 – order of elements: Cr > Fe > Al > Mg > Si + O
Spectre 2 – order of elements: Si > Mn > Al > Mg > Na > Ca > K > Ti > Cr + O
Spectre 3 – order of elements: Cr > Mn > Al > Mg > Fe > V > Ti > Si + O
Spectre 4 – order of elements: Si > Mn > Al > Na > Ca > Mg > Fe > K + O

Table 7: Chemical composition of non-metallic materials used during the production of steel
Tabela 7: Kemična sestava nekovinskih materialov, uporabljenih pri izdelavi jekla

Sample	O	Al	Si	K	Mg	Na	Ca	Cr	P	S	Mo	Ti	Fe	Total
	(*w*/%)													
Refining slag VD-EU2	45.2	8.2	0.9		1.3		43.0						1.3	100
Refractory shotcrete of ref. ladle – Kalinovo	55.2	22.9	6.8		3.0		9.6						2.5	100
Sand in slide gate Chromix 8/5	30.2	8.3	1.5		7.5			33.6		0.2			18.7	100
Pouring channel – main gate of the system	55.1	21.0	19.5	1.7								1.0	1.8	100
Mortar for gluing of pouring channels – Regnalit	57.7	12.5	26.0	1.7								0.6	1.6	100
Mortar for gluing of pouring channels – ŽĎAS	52.9	16.4	24.2	0.7		4.7						0.6	0.8	100
Sand SiO_2	58.8	0.2	40.5									0.2	0.3	100
Sand SiO_2 – recycled	58.2	0.6	38.4	0.3				1.0					1.6	100
Casting powder PC 20	51.3	13.8	20.7	2.4	0.5	2.4	1.9		0.6		1.7	1.2	3.6	100

The agreement of both is acceptable for all elements, with the exception of the contents of nitrogen and particularly of oxygen. It can be concluded that the difference could be resolved by a change of methodology of taking the samples for a determination of the contents of gases in the hot metal.

On the basis of the evaluation of the micro-cleanness of the steel according to the standard DIN 50 602 by method K4, a very good micro-cleanness $K_4 < 10$ was assessed for 45 heats out of 54 heats, thus for 83.3 % of the production.

The metallographic analyses of 7 rejected rotors with use of the electron microscope showed that 6 shafts out of 7 were unsatisfactory due to the presence of isolated massive rows of clusters of non-metallic particles with lengths up to 15 mm consisting of 2 phases – casting powder and chromite sand (Cr_2O_3), which was used as fill sand for refining the ladle slide gate.

The measures for ensuring the stable level of metallographic cleanliness and for the prevention of the occurrence of exogenous inclusions may consist of the optimisation of slag mode or in its possible modification, as well as of interventions into casting technology, including the solution of the issues for ceramics used for the pouring and filtration of steel.

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