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RE-OXIDATION PHENOMENA DURING THE FILTRATION OF STEEL BY MEANS OF CERAMIC FILTERS

REOKSIDACIJSKI PROCESI MED FILTRIRANJEM JEKLA S KERAMIČNIMI FILTRI

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This paper presents the results of experiments on the filtering of the melt of carbon steel with the use of five types of ceramic filters with direct holes, which differed in terms of their basic ceramic nature. The objective of the experiments was to determine the influence of filter ceramics on the re-oxidation reactions and the reactions between the filter ceramics and molten steel flowing through the filter capillaries. The metallurgical and metallographic cleanliness of the steel filtered through individual types of filters was also assessed.

Key-words: filtration of steel, ceramic filters, capillary tube re-oxidation, micro-cleanliness of steel

V članku so prikazani rezultati preizkusov filtriranja ogljikovega jekla s filtri iz keramike različne sestave in z neposrednimi kapilarami. Cilj preizkusov je bil ugotoviti vpliv filtrne keramike na reakcije reoksidacije in naravo reakcij med to keramiko in jeklom, ki teče skozi kapilare. Metalurška in metalografska čistota jekla sta bili tudi ocenjeni.

Ključne besede: filtriranje jekla, keramični filtri, reoksidacija v filtrnih kapilarah, mikročistost jekla

1 INTRODUCTION

Re-oxidation processes accompany the de-oxidised steel from the furnace or from the ladle till its final solidification in the mould or in the ingot-mould. The main products of re-oxidation processes are usually non-metallic oxide inclusions formed first from the elements with a higher affinity for oxygen, and progressively with the re-oxidation of elements with decreasing and finally with a very low affinity for oxygen. Among the elements present in the molten steel, iron and manganese, silicon, and chromium, etc. [1–4] are re-oxidised.

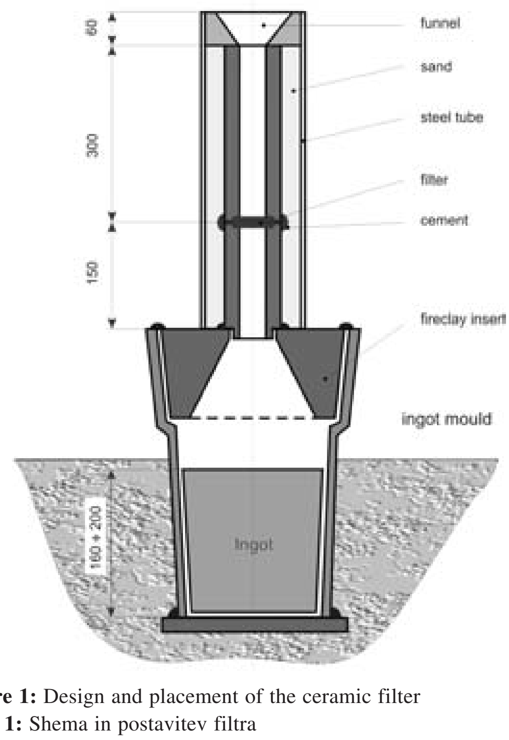

Figure 1: Design and placement of the ceramic filter
Slika 1: Shema in postavitev filtra

The paper presents the results of experiments of the filtration of molten carbon steel using five types of ceramic filters with direct holes, which differed in terms of their primary ceramic basis. The experiments and analyses of the chemical composition were aimed at determining the influence of filter ceramics on the course of re-oxidation processes and at assessing the reactions between the filter ceramics and the molten steel flowing through the filter capillaries. The aim of the experiments was also to evaluate the metallurgical and metallographic cleanliness of the steel filtered with use of individual types of filters.

2 CHANGES OF THE CHEMICAL COMPOSITION OF THE CAPILLARIES' CERAMIC SURFACE DURING FILTRATION

The five types of ceramic filters used for the verification of re-oxidation processes consisted of combinations of the following types of oxides: A – TiO_2 ·

ZrO_2; B – $Al_2O_3 \cdot TiO_2$; C – $MgO \cdot Al_2O_3$; D – $Al_2O_3 \cdot ZrO_2$; E – $Al_2O_3 \cdot SiO_2$. The specimens of ceramic filters were prepared in the company KERAMTECH, spol. s. r. o., Žacléř, Czech Republic. The sequence of the preparation of the experimental steel samples was melting of the steel, stabilisation at a temperature of 1650 °C, addition of pure aluminium and silicon-calcium for de-oxidation of the molten steel prior to filtration and at the same time the addition of a determined quantity of iron sulphide (FeS) into the molten steel intended to determine the reduction of sulphur content during the flow of the molten steels through the filter. Then the specimens for the determination of the initial chemical composition and filtration of the steel through individual types of filters were cast. During filtration the steel flowed through the filter and (*solidified*) above the filter, in the filter itself and in the filtered casting (sample). **Figure 1** shows the filtering scheme.

The chemical composition was determined with energy-dispersive X-ray spectral micro-analysis using the analytical systems JEOL JXA-8600/ KEVEX and JEOL JSMU 840/LINK. The results of the chemical analysis at the surface layer of the capillaries of the ceramic filters during the filtration of the initial chemical composition of the filter ceramics, which had no contact with the filtered melt, are summarised in **Table 1**. The working identification *"coating"* was used for the different chemical compositions of the surface of the ceramics after filtration. In **Table 1** the *differences* in the chemical composition of the *ceramics-coating,* (i.e., the difference between the original chemical composition of the ceramics and the chemical composition of the coating), in which the symbol (–) means decrement, and the symbol (+) means increment of an oxidic component of ceramics on the surface of the coating in mass fractions (%), are shown. The chemical composition of the used ceramics is marked in **Table 1** in bold characters. The chemical composition of basic oxidic components of the filter ceramics and the chemical composition of the oxidic components of the coating were determined as an arithmetic mean of two measurements.

It follows from the analyses of the chemical composition in Table 1 that in the whole series of five ceramic filters, which have a different oxidic base, the processes of adsorption of the flowing molten steel occur, which are related to the formation of the coating on the surface of the filter capillaries. Physical-chemical reactions occur between the flowing molten steel and the ceramic of the filter capillaries, and the initial ceramic composition is changed and a coating is formed on the surface of the capillaries. In this coating the chemical composition of the primary thermodynamically stable oxides is reduced and particularly the share of the oxides MnO and Fe_2O_3 is increased. The sum of the contents of both types of oxides in the capillaries' coating, i.e., MnO + Fe_2O_3, has a positive value for the whole series of filters A to E (see the **Table 1**). Both types of oxides are formed as a result of re-oxidation processes.

The ratios given in Table 1 are also given in a graphical representation. The changes of the chemical composition of the coating on the surface of filter capillaries were compared as a ratio of the sums of the concentrations of the decrements of the basic ceramic components for the investigated series of five filters A to E to the increments of the sums of the oxide MnO and Fe_2O_3 contents formed in the coating as a result of re-oxidation. This comparison is shown in bar form in **Figure 2**. It can be concluded from **Figure 2** that the sum of the changes in the composition of basic oxidic components in the filter ceramics on the coating of the capillaries (which – according to the analyses in **Table 1** – always has a negative value) is in all the investigated

Table 1: Changes in the chemical composition of the ceramics on the surface of the walls during the coating of the filter capillaries. The symbol (–) means decrement, the symbol (+) means increment of an oxide component of ceramics on the surface of the coating (*w*/%)

Tabela 1: Sprememba sestave keramike na površini kapilar. Simbol (–) pomeni zmanjšanje, simbol (*) pa povečanje neke oksidne komponente keramike na površini kapilare.

Filter	MgO	Al_2O_3	SiO_2	TiO_2	S	K_2O	CaO	ZrO_2	MnO	Fe_2O_3	
A	ceramics	2.09	7.55	13.04	**41.60**	0.00	0.62	0.16	**33.42**	0.07	1.96
	coating	0.82	3.16	4.08	**35.94**	0.00	0.14	0.09	**45.14**	0.73	9.92
	difference	–1.27	–4.39	–8.96	**–5.66**	0.00	–0.48	–0.07	**+11.72**	+0.66	+7.96
B	ceramics	0.23	**48.48**	11.62	**37.17**	0.15	0.50	0.07	0.00	0.08	1.12
	coating	0.51	**48.99**	12.34	**30.55**	0.12	0.20	0.47	0.00	4.55	1.67
	difference	+0.28	**+0.51**	+0.72	**–6.62**	–0.03	–0.30	+0.40	0.00	+4.47	+0.55
C	ceramics	**21.52**	**49.50**	22.97	0.75	0.22	0.67	0.41	0.00	0.11	3.29
	coating	**20.06**	**48.80**	23.88	0.69	0.11	0.64	0.53	0.00	1.95	2.92
	difference	-1.46	-0.70	+0.91	–0.06	–0.11	–0.03	+0.12	0.00	+1.84	–0.37
D	ceramics	3.58	**54.63**	11.52	0.30	0.00	0.30	0.12	**27.41**	0.15	2.51
	coating	1.95	**27.68**	22.80	0.18	0.00	0.40	0.35	**13.15**	13.51	20.01
	difference	–1.63	-26.9	+11.30	–0.12	0.00	+0.10	+0.23	–14.26	+13.36	+17.50
E	ceramics	3.78	**31.62**	**57.17**	1.01	0.10	0.93	0.32	0.00	0.09	4.45
	coating	2.73	**34.00**	**53.47**	1.13	0.11	1.56	0.62	0.00	0.27	5.24
	difference	–1.05	**+2.38**	-3.70	+0.12	+0.01	+1.24	+0.30	0.00	+0.18	+0.79

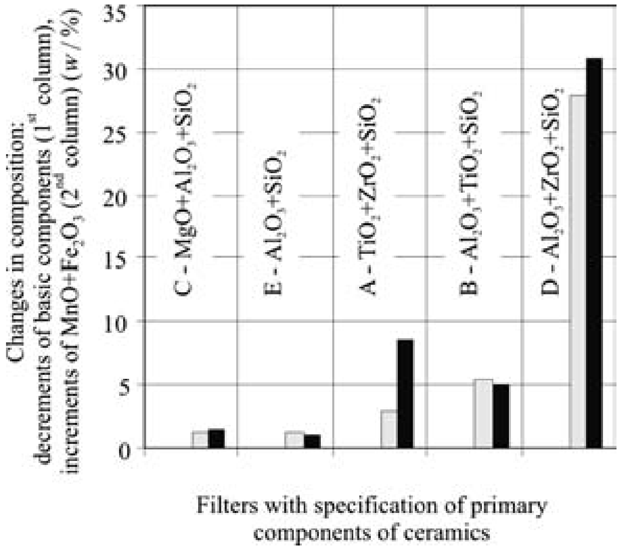

Figure 2: Decrements and increments of oxides in the coating of the filter capillaries

Slika 2: Zmanjšanje in povečanje vsebnosti oksidov v oblogi v kapilarah

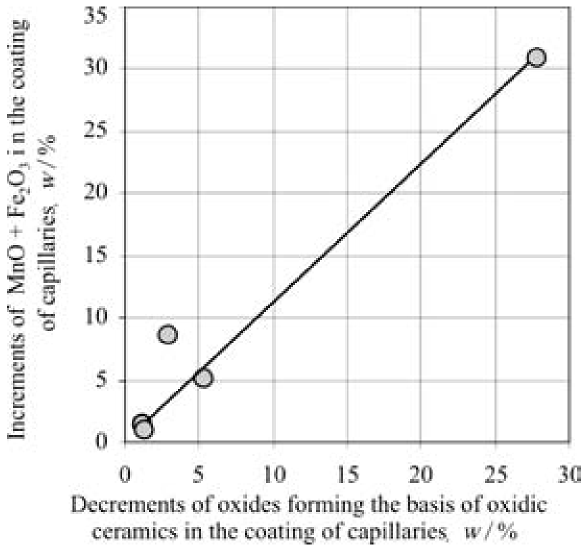

Figure 3: Relation between the decrements and increments of the oxides in the coating of the filter capillaries

Slika 3: Razmerje med zmanjšanjem vsebnosti enih in povečanjem vsebnosti drugih oksidov v oblogi v kapilarah filtrov

types of filter compensated by an increment of the sum of the less-stable manganese and iron oxides, formed with the re-oxidation of the filtered molten steel.

The relationship between the sum of the decrements and increments in the coating can also be expressed analytically with the diagram in **Figure 3**, which corresponds to the straight-line equation

(Increment of MnO + Fe_2O_3) = 3.97 + 0.606*(sum of the decrements in the composition of the oxides of the basis of filter ceramics), (1)

with a correlation coefficient of $r = 0.9069$, while the critical value of the same quantity for $\nu = 5 - 2 = 3$ degrees of freedom has the confidence level $\alpha = 0.05$ and $r_{krit} = 0.8783$.

The obtained results of the analyses show that the decrement of the sum of the oxides of the basic ceramics is replaced by the increment (in fact with the sum) of the oxide MnO and the iron oxides (Fe_2O_3) in the coating of the capillaries of individual filters. This observation is related to the physical-chemical reactions of re-oxidation processes during the filtration that should be considered during the steel filtration.

3 METALLURGICAL CLEANLINESS OF THE FILTERED STEEL

The results of the assessment of the metallurgical cleanliness of the molten steel filtered with the checked filters A to E are summarised in **Table 2**. The chemical composition of the non-filtered steel was determined from a sample taken above the filter, while the chemical composition of the filtered steel was determined from a sample taken from the casting below the filter.

The table also gives an efficiency of the filtration of the individual filters. It is obvious from the data that the filtration efficiency is different for elements that form oxides – i.e., calcium, aluminium and oxygen – and for elements that form nitrides and sulphides – i.e., nitrogen and sulphur – as shown in **Figure 4**. The filtration efficiency for elements forming oxides in steel is, on average, i.e., without consideration of the type of ceramic filter (for all types of filter), approximately four times higher than for elements forming in steel nitride or sulphide inclusions.

The symbols in **Figure 4** mean the following: η (Ca_Σ), η (Al_Σ), η (O_Σ) – average efficiencies of the whole series of five filters for the elements forming oxides, and η (N_Σ) and η (S) – average efficiencies of the

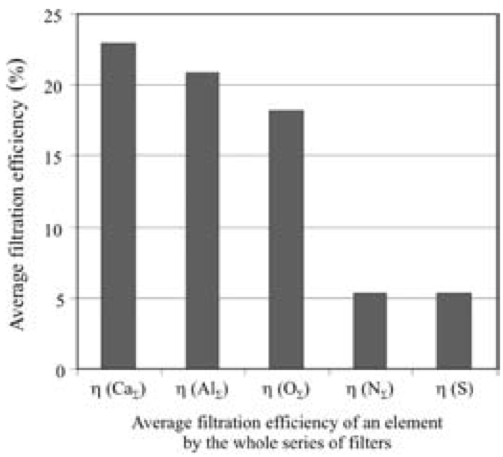

Figure 4: Filtration efficiency for the elements Ca, Al, O, N, S

Slika 4: Povprečna učinkovitost za elemente Ca, Al, O, N in S. Simboli η (Ca_Z) η (Al_Z), η (O_Z) – povprečje učinkovitosti vseh filtrov za elemente, ki tvorijo okside; η (N_Z) in η (S) – povprečje vseh filtrov za elemente, ki tvorijo sulfide in nitride.

Table 2: Metallurgical cleanliness of steel – chemical composition of steel prior to filtration and after filtration with the checked five filters *w*/% and the filtration efficiency η/%
Tabela 2: Metalurška čistost jekla; kemična sestava jekla pred filtriranjem in po njem za vse preizkušane filtre *w*/% in učinkovitost filtriranja η/%

Element	Non-filtered	After filtration of molten steel by the given type of filter				
		A	B	C	D	E
S	0.045	0.042	0.044	0.040	0.043	0.044
Al_{Σ}	0.189	0.163	0.128	0.164	0.134	0.159
O_{Σ}	0.0278	0.0256	0.0240	0.0122	0.0257	0.0250
N_{Σ}	0.0189	0.0184	0.0181	0.0168	0.0181	0.0180
Ca_{Σ}	0.0028	0.0023	0.0021	0.0023	0.0023	0.0018
Efficiency η		A	B	C	D	E
η (S)	–	6.7	2.2	11.1	4.4	2.2
η (Al_{Σ})	–	13.8	32.3	13.2	29.1	15.9
η (O_{Σ})	–	7.9	9.1	56.1	7.6	10.1
η (N_{Σ})	–	2.6	4.2	11.1	4.2	4.8
η (Ca_{Σ}),	–	17.9	25.0	17.9	17.9	35.7
$\eta_{(\varnothing)}$: x	–	9.8	14.6	21.9	12.6	13.7
s_x	–	6.1	13.4	19.3	10.8	13.4

whole series of five filters for the elements forming nitrides and sulphides.

Notes: filtration efficiency

$$\eta = \frac{w(x_{\text{non-filtered}}) - w(x_{\text{filtered}})}{w(x_{\text{non-filtered}})}$$

symbol X_c means total content of the element in steel; x is the arithmetic mean; and s_x is the standard deviation.

The average filtration efficiency also depends on the type of ceramic filter (see **Table 1**) and it is different for each filter. The difference between the highest filtration efficiency of the filter C – $MgO \cdot Al_2O_3$ and lowest filtration efficiency of the filter A – $TiO_2 \cdot ZrO_2$, is more than double. The relation between the filtration efficiency of individual types of ceramic filters is shown in **Figure 5**. It is apparent from this figure that the filtration efficiency of the individual types of filters decreases in the given series of filters in the order C, B, E, D, A.

4 METALLOGRAPHIC CLEANLINESS OF THE FILTERED STEEL

The assessment of the metallographic cleanliness of the filtered steel in terms of the quantity of the oxide and sulphide inclusions was performed in accordance with the standard DIN 50 602 and according to the K0 methodology, for the filtered and non-filtered steels.

A graphical representation of the metallographic cleanliness for the individual types of filters is shown in **Figure 6** and the filtration efficiency in % for the filters as an evaluation of the micro-cleanliness according to the DIN 50 602, scale K0 I, is shown in **Figure 7**.

The assessment of the metallographic micro-cleanliness of the steel according to DIN 50602, scale K0, indicates that the micro-cleanliness of the filtered steel decreases in the order C, E, D, A, B for the filters (**Figure 6**). Also, the filter efficiency – in terms of

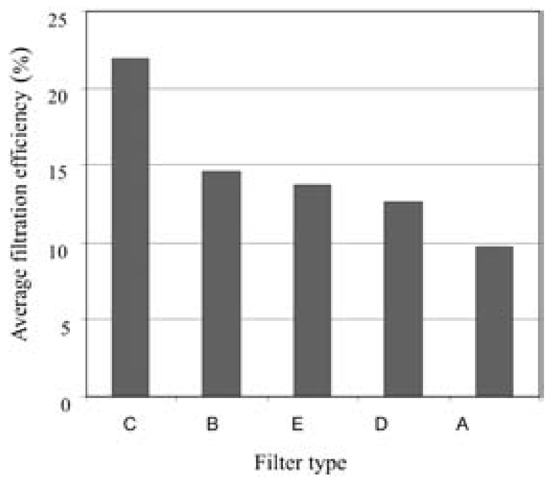

Figure 5: Filtration efficiency by type of filter
Slika 5: Učinkovitost za vsak prezkušen filter

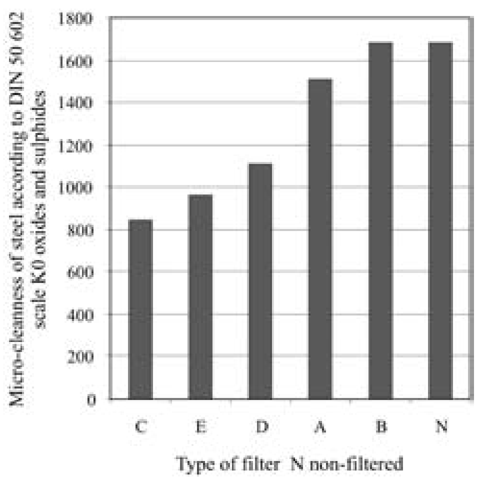

Figure 6: Micro-cleanliness of filtered steel according to DIN 50 602
Slika 6: Mikročistota filtriranega jekla po DIN 50 602

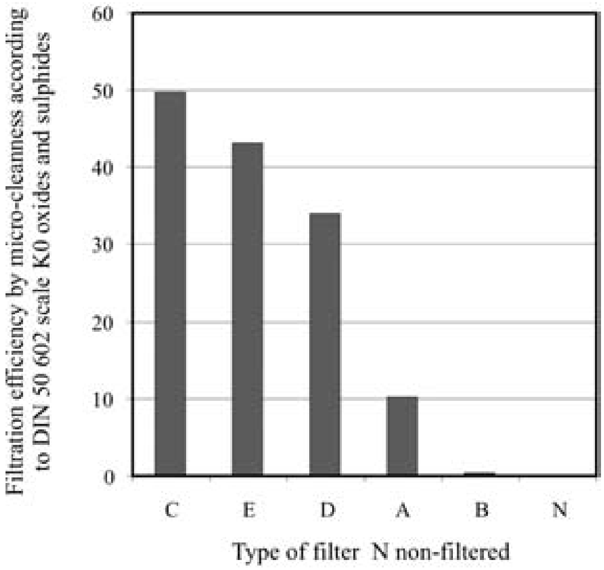

Figure 7: Filtration efficiency as micro-cleanliness according to DIN 50 602
Slika 7: Učinkovitost filtriranja po DIN 50 602

ensuring the minimum number of sulphide and oxide inclusions – decreases in the same order. Thus, the best micro-cleanliness is therefore ensured with filtration with the ceramic filter C –$MgO \cdot Al_2O_3$, and the lowest are the filter A - $TiO_2 \cdot ZrO_2$ and, particularly, the filter B – $Al_2O_3 \cdot TiO_2$, with an efficiency of almost zero.

5 CONCLUSION

The paper presents results from the filtering of molten carbon steel with five types of ceramic filters with direct holes of different primary ceramic bases. The objective of the experiments was to determine the influence of filter ceramics on the re-oxidation reactions and to evaluate the reactions between the filter ceramics and the molten steel flowing through the filter capillaries. The metallurgical and metallographic cleanliness of the steel filtered by individual types of filters was also assessed.

It was established that during the filtration of the molten steel with ceramic filters of different oxide bases of the used ceramics, the molten steel flowing through the filter reacted with the surface of the filter capillaries. The physical-chemical reactions between the molten steel and the filter ceramic form a coating on the surface of the capillaries in the coating. The chemical composition of the used ceramics is changed and it is enriched in the oxides of manganese and iron, which are formed as a result of re-oxidation processes during the filtration. The extent of the changes of the chemical composition is a function of the thermodynamic stability of the oxides forming the initial composition of the ceramic filters. The metallurgical and metallographic cleanliness of the same steel filtered through the different ceramic filters is very different.

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