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STUDY OF THE METALLURGICAL ASPECTS OF STEEL MICRO-ALLOYING BY TITAN

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The metal properties upgrading applying it's alloying with the simultaneous limitation of the impurities represents a prospective possibility of the metallurgical production further development. The interaction of the alloying substance active element with oxygen in metal and adjacent multiphase environment occurs under the actual conditions. Present paper is oriented particularly to the thermodynamic aspects of deoxygenation by titan in process of production of micro alloyed low carbon steel in two plants (oxygen converter 1-OC1 and 2-OC2) with the different effect of micro-alloy exploitation. Analysis of the effect of the metallurgical factors on the titan smelting loss in micro-alloyed steel production points at the need to master the metal preparation for the alloying and especially has got the decisive effect upon the oxidizing ability and rate of the slag phase availability. When comparing the micro-alloying matter yield among the individual production units, disclosed have been better results obtained in plant OC 2. Confirmed has been the effect of the slag amount (average amount of 7,3 t at OC 1 and 5,83 t at OC 2) and its quality during the steel tapping as one among the most significant factors affecting the alloying process and which also represent its oxidizing potential.

Key words: *steel, micro-alloying by titan, deoxygenation ability, role of slag, metal smelting loss*

Studij mikrolegiranja čelika s metalurškog stajališta. Povećanje svojstava metala primjenom legiranja uz istodobno ograničenje nečistoća predstavlja mogući daljnji razvoj metalurške proizvodnje. U stvarnim uvjetima proizvodnje dolazi do interakcije legirajućih aktivnih elemenata s kisikom u metalu i okružujućom višefaznom okolinom. Ovaj je rad usmjeren na pojedinačna termodinamička stajališta dezoksidacije titanom tijekom proizvodnje mikrolegiranog niskougljičnog čelika u dvama kisikovim konvertorskim postrojenjima (OC1 i OC2) s različitim utjecajem iskorištenja mikrolegiranja. Analiza utjecaja metalurških čimbenika na gubitak titana pri proizvodnji mikrolegiranog čelika ima presudan utjecaj na oksidativnu sposobnost i korisnost troske. Usporedba iskorištenja mikrolegirajuće tvari kod pojedinih proizvodnih jedinica je pokazala da su bolji rezultati postignuti u kisikovom konvertoru 2. Potvrđeno je da je utjecaj količine troske (prosječna količina 7,3 t za kisikov konvertor 1, a 5,83 t za kiskov konvertor 2) i njen kvalitet za vrijeme izlijevanja čelika djeluju kao najznačajniji utjecajni čimbenici na proces legiranja.

Ključne riječi: *čelik, mikrolegiranje titanom, dezoksidacijska sposobnost, uloga troske, gubitak metala pretaljivanjem*

INTRODUCTION

The metal properties upgrading applying its alloying with the simultaneous limitation of the impurities represents one of the most prospective possibilities of the further increase of the metallurgical production technical and economical effectiveness.

The interaction between the oxygen from metal and the added elements occurs under the actual conditions and consequently the non-metallic phase is formed [1, 2]. It means that depending upon the oxygen content and its momentaneous activity, the active element is differently reacting from the point of its metallurgical exploitation. Under the condition of high over balance activities of oxygen, the element will act as deoxygenating agent, i. e. there will be rather significant beneficial smelting loss of the active element depending on its deoxygenating ability under given conditions. Under the condition of lower oxygen activity under the thermodynamic equilibrium of the system Fe-O-R the element will be prevailingly exploited in the form of the alloying matter [3].

It is obvious that the situation will be far more complex if more components will react under the actual conditions.

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Deoxygenation ability of the element will be also changed with the presence of other components in the metallic melt, as the third, fourth and further elements act in two directions. On one hand they affect the oxygen activity and on other hand they adjust the activity coefficients not only of deoxygenating agents but also further alloying substances.

Moreover, the level of the metallurgical processes will be also directly linked with the level of the methods of their control and control of the applied raw materials. New methods of the reliable representative data acquisition on the heat chemical composition will further enable to specify the regularity of the metallurgical processes. Especially in this case it is true that accuracy and perfection of the method of obtaining the principal information determine not only our knowledge about the course of the metallurgical processes but also our possibilities of these processes control based on the latest technology.

The example of highly attractive method to estimate the immediate state of the melt is the method of direct estimation of the oxygen activity based on the cells, based on the solid electrolytes, electromotive voltage measurement. Works on this topic have underwent world-wide and also in out country for longer period and provide highly promising and applicable results. Application of the developed probes enables to estimate under the given temperature the relation between the carbon content and oxygen activity in the steel, also enables to estimate the amount of the deoxygenation elements for deoxidization, enables to prevent the steel re-oxidation and to control the efficiency of various additives in ladle [4 - 6].

The goal of the presented paper is to insect the efficiency of the steel micro-alloying by titan under the conditions of two converter plants OC1 and OC2 from the point of laboratory research results, oriented in the titan deoxygenation capacity estimation. Aluminium as a deoxygenation agent is commonly used for such melted metal adjustment.

LABORATORY EXPERIMENTS AND ANALYSIS

The present paper directs the attention particularly to the thermodynamic aspects of the deoxygenation by the element having high affinity oxygen but also to other non-metallic elements, acting most frequently in role of alloying elements, such may be titan in compliance with the most effective yield of this metal. The study exploited EMN method. The estimation of the deoxygenation ability of the above element was realized in Tammann resistance furnace with the charge of the pentacarbonyl iron of V3 class (99,98 % Fe) under the protective atmosphere of argon. Used was the crucible made of alumina.

To estimate the titan deoxygenation ability used was the solid electrolyte of VOSTIO 10 type produced from alumina with 10 % $Zr0_2$ and 1 % of TiO_2. As the potential indicating sensors used were the tungsten wires [6].

The reference oxygen - carbon (graphite) electrode was prepared by ramming the spectrally clean powder graphite. The corresponding activity of oxygen within the considered temperature range was 0,00024 +/– 4×10^{-5} [7].

The metal melt temperature was measured by WRe 5/20 thermocouple.

The samples were taken by the metal suction into the ceramic tube from the immediate vicinity of the solid electrolyte. Then the samples were immediately quenched in water. The precondition for the samples taking was the temperature and EMN stabilization.

To calculate the oxygen activity applied was the formula

$$E = 0,099 t_i \cdot T \log \frac{a'_O}{a''_O} \approx 0,1 t_i \cdot T \log \frac{a'_O}{a''_O} \tag{1}$$

where:

a'_O - oxygen activity in the observed melt,
a''_O - activity of the reference electrode,
t_i - ration of the ion conductivity of the solid electrolyte.

Obtained sets of the oxygen activity and balance concentration of the active element were processed using the least squares method.

With the objective to specify the titan deoxygenation characteristics realized have been nine heats in corundum (oxal) crucible using the titan of cleanness of 99,7 %, class VT 1-0 in balance concentrations up to 6,88 % within the temperature interval 1843 - 1923 K.

Determination of the region of the equilibrium oxydic phase existence within the reaction system Fe-O-Ti was realized based on the published literature data and the regression analysis of the experimental values set (%Ti) and $a_{[O]}$ with the condition that the equilibrium with Ti_3O_5 may be considered up to 0,17 % Ti and the balance with Ti_2O_3 for the higher contents [8].

Based on the measured values of oxygen activity in the system Fe-O-Ti, estimated was the relation for the equilibrium constant deoxygenation by titan.

Within the range of 0,003 - 0,17 % Ti

$$\log K_{Ti_3O_5} = -\frac{91309}{T} + 32,527, \tag{2}$$

and within the region 0,30 - 6,88 % Ti

$$\log K_{Ti_2O_3} = -\frac{50946}{T} + 18,543. \tag{3}$$

The comparison of the equilibrium constant value pre the temperature 1973 K, $K_{Ti_2O_3} = 2,203 \times 10^{-9}$ with the data from [9, 10] $8,16\times10^{-8}$ shows the rather good agreement, noteworthy for rather high scattering of other data.

The temperature dependant behavior of the interaction coefficient between titan and oxygen is defined by the following formulas:
- in the region of equilibrium with Ti_3O_5

$$\log\left(-e_{O}^{Ti}\right)_{Ti_3O_5} = \frac{7829}{T} - 4,597, \qquad (4)$$

- in the region of equilibrium with Ti_2O_3

$$\log\left(-e_{O}^{Ti}\right)_{Ti_2O_3} = \frac{7302}{T} - 4,398. \qquad (5)$$

As this is an element with the strong deoxygenation effect, to prepare the metal for micro - alloying it is necessary

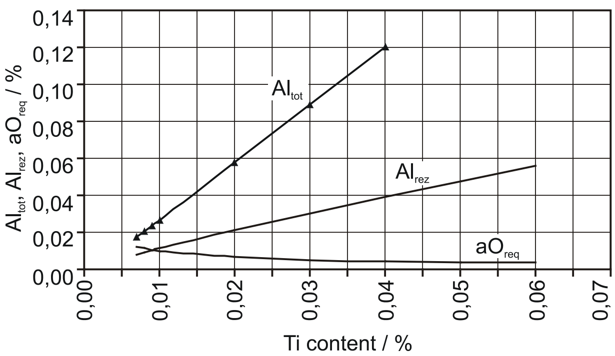

Figure1. **Relation between the oxygen required activity, residual and total aluminium as depending on the Ti content at the temperature of 1873 K / Al_{tot}, Al_{res}, Al_{req} /**
Slika 1. **Odnos između traženog aktiviteta kisika, zaostalog i ukupnog aluminija ovisno o sadržaju titana kod temperature 1873 K / Al_{tot}, Al_{res}, Al_{req} /**

to use the strong deoxygenation agent as aluminium [8, 11]. To estimate the conditions for alloying and deoxygenation, used may be formulas, Figure 1.:

$$a_{[O]} = 10e^{\log \frac{K_{Me_mO_n}}{n}} \times [\%Me]^{-\frac{m}{n}}, \qquad (6)$$

$$[\%Al]_{rez} = 0,70514 \times [\%Ti]^{0,9}. \qquad (7)$$

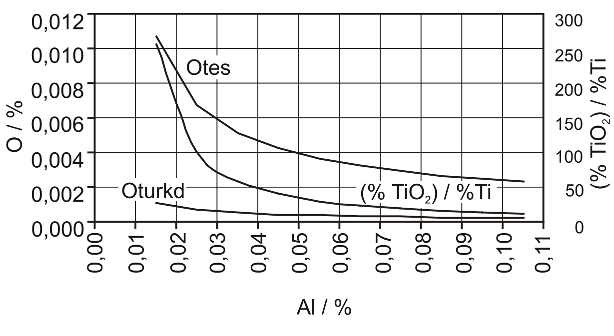

Figure 2. **Relation of the oxygen equilibrium content and titan smelting loss on the Al content**
Slika 2. **Odnos ravnotežnog sadržaja kisika i gubitka titana pretaljivanjem o sadržaju aluminija**

As the information related to the deoxygenation ability of aluminium are in broad interval of values, Figure 2. provides the comparison with the data of Turkdogan [12, 13] simultaneously with the impact on the equilibrium of metallic titan and its oxide.

Figures 1. and 2. illustrate the conditions of the metal oxidation and limits of the safe steel alloying by titan in metallic aluminium preparation.

PLANT EXPERIMENTS AND DISCUSSION

The alloying is one of the possibilities for high quality steel acquisition. Their act actively on the steel cleanness, grain size, composition and morphology of the residual phases and in such a manner affects the entire spectrum of its technological and yield properties.

The practical implementation of the alloying is a complex problem as this is to consider multiply and sometimes even contradictory aspects as:
- specified composition,
- composition of the alloying additives,
- affinity of elements as dependent on the concentration and temperature,
- content of gases and non-metallic inclusions in steel,
- related costs,
- type of the steelmaking aggregate and its parameters.

The differences in the principles of the individual alloying elements application will first of all depend on their

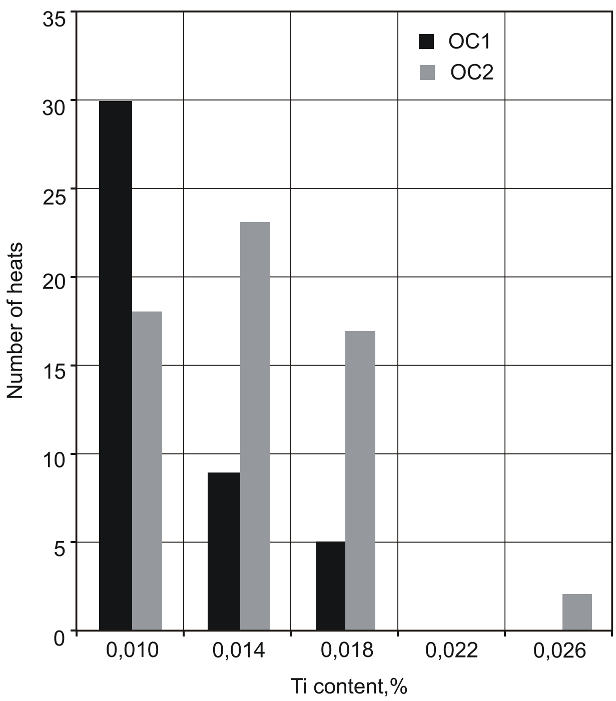

Figure 3. **Titan content obtained from heat analysis**
Slika 3. **Sadržaj titana dobiven analizom talina**

physical and chemical properties, possibly on the physical and chemical properties of the substances in form in which these are added to the melted metal or to the charge. It is known from the science of physical chemistry that the individual alloying elements differ by the value of affinity to oxygen. In case of micro-alloyed low carbon steel with low content of sulphur, phosphorus and limited content of carbon according to DIN EN 10149, they achieve in two plants the titan contents as shown in Figures 3. and 4.

The titan yield in plants OC1 and OC 2 is shown in Figure 4.

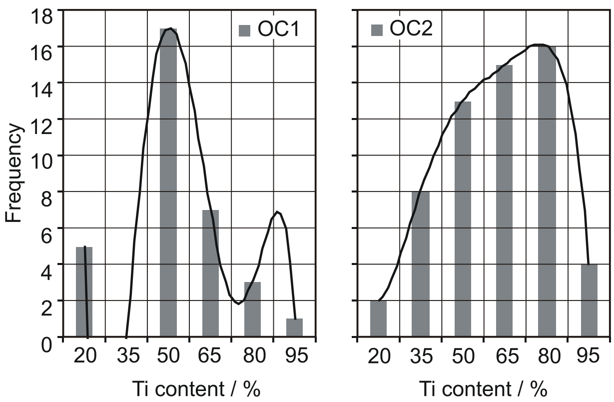

Figure 4. **Titan yield of the alloying agent**
Slika 4. **Iskorištenje titana kao legirajućeg elementa kod kisiko-**

Along with the physical and chemical properties of the alloying agent, significant effect on its yield show several technological factors of the steel production. As the previous two figures show, even two plants in the same steelwork achieve rather different level of yield.

Table 1. gives for comparison several selected parameters of production.

Table 1. **Comparison of the production parameters**
Tablica 1. **Usporedba proizvodnih parametara**

	$Ti_{released}$ / %		$Al_{released}$ / %		$Yield_{liquid\ steel}$ / %	
	OC 1	OC 2	OC 1	OC 2	OC 1	OC 2
Min.	0,0010	0,0010	0,024	0,025	76,80	83,9
Max.	0,0180	0,0250	0,053	0,046	95,90	93,2
Mean	0,0079	0,0122	0,035	0,036	89,05	89,9
	FeTi per ton / kg		Weight of slag / t		Fe_{tot} / t	
	OC 1	OC 2	OC 1	OC 2	OC 1	OC 2
Min.	0,08	0,16	2,20	1,04	0,35	0,15
Max.	0,57	0,77	14,9	14,3	4,64	3,72
Mean	0,35	0,36	7,30	5,83	1,52	1,17

Figures 5. and 6. shows relations of the obtained titan content and the residual and total aluminium in the different plants.

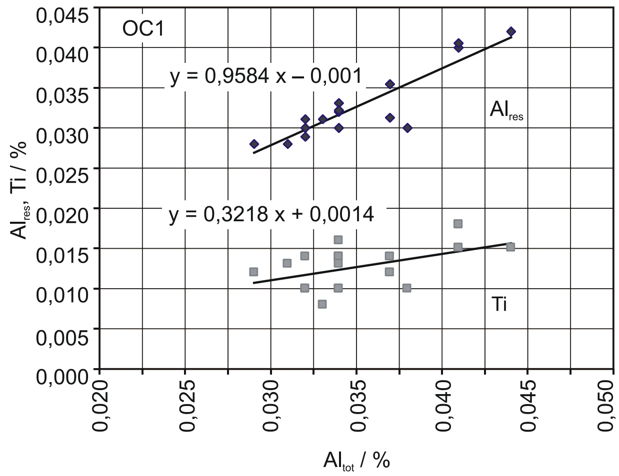

Figure 5. **Relation between titan content and Al_{res} on Al_{tot} in plant OC 1**
Slika 5. **Odnos između sadržaja titana i zaostalog aluminija o ukupnom aluminiju za kisikov konvertor 1**

The philosophy of the steel processing is obvious from the presented evidence, nest the steel preparation for alloying as well as the assurance of alloying by titan at the individual plants. The metal processing in the ladle is embarrassed by the amount and properties of the slag which enters into it in

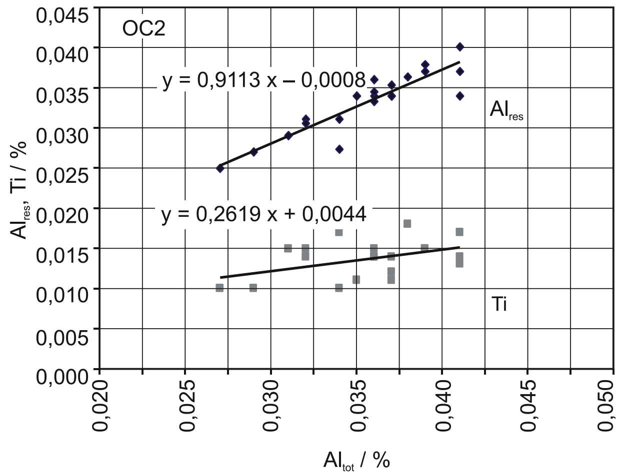

Figure 6. **Relation between titan content and Al_{res} on Al_{tot} in plant OC 2**
Slika 6. **Odnos između sadržaja titana i zaostalog aluminija o ukupnom aluminiju za kisikov konvertor 2**

course of tapping. Present components of slag and the lining as well enter into the interaction with titan in the melt. Under the above conditions the titan yield varies significantly. Though the oxygen availability for these reactions, which is present in form of iron oxides, is dominant, even further oxides may participate in the above oxy-reduction processes, particularly those of manganese and silicon.

The values of the micro alloying agent loss depending on the aluminum content are shown in Figure 7.

Simultaneous activities of the liquid metal with slag melt influence along with the thermodynamic characteristics also the kinetic factors. The high temperature, time and method of interaction in case of ladle metallurgy when created are favorable conditions for the mass transfer, may be the significant variable controlling the alloying agents loss by smelting.

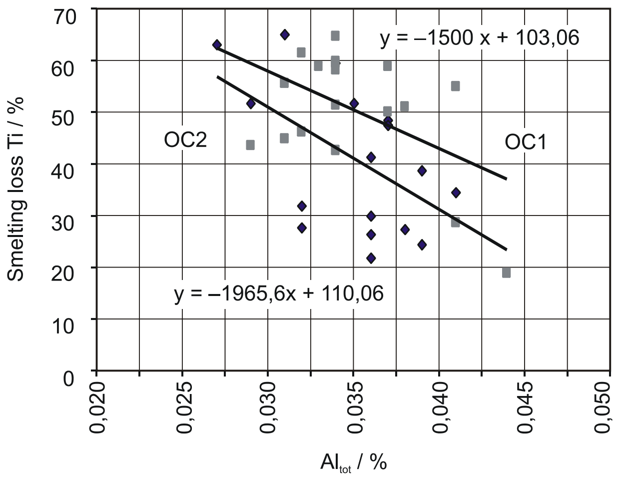

Figure 7. **Relation between the titan smelting loss in alloying and aluminium content in metal**

Slika 7. **Odnos između gubitka titana pretaljivanjem tijekom legiranja i sadržaja aluminija u metalu**

Though the metal preparation for the steel alloying by titan along with aluminium application influences the alloying agent yield, when comparing the plants OC1 and OC2, we can see another significant effect - particularly that of slag amount and its composition, Table 1. and Table 2.

Table 2. **Converter slag analysis**

Tablica 2. **Analiza konvertorske troske**

	Converter slag analysis / %					
	Fe_{tot}		MnO		SiO_2	
	OC 1	OC 2	OC 1	OC 2	OC 1	OC 2
Min.	15,97	14,26	2,80	2,70	4,65	6,56
Max.	31,13	25,99	4,91	5,25	14,98	15,52
Mean	20,80	20,05	3,81	3,78	10,09	10,80
	Al_2O_3		CaO		MgO	
	OC 1	OC 2	OC 1	OC 2	OC 1	OC 2
Min.	0,34	0,51	36,38	40,21	4,65	5,20
Max.	1,28	1,20	53,90	53,14	9,52	12,32
Mean	0,75	0,81	46,75	46,33	6,80	7,69

The amount and composition of the present slag, as one of the technology factor influencing the steel alloying process, participate significantly in the alloying substance yield along with its oxidation. For example:

$$(SiO_2)+[Ti]=[Si]+(TiO_2), \tag{8}$$

$$\log[Ti]=\log K_{Ti}-\log K_{Si}+\log\frac{[Si]}{a_{SiO_2}}+\log a_{TiO_2}. \tag{9}$$

The principal characteristics of the slag composition in both plants are presented in Table 2. From the used data obvious is the difference in the slag amount and degree of its oxidation in the individual plants.

$$Fe_s+[O]=(FeO), \tag{10}$$

$$\log K_{[O]}=\log\frac{a_{(FeO)}}{a_{[O]}}=\frac{6150}{T}-2,604, \tag{11}$$

$$\log[O]=-\log K+\log a_{(FeO)}-\log f_{[O]}. \tag{12}$$

The values of the difference between the balanced metal oxidization by such slag and activity of the oxygen diluted in metal as depending on the present titan content are given in Figure 8.

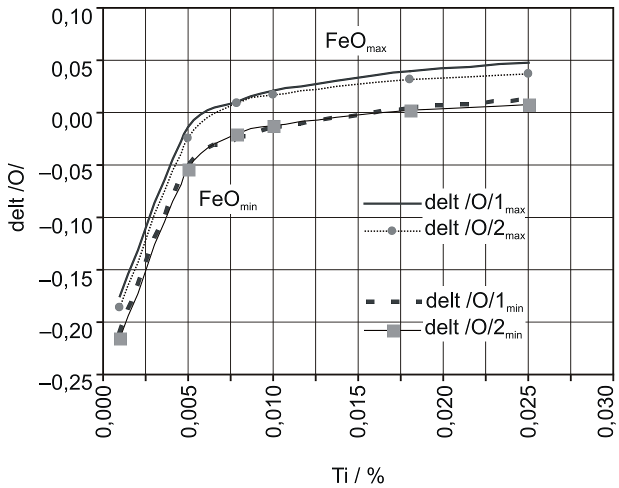

Figure 8. **Relation between the oxidizing potential of the slag and titan content**

Slika 8. **Odnos između oksidacijskog potencijala troske i sadržaja titana**

The metal and slag oxidation control, slag free tap, balanced and suitably reproducible preparation of the melt prior its micro alloying, suitable system of alloying substance addition, namely those with higher affinity to oxygen and elimination of the secondary interactions with the slag and lining with higher potential of oxygen, with enable to assume and preserve the required level of the alloying agent in steel.

The depth of the necessary metal deoxygenation may be specified based on the results of the combined laboratory and in plant research of the titan behaviour under the actual conditions of the steel production, as well as the slag amount a composition and namely of its oxidation ability.

CONCLUSION

The present metallurgy s able to utilize effectively the tools of the chemical thermodynamics and chemical kinetics for creating the requested properties of the metals when exploited are the means of the steel ladle metallurgy. Analysis of the metallurgical factors effect upon the titan loss by smelting in micro - alloyed steels production points at the need to master the metal preparation for the alloying and particularly at the decisive effect of the oxidizing ability and degree of availability of the slag phase.

When assessing the micro - alloying agents yield among the individual production units, observed have been better results at the plant OC2. As one of the most significant factor influencing the alloying process, confirmed has been the effect of the slag amount and quality (average amount of 7,3 t at OC 1 and 5,83 t at OC 2) in steel tapping, representing its oxidizing potential.

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