

ALUMINIUM PROTECTIVE COATINGS PRODUCED ON CREEP-RESISTING STEEL DIRECTLY IN A CASTING MOULD

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The structure of coatings and their ability to protect the castings made of G-X25NiCrSi 36-17 (DIN 17006) cast steel against carburization have been described. Al-Cu and Al-Si protective coatings, produced directly in a casting mould, have a considerable thickness (400 - 2000 μm), and complex multiphase structure. Its main structural constituents are: $\gamma(\text{Fe, Ni, Cr})$, $\alpha(\text{Fe, Ni, Cr})$, $\beta\text{Al}(\text{Ni, Fe})$, carbides M_{23}C_6 and M_7C_3 . In Al-Si ferritic coatings are also present: $\gamma(\text{Ni, Fe})$, $\alpha(\text{Fe, Al, Ni, Cr})$ and $(\text{Cr, Si})_3\text{Ni}_2\text{Si}$. Carburisation changes substantially the structure of coatings, what results in an increase of the amount of $\gamma(\text{Fe, Ni, Cr})$ or $\gamma(\text{Ni, Fe})$ and carbides, and a decrease of the amount of $\alpha(\text{Fe, Ni, Cr})$ and $\beta\text{Al}(\text{Ni, Fe})$. Apart from above mentioned changes, the investigated coatings reduce the carbon diffusion by 20 - 65 % Al-Cu, about 55 % Al-Si (austenitic), and 75 % Al-Si (ferritic), so they can provide a temporary protection against high-temperature corrosion.

Key words: protective coatings, high-temperature corrosion, resistance against carburization

Zaštitna aluminijska prevlaka izvedena izravno u ljevačkom kalupu na čeliku otpornom prema puzanju.

U radu je opisana struktura prevlaka i njihova sposobnost lijevanja od G-X25NiCrSi 36-17 (DIN 17006) u svrhu zaštite protiv naugljičavanja. Zaštitne prevlake Al-Cu i Al-Si, napravljene izravno u ljevačkom kalupu, imaju znatnu debljinu (400 - 2000 μm) i složenu multifaznu strukturu. Glavni strukturni element su: $\gamma(\text{Fe, Ni, Cr})$, $\alpha(\text{Fe, Ni, Cr})$, $\beta\text{Al}(\text{Ni, Fe})$, karbidi M_{23}C_6 i M_7C_3 . U feritnim prevlakama Al-Si prisutni su i: $\gamma(\text{Ni, Fe})$, $\alpha(\text{Fe, Al, Ni, Cr})$ i $(\text{Cr, Si})_3\text{Ni}_2\text{Si}$. Naugljičavanje mijenja suštinu strukture prevlaka, a to dovodi do povećanja količine $\gamma(\text{Fe, Ni, Cr})$ ili $\gamma(\text{Ni, Fe})$ i karbida, a smanjuje količinu $\alpha(\text{Fe, Ni, Cr})$ i $\beta\text{Al}(\text{Ni, Fe})$. Neovisno o gore spomenutim promjenama prevlake smanjuju difuziju ugljika za 20-60 % Al-Cu, oko 55 % Al-Si (austenitni) i 75 % Al-Si (feritni) pa mogu osigurati privremenu zaštitu protiv korozije na visokoj temperaturi.

Ključne riječi: zaštitne prevlake, visoko temperaturna korozija, otpornost protiv naugljičavanja

INTRODUCTION

To improve the service life of cast elements (made of creep-resisting cast steels Fe-Ni-Cr) of industrial furnaces and plants, a method of production of Al-Cu and Al-Si protective coatings directly in a casting mould was worked out [1-3]. These coatings provide a temporary protection of casting material against aggressive carburizing atmospheres present during pyrolysis of crude oil and carburization of steel parts of machines and vehicles. The authors, paid a special attention to the carburization, as during this process extremely difficult conditions prevail at being a result of rapid temperature changes during hardening, and also because the castings are put into service without previous machining [2]. The reason of taking them out of service is first of all moving from the carburized surface into the depth of the material, Figure 1.

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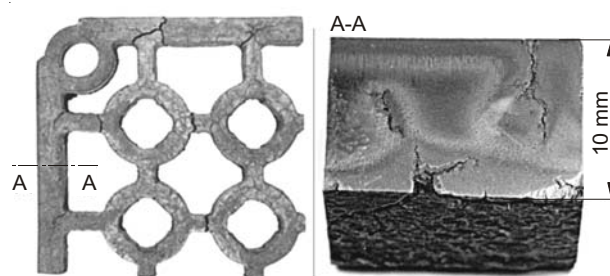


Figure 1. Casting of pallet taken out of service from carburizing furnace:

a) corner with visible surface net of cracks and cracks in joints of "T" type,
b) macrostructure of cross-section of wall with visible carburized case and cracks

Slika 1. Odljevi paleta povučeni iz rada peći za naugljičavanje:
a) kut s vidljivim površinskim pukotinama i na T-spojevima,
b) makrostruktura presjeka stijenki s vidljivim naugljičenim slojem i pukotinama

EXPERIMENTAL AND RESULTS

On the basis of previous investigations [2], it was decided that Al-Cu and Al-Si coatings would be produced by a casting method. The material for investigations was obtained by applying on the inside surface of the casting mould an activating mixture.

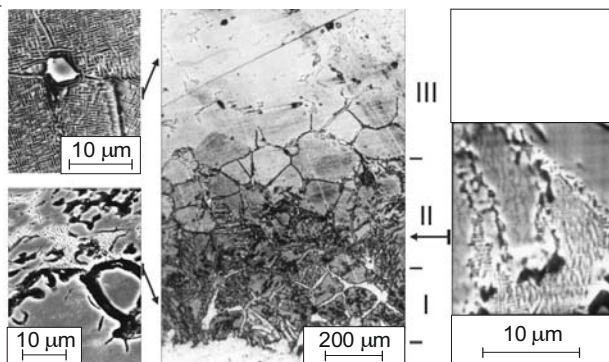


Figure 2. Microstructure of a typical coating Al-Cu obtained by a casting method
Slika 2. Mikrostruktura tipične prevlake Al-Cu dobivene metodom ljevanja

After pouring G-X25NiCrSi 36-17 cast steel and solidification, the appropriate coatings were produced. The activating mixtures consisted of:

- Al and Cu powders (granularity of 71 - 100 μm) for Al-Cu coatings,
- Al, Fe-Si 75A or Si powders (granularity as above) for Al-Si coatings,
- water glass R145, 12% in relation to powders mass,
- flux KCl+ NaCl+ NaF, 5% in relation to powders' mass.

The procedure and variable parameters of production process of Al-Cu and Al-Si coatings are described in pa-

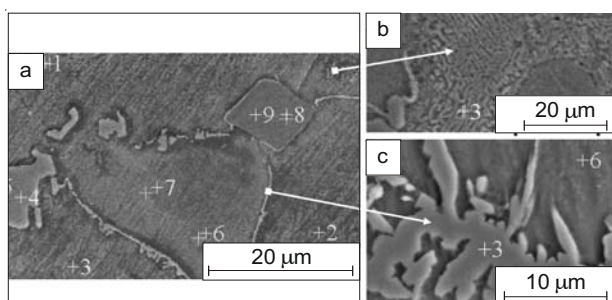


Figure 3. Structure of middle part of coating type Al-Si as-cast.
a) 1, 2, 3 - $\gamma(\text{Fe, Ni, Cr})$; 4 - $(\text{Cr, Fe})_3\text{C}_3$; 6, 7 - $\gamma(\text{Ni, Fe})$; 8, 9 - Cr_3S_2 ,
b) 3 - $\alpha(\text{Fe, Ni, Cr}) + \beta\text{Al}(\text{Ni, Fe})$,
c) 3 - $(\text{Cr, Si})_3\text{Ni}_3\text{Si}$; 6 - $\alpha(\text{Fe, Al, Ni, Cr})$
Slika 3. Struktura srednjeg dijela prevlake tipa Al-Si u ljevanom stanju.
a) 1, 2, 3 - $\gamma(\text{Fe, Ni, Cr})$; 4 - $(\text{Cr, Fe})_3\text{C}_3$; 6, 7 - $\gamma(\text{Ni, Fe})$; 8, 9 - Cr_3S_2 ,
b) 3 - $\alpha(\text{Fe, Ni, Cr}) + \beta\text{Al}(\text{Ni, Fe})$,
c) 3 - $(\text{Cr, Si})_3\text{Ni}_3\text{Si}$; 6 - $\alpha(\text{Fe, Al, Ni, Cr})$

pers [1, 3]. About 50 various tests were carried out for Al-Si and Al-Cu coatings respectively.

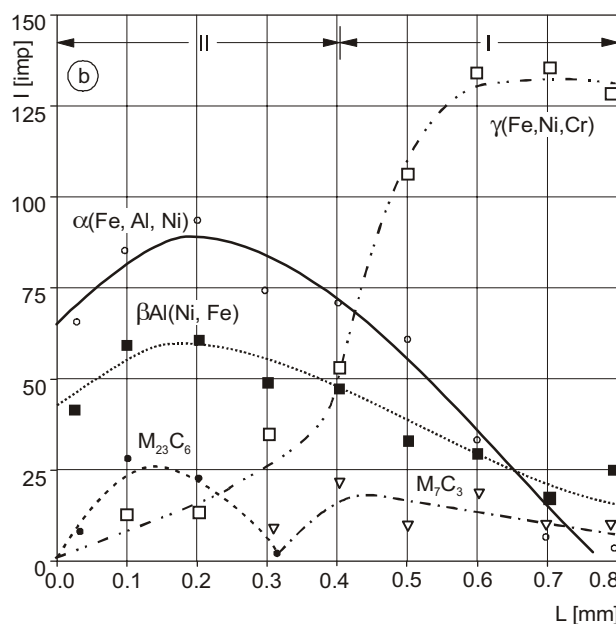
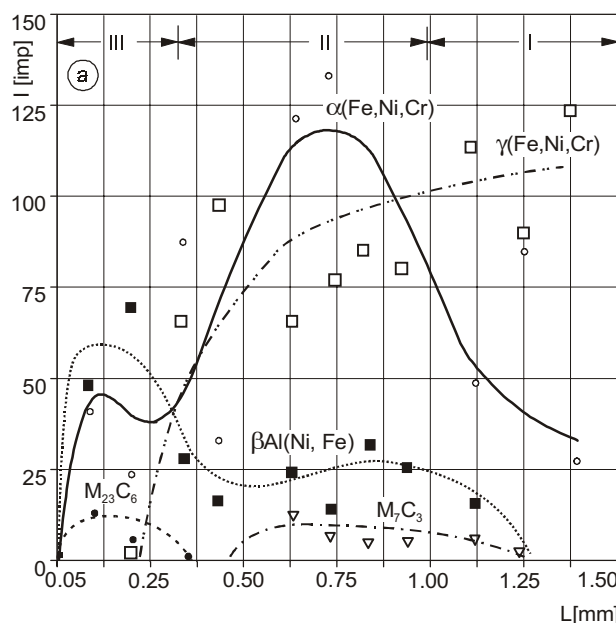


Figure 4. Distribution of main phase constituents on cross-sections of coatings as-cast:

- a) Al-Cu
 - b) Al-Si
- Slika 4. Raspored glavnih faza elemenata na presjeku prevlake u ljevanom stanju:
a) Al-Cu
b) Al-Si

The following techniques were used to examine the obtained material:

- chemical analysis to determine average contents of Al and Cu, or Al and Si in coatings,
- optical microscopy with quantitative image analysis,

- electron microscopy with X-ray microanalysis,
- X-ray diffraction.

The two latter of the above mentioned techniques enabled the identification of structural constituents present in the coatings having the thickness in the range of 400 - 2000 μm . A typical structure of Al-Cu coating as-cast is shown in Figure 2., which consists of three zones, whereas Al-Si coatings do not have a zone III. A typical picture of zone II of Al-Si coating is shown in Figure 3., in which identified structural constituents are also marked.

The diffractometric analysis was carried out on parallel microsections prepared by grinding off the successive layers. In this way, from 6 to 10 diffraction patterns were obtained for each of examined coatings. These enabled not only the identification of the phase constituents, but also (by measuring specimens after every single analysis) the attribution of the results to the strictly defined spot on the cross-section of the coating.

The diagrams in Figure 4. show the distribution of the main phase constituents of Al-Cu and Al-Si coatings. From this diagrams phase composition and the thickness of the individual zone can be read.

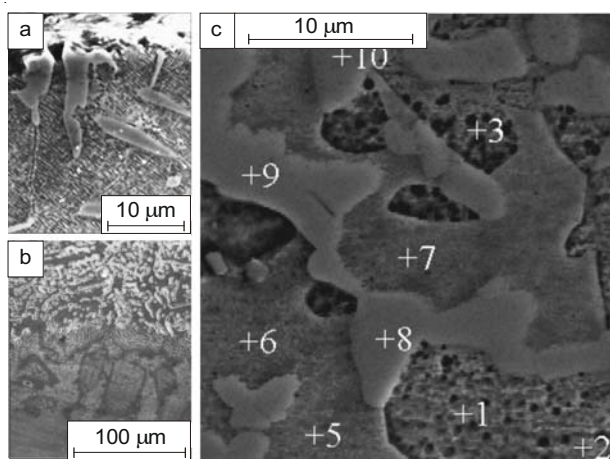


Figure 5. Structure of Al-Cu (a, b) and Al-Si (c) coatings after carburization and thermal fatigue:

- a) external zone of Al-Cu coating,
- b) internal zone of coating with visible boundary of "carburization front",
- c) central part of Al-Si coating (ferritic): 1, 2, 3 - $\gamma(\text{Fe, Ni, Cr}) + \beta' \text{Al}(\text{Ni, Fe}) + \alpha(\text{Fe, Ni, Cr})$; 5, 6, 7 - $\gamma(\text{Ni, Fe})$; 8 (Cr, Fe)₂₃C₆; 9, 10 (Cr, Fe)₇C₃

Slika 5. Struktura prevlaka Al-Cu (a, b) i (Al-Si (c) nakon procesa naugljičavanja i toplinskog zamora:

- a) eksterna zona prevlake Al-Cu,
- b) interna zona prevlake s vidljivom granicom "fronta naugljičavanja",
- c) središnji dio prevlake Al-Si (feritni); 1, 2, 3 - $\gamma(\text{Fe, Ni, Cr}) + \beta' \text{Al}(\text{Ni, Fe}) + \alpha(\text{Fe, Ni, Cr})$; 5, 6, 7 - $\gamma(\text{Ni, Fe})$; 8 (Cr, Fe)₂₃C₆; 9, 10 (Cr, Fe)₇C₃

The characteristics of the main identified phases and the measured values of the lattice parameters "a" are presented in Table 1.

It was stated that Al-Si coatings, depending on a type of Si carrier (Fe-Si or Si), can have either austenitic (Fe-Si) or ferritic (Si) structure.

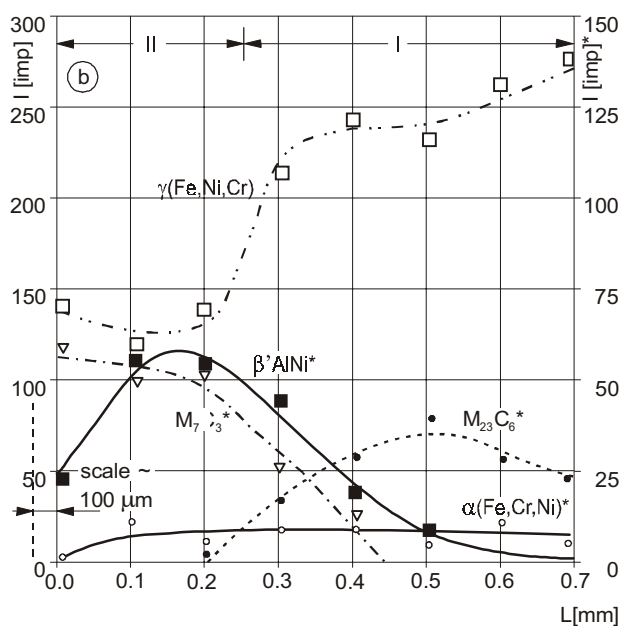
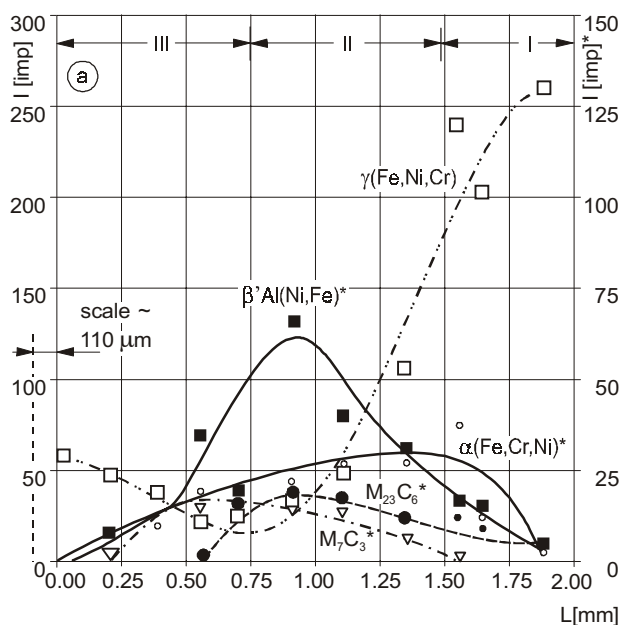


Figure 6. Distribution of main phase constituents on cross-sections of coatings after carburization and thermal fatigue:

- a) Al-Cu
- b) Al-Si

Slika 6. Raspored glavnih faza elemenata na presjeku prevlaka nakon procesa naugljičavanja i toplinskog zamora:

- a) Al-Cu
- b) Al-Si

The picture of the austenitic structure of the Al-Si coating and the distribution of phase constituents are not different from those of the ferritic one (Figure 3.). The difference lies in altered proportions of the phases α and γ , and

Table 1. Characteristics of main identified phases present in Al-Cu and Al-Si coatings, and measured values of lattice parameter 'a', obtained from analysis of 3-6 peaks for each phase..

Tablica 1. Svojstva glavnih identificiranih faza prisutnih u prevlakama Al-Cu i Al-Si i izmjerenim vrijednostima "a" parametra rešetke dobivenim iz analize 3-6 vrhova (pikova) za svaku fazu

Phase	Definition	Crystal lattice	Lattice parameter "a" x 10 ⁻¹⁰ m		Index No JCPDS
			as cast	after carb. therm. fat	
γ (Fe, Ni, Cr)	solid solution Ni, Cr and Al in Fe γ	fccA ₁	Al-Cu-3.605 Al-Si-3.599	3.604 3.586	33-0397
γ (Ni, Fe)	solid solution Fe, Al, Cr and Si in Ni	fccA ₁	Al-Si-3.604	3.588	23-0297
γ (Fe, Ni, Cr) matrix	solid solution Ni and Cr in Fe γ	fccA ₁	Al-Cu-3.588 Al-Si-3.588	3.593	[6]
α (Fe, Ni, Cr)	solid solution Ni and Cr in Fe α	bccA ₂	Al-Cu-2.873	2.877	[6]
α (Fe, Al, Ni, Cr)	solid solution Al, Ni and Cr in Fe α	bccA ₂	Al-Cu-2.869	2.865	35-1375
β Al(Ni, Fe)	intermetallic phase, disordered of AlNi type	bcc type C ₅ Cl	Al-Cu-2.869 Al-Si-2.888	- -	20-0097
β 'Al(Ni, Fe)	Superstructure	type B ₂	-	Al-Cu-2.875 Al-Si-2.865	02-1261

also in the fact that the presence of chromium sulfides was not confirmed [3].

The final identification of the structural constituents of the investigated coatings was based on the results ob-

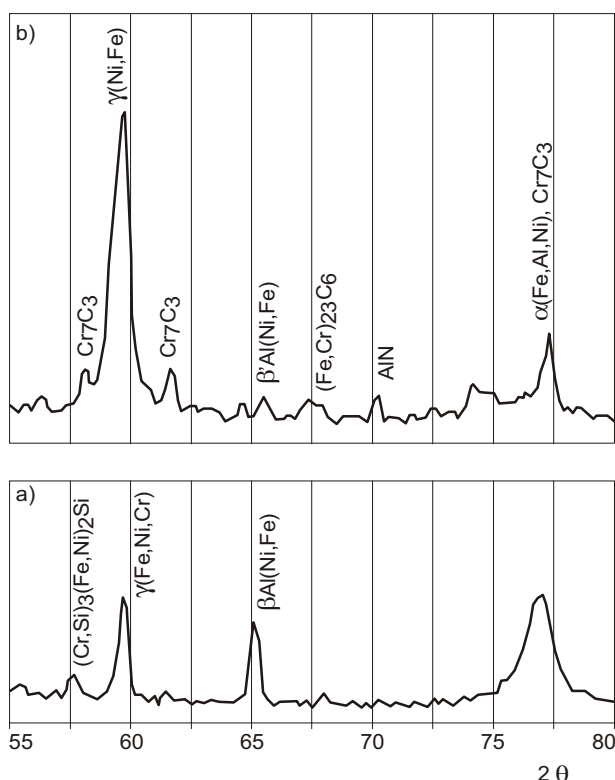


Figure 7. Fragments of diffraction patterns for Al-Si ferritic coating:

- a) for as-cast,
- b) after carburization and thermal fatigue

Slika 7. Fragmenti difrakcije uzoraka za feritnu prevlaku Al-Si: a) u ljevanom stanju, b) nakon procesa naugličavanja i toplinskog zamora

tained from diffractometric tests and local chemical analysis (X-ray micro-analyzer beam $\phi = 2$ mm). The results are shown in Table 2.

The coatings (and specimens without coatings) were carburized at the temperature 900 °C in carburizing box and then subjected to thermal shocks (900 °C/50 °C, oil). For Al-Cu and Al-Si coatings the times of carburisation were 400 h and 380 h, and the number of thermal shocks 40 and 38 respectively.

As a result of this process, a brittle scale was formed on the surface of the coatings. The thickness of the scale was about 100 mm, and its constitution was made of: NiFe₂O₄, AlFe₃C_x, FeCr₂O₄, Fe₂O₃ and AlN, what is shown in Figure 6.

Afterwards, by counting up of the amount of carbides with the use of image analyzer, the depth of carburization was determined, as this value was assumed as an initial stage of high-temperature corrosion [4]. The structure of the coatings was analyzed using the same techniques as before. Figure 5. shows the structure of the coatings after carburization and thermal fatigue. Figure 6. shows the distribution of the main phase constituents on the cross-sections of coatings, whereas the other results are presented in Tables 1. and 2.

It should be mentioned, that the pictures of the austenitic structures of Al-Si coatings, as well as their chemical composition and phase constitution, were very much alike those presented in Figure 5.c and 6.b.

To observe the changes being a result of carburization and thermal fatigue, the diffraction patterns were compared, as it is shown in Figure 7.

The results of the measurements of the carburization depth (GN), and the values of the relative depth of carburization (WGN), calculated in relation to the carburized material without coating are presented in Table 3.

Table 2. Results of chemical analysis of structural constituents of Al-Cu and Al-Si coatings and final identification of phases

Tablica 2. Rezultati kemijske analize strukturnih elemenata prevlaka Al-Cu i Al-Si i završnih identifikacijskih faza

Average chemical composition *, %-wt					Structural constituent
Ni	Fe	Cr	Cu	Al	
Al-Cu as cast					
28.5	42.4	19.0	2.7	3.8	$\gamma(\text{Fe,Ni,Cr})$
35.8	46.6	16.1	0.3	0.1	$\gamma(\text{Fe,Ni,Cr})$ matrix
29.5	40.8	19.1	1.7	1.3	$\alpha(\text{Fe,Ni,Cr})$
37.7	24.7	12.6	3.2	16.2	$\beta\text{Al}(\text{Ni,Fe})$
Al-Cu after carburisation and thermal fatigue					
22.1	61.2	6.7	3.7	3.8	$\gamma(\text{Fe,Ni,Cr})$
35.2	48.5	14.2	1.7	0.5	$\gamma(\text{Fe,Ni,Cr})$ matrix
7.1	72.1	9.4	2.4	3.2	$\alpha(\text{Fe,Ni,Cr})$
42.1	29.7	2.3	6.35	18.1	$\beta'\text{Al}(\text{Ni,Fe})$
Al-Si as cast					
				Si	
31.8	44.8	18.3	2.6	2.6	$\gamma(\text{Fe,Ni,Cr})$
49.9	33.0	5.7	4.2	7.2	$\gamma(\text{Ni,Fe})$
34.3	45.8	18.0	1.3	0.6	$\gamma(\text{Fe,Ni,Cr})$ matrix
16.1	45.2	15.4	5.4	17.3	$\alpha(\text{Fe,Al,Ni,Cr})$
41.1	32.0	10.1	2.4	14.2	$\beta\text{Al}(\text{Ni,Fe})$
Al-Si after carburisation and thermal fatigue **					
46.7	45.3	2.8	2.4	2.8	$\gamma(\text{Ni,Fe})$
34.3	46.1	17.2	1.5	0.9	$\gamma(\text{Fe,Ni,Cr})$ matrix
* average values from 6 -12 measurements. ** sizes of precipitates of other structural constituents were too tiny to accept results of microanalysis as reliable.					

Table 3. Depth of carbonization of investigated coatings
Tablica 3. Dubina naugljičavanja na istraživanim prevlakama

Type of coating	Depth of carburisation GN* [μm]	Relative depth of carburisation WGN [%]
Sample without coating	1784	100.0
Al-Cu (the worst)	1422	79.7
Al-Cu (middle)	810	45.4
Al-Cu (the best)	607	34.0
Sample without coating	1950	100.0
Al-Si (austenitic)	850	43.6
Al-Si (ferritic)	480	24.6
* average values from 6 -12 measurements		

DISCUSSION

The casting coatings reveal a specific different structure in comparison with the coatings having the same

chemical composition, but obtained by other methods [4]. that is characterized by: The more important differences lie in the following:

- they have developed intermediate zone (I, Figure 4.),
- they have diverse different structure of internal zone (II, Figure 4.),
- mixture of phases on outer surface there is mixture of phases instead of uniform layer of $\gamma\text{Al}(\text{Ni,Fe})$. (Figure 2., Figure 4.).

The main structural constituents of Al-Cu and Al-Si austenitic coatings comprise: $\gamma(\text{Fe, Ni, Cr})$, $\alpha(\text{Fe, Ni, Cr})$, $\beta\text{Al}(\text{Ni, Fe})$ and carbides M_{23}C_6 and M_7C_3 (Tables 1. and 2.).

Al-Si ferritic coatings, apart from a.m. constituents, also consist of: $\gamma(\text{Ni, Fe})$, $\alpha(\text{Fe, Al, Ni, Cr})$ and complex silicide $(\text{Cr, Si})_3\text{Ni}_2\text{Si}$ (Table 1. and Figure 3.c).

Carburization changes considerably the structure of the coating, which afterwards consists of the following phases (presented in decreasing sequence):

- Al-Cu coatings: $\gamma(\text{Fe, Ni, Cr})$, $\beta'\text{Al}(\text{Ni, Fe})$, $\alpha(\text{Fe, Ni, Cr})$, M_7C_3 , M_{23}C_6 (Table 2.),
- Al-Si ferritic coatings: $\gamma(\text{Ni, Fe})$, $\beta'\text{Al}(\text{Ni, Fe})$, $\alpha(\text{Fe, Ni, Cr})$, $\gamma(\text{Fe, Ni, Cr})$, M_7C_3 , M_{23}C_6 (Table 2. and Figure 5.c).

An double increase in the volume fraction of $\gamma(\text{Fe, Ni, Cr})$ in Al-Cu coatings, and $\gamma(\text{Ni, Fe})$ in Al-Si coatings are observed (Figure 6.a and 6.b). Moreover, an increase in the fractions of carbides M_7C_3 and M_{23}C_6 take place accompanied by a simultaneous decrease in the content of $\alpha(\text{Fe, Ni, Cr})$ and $\beta\text{Al}(\text{Ni, Fe})$, which undergoes the transformation into super structure $\beta'\text{Al}(\text{Ni, Fe})$ (Figure 7.a and 7.b). The decrease of values of the lattice parameters that are presented in Table 1. and the alterations in the chemical composition of the phases, that are shown in Table 2., indicate, that chromium, initially comprised in $\gamma(\text{Fe, Ni, Cr})$, $\alpha(\text{Fe, Ni, Cr})$ and $\beta\text{Al}(\text{Ni, Fe})$ undergoes reaction with the diffused carbon and creates carbides. The thickness of coatings and concentration gradients of particular phase constituents on cross-sections are also reduced, what can clearly be seen if the Figure 4.a and 6.a or Figure 4.b and 6.b are compared. The process taking place in the structure of coatings, as a result of carburisation and thermal fatigue are described in papers [1-3, 5].

The measured values of the carburization depth showed, that the coatings reduce the carbon diffusion into material by: 20 - 65 % Al-Cu, 55 % Al-Si (austenitic) and 75 % Al-Si (ferritic), in comparison with material unprotected by a coating. Moreover, all investigated coatings reveal a considerable resistance to thermal shocks, which positively distinguishes them from similar coatings obtained by other methods [3].

As a result of investigations, it was also found out that the structure and protective properties of coatings depend on some production parameters. The statistical models,

derived on the basis of these dependencies, allowed for working out the principles of selection of production parameters by casting method [11].

CONCLUSIONS

1. Al-Cu and Al-Si coatings produced by casting method have complex multiphase structure, and its main constituents are: $\alpha(\text{Fe, Ni, Cr})$, $\gamma(\text{Fe, Ni, Cr})$, $\beta\text{Al}(\text{Ni, Fe})$ and carbides M_7C_3 and M_{23}C_6 .
2. During carburization, combined with thermal shocks, the coatings reduce the depth of carburization by 20 - 75 % in comparison with material unprotected by a coating.
3. During carburization, on the surface of the coatings, a brittle scale is formed. The structure undergoes the complex transformations, which give in the result an increase of the amount of $\gamma(\text{Fe, Ni, Cr})$ or $\gamma(\text{Fe, Ni})$ and carbides, at the expense of $\alpha(\text{Fe, Ni, Cr})$ and $\beta\text{Al}(\text{Ni, Fe})$.

4. Al-Cu and Al-Si coatings produced by casting method can provide a temporary protection of castings made of creep-resisting cast steels against carburization.

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