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MICROSTRUCTURAL INVESTIGATION OF A COMPLEX COBALT BASED THERMAL BARRIER COATING TESTED BY QUICK THERMAL SHOCK

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Este prezentată influența testului la şoc termic rapid asupra structurii unor straturi metalice rezistente la uzare, coroziune şi eroziune la temperaturi înalte, din sistemul Co-Cr-W-C-Fe-Ni-Si-Mn, depuse pe suport din cupru. Acoperirile metalice au fost obținute prin sudare în arc electric, cu electrod nefuzibil, în atmosferă de gaz inert (TIG).

Investigările structurale ale epruvetelor din cupru cu depuneri metalice, atât netestate, cât şi testate la şoc termic rapid, au fost efectuate prin intermediul difracției de radiații X şi al microscopiei electronice cu baleiaj (SEM).

Depunerile netestate şi cele supuse testului la şoc termic rapid au fost cercetate comparativ în vederea evaluării modificărilor structurale şi de proprietăți pentru aprecierea statutului de barieră termică al aliajului utilizat ca acoperire.

The quick thermal shock test influence on the structure of some high temperature wear, corrosion and erosion resistant Co-Cr-W-C-Fe-Ni-Si-Mn metallic layers has been investigated. The coatings deposited on a copper substrate were obtained by electric arc welding, with non-fusible electrode, in inert gas atmosphere (TIG). Structural investigations of the metallic coatings on copper support samples, both non-submitted and submitted on quick thermal shock, were done by X-ray diffraction and scanning electron microscopy (SEM).

The results obtained for both types of samples were compared in order to evaluate the properties and structural changes. Tthe conclusions allowto evaluate the ability of the above mentioned alloy to act as a thermal shock barrier.

Keywords: thermal barrier layers, copper support, SEM, XRD, quick thermal shock

1. Introduction

Metallic coatings (Co-Cr-C-W-Fe-Ni-Si-Mn-Mo) deposited on copper support were tested by quick. The choice of these materials as surface layers had in view their appliccation for improving the lifetime of blast tuyere of a blast furnace [1, 2].

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The blast tuyere is a highly pure copper fitting used for air blast in the burning zone of a blast furnace. This device is severely thermally and mechanically stressed (thermal shock, piercing due to hot metal or slag, galling and wear).

In order to improve the blast tuyere reliability, it has been proposed to plate the tuyere's front zone with thermal barrier coatings, which are wear and corrosion resistant at high temperatures [3]. To this purpose, it has been chosen to test and investigate a cobalt based alloy, well known for its high temperature wear, corrosion and erosion resistance properties, in order to establish and estimate its blast tuyere protection layer's status.

The applied test was quick thermal shock, due to its best simulation of blast tuyere working conditions.

2. Materials and methods

In order to run quick thermal shock tests copper samples covered with a cobalt based complex alloy (Stellite 6) were obtained by electric arc welding in inert gas atmosphere (TIG).

The chemical composition of the alloy used for the coatings is indicated in Table 1.

Table 1

Chemical composition of the deposited layers.

Sample type	Sample	Chemical compozition of deposited layer (%)	Submitted to quick thermal shock
Metallic layer STELLITE 6	MS 10	C=1,24; Cr=30,8; Si=1,35; W=4,70; Fe=2,35; Ni=2,56; Mn=0,12; Mo=0,11; Co= balance	No
	MS 14		Yes

The coated copper samples are of a parallelepiped form, having the following dimensions:

- Height of deposited material H_d = 3...5,5 mm
- Height of the copper support H_{cs} = 9 mm
- Total height of the sample $H_t = H_{cs} + H_d$ = 12...14,5 mm

Testing method

The thermal shock consists in the apparition of mechanical stresses following to a rise or a drop of temperature.

Sample MS 30 was submitted to quick thermal shock test at 950°C, for 25 cycles. A cycle consists in heating a sample in the furnace for 5 minutes at the designed temperature followed by cooling, also for 5 minutes, in a cool air spray.

3. Results

The investigations of the structural changes induced by quick thermal shock were performed by X-ray diffraction and scanning electron microscopy.

X-ray diffraction

Figures 1 and 2 present the X-ray diffraction patterns obtained for MS 10 and MS 14 sample, respectively.

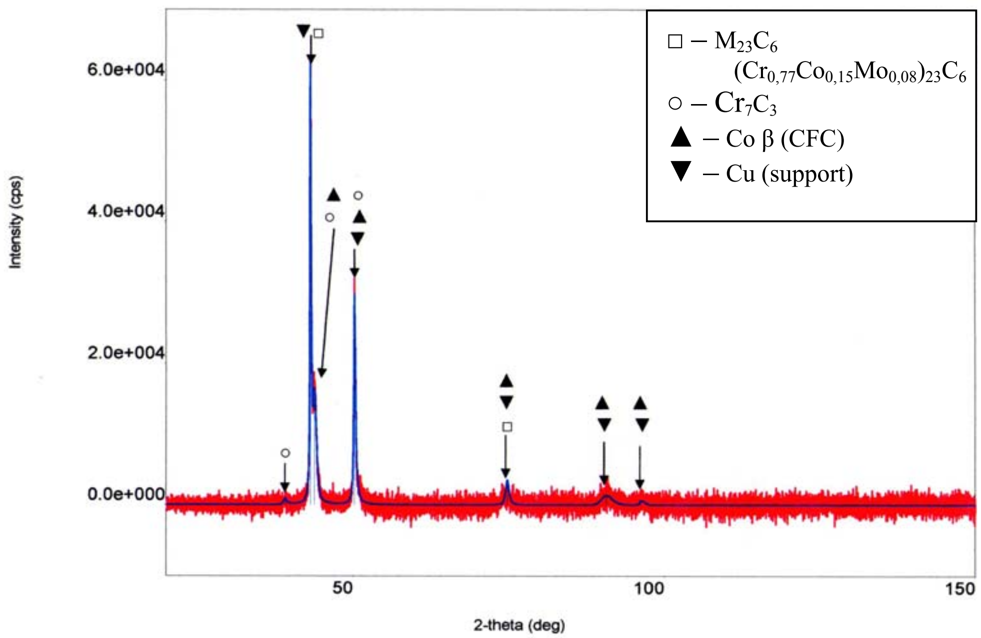


Fig. 1. X-ray diffraction pattern of the Stellite 6 coating deposited by electric arc welding (MS 10 sample)

The unit cell parameter of the phase identified Co β are presented in Table 2.

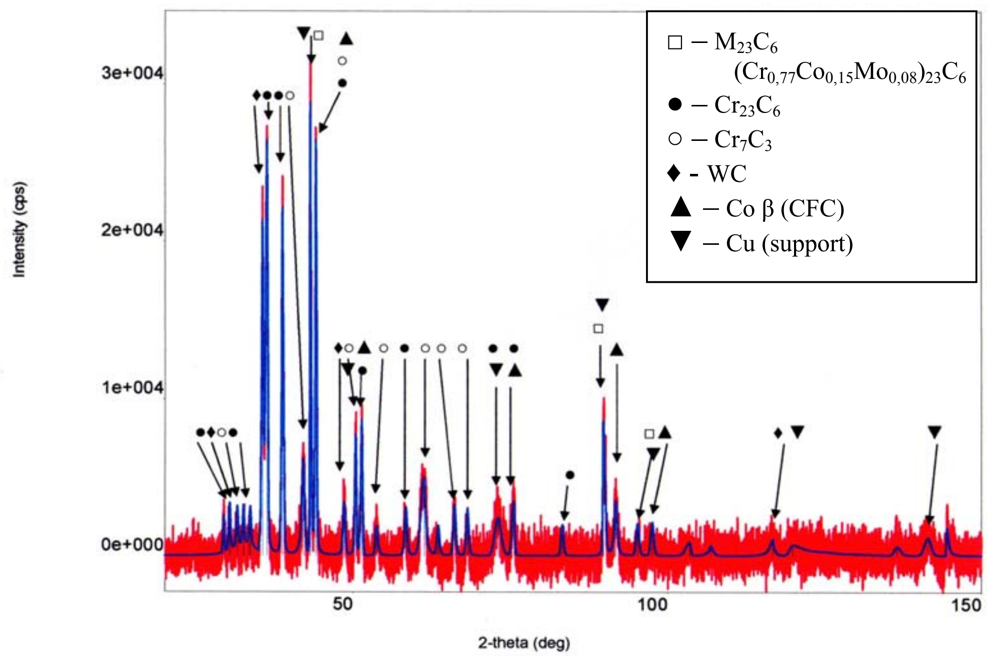


Fig. 2. X-ray diffraction pattern of the Stellite 6 coating submitted to quick thermal shock at 950° C (MS 14 sample)

Table 2.

The unit cell parameter of the Co based solid solution phase determined for MS 10 and MS 14 samples

Interplanar distance d [Å]		Unit cell parameter a [Å]	
		Calculated for each peak	Average
MS 10	d_{111}=2,065	a_1=3,5767	a_{Co}=3,5926
	d_{200}=1,813	a_2=3,6260	
	d_{220}=1,268	a_3=3,5864	
	d_{311}=1,083	a_4=3,5919	
	d_{222}=1,034	a_5=3,5819	
	d_{200}=1,786	a_2=3,5720	
	d_{220}=1,273	a_3=3,6006	
MS 14	d_{111}=2,054	a_1=3,5576	a_{Co}=3,5536
	d_{200}=1,778	a_2=3,5560	
	d_{220}=1,257	a_3=3,5553	
	d_{311}=1,072	a_4=3,5554	
	d_{222}=1,023	a_5=3,5438	

The qualitative phase analysis made by indexing the X-ray diffraction pattern in Figure 1 revealed that the Stellite 6 coating on copper support unsubmitted to quick thermal shock has a phase composition consisting of a Co based solid solution (having a face-centered cubic (FCC) crystal lattice) also containing mainly chromium carbides Cr_7C_3 and possibly $M_{23}C_6$ – type carbides $((Cr_{0,77}Co_{0,15}Mo_{0,08})_{23}C_6)$.

The increase of the carbides chromium content and the appearance of the tungsten carbide in MS 14 sample's layer is correlated with a change of the solid solution unit cell parameter from 3,5926 Å in MS 10 sample to 3,5536 Å in MS 14 sample (Table 2). As it can be observed, its value evolves towards that of pure cobalt ($a_{Co\ FCC}$ = 3,5447 Å). Thus, it seems that after quick thermal shock the solid solution undergoes a dilution process, leading to a depletion in alloying elements (tungsten and chromium). As a result, carbides having the highest chromium content ($Cr_{23}C_6$) will be found in the quick thermal shock sample.

Scanning electron examination

Figures 3 and 4 present the microstructures of the Stellite 6 layers in MS 10 and MS 14 samples.

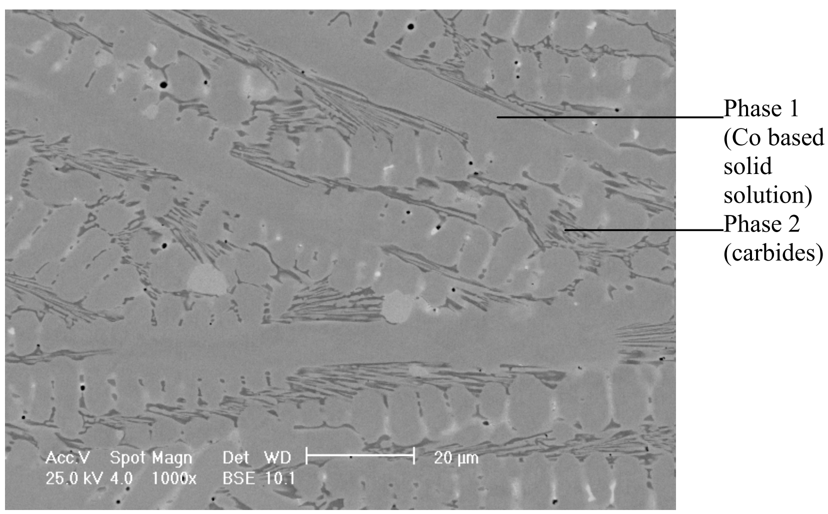


Fig. 3. SEM micrograph of the MS 10 sample's protection layer

In Figure 3 we can see in light grey the cobalt based solid solution *(phase 1)* and, in different shades of dark grey, the carbides *(phase 2)* which, according to the X-ray diffraction pattern, are of the Cr_7C_3 and $M_{23}C_6$ type. These carbides are to be found in an interdendritic eutectic along with the solid solution.

The microstructure shown in Figure 4 exhibits two types of carbides, a first one of a dark grey colour and morphologically close to *phase 2* in Figure 3, and a second one almost black, of a more compact aspect *(phase 2')*, both included in the solid solution *(phase 1)*.

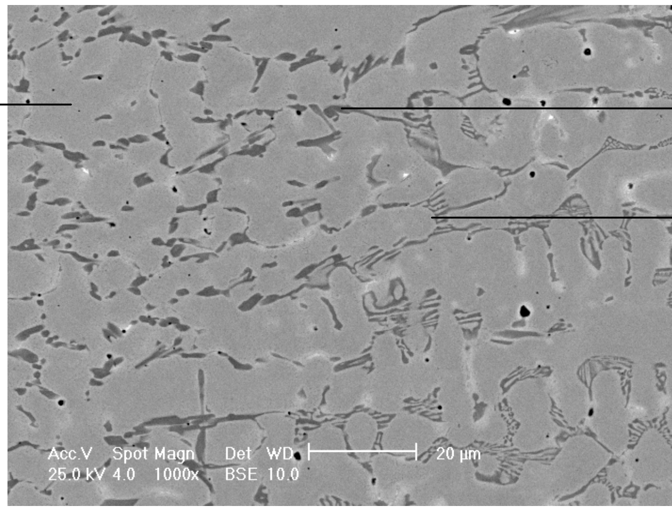


Fig. 4. SEM microstructure of the MS 14 sample's protection layer

In order to obtain further informations concerning the *phases 1, 2 and 2'*, EDS chemical compositions analyses were performed, as shown in figures 5 to 9.

Phase 1 in figure 3

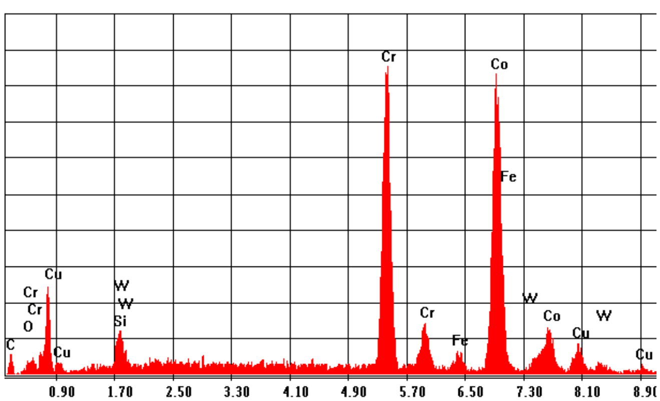
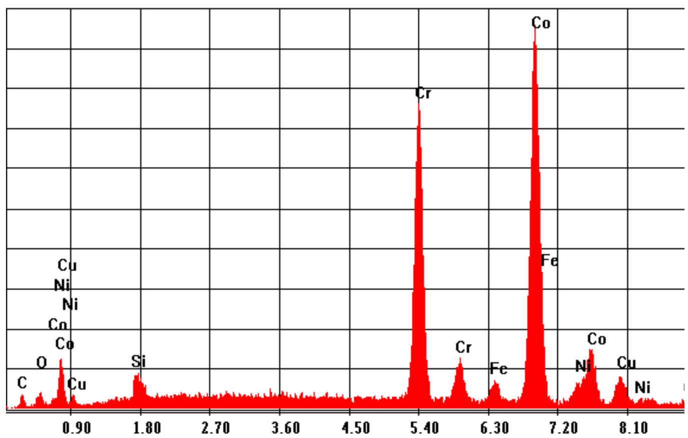


Fig. 5. a) EDS for phase 1 in Stellite 6 layer

Element	[%] weight
C K	8.3
O K	0.3
SiK	2.16
CrK	27.54
FeK	2.04
CoK	50.51
CuK	3.23
W L	5.92
Total	100

Fig. 5. b) Quantitative analysis for phase 1

Phase 1 in figure 4

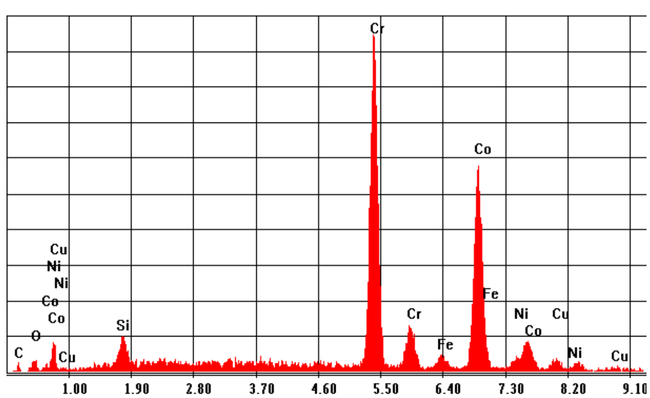


Element	[%] weight
C K	8.32
O K	1.72
SiK	2.25
CrK	22.03
FeK	2.23
CoK	54.45
NiK	3.60
CuK	5.40
Total	100.00

Fig. 6. a) EDS for phase 1 in Stellite 6 layer submitted to quick thermal shock at 950°C

Fig. 6. b) Quantitative analysis for phase 1

Phase 2 in figure 3

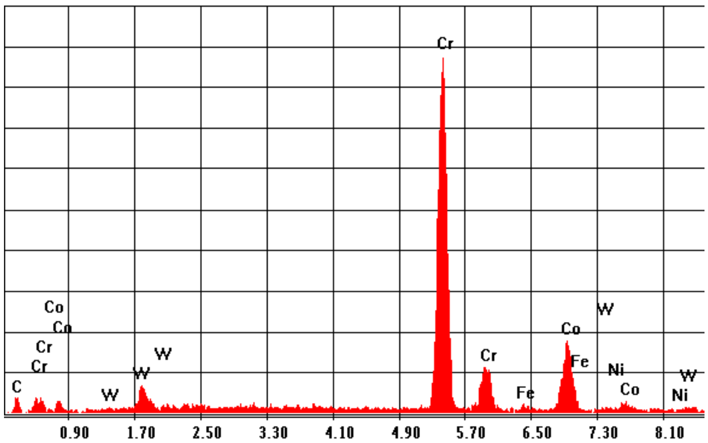


Element	[%] weight
C K	5.76
O K	0,76
SiK	3.04
CrK	40.59
FeK	2.26
CoK	39.97
NiK	4.01
CuK	3.61
Total	100.00

Fig. 7. a) EDS for phase 2 in Stellite 6 layer

Fig. 7. b) Quantitative analysis for phase 2

Phase 2 in figure 4

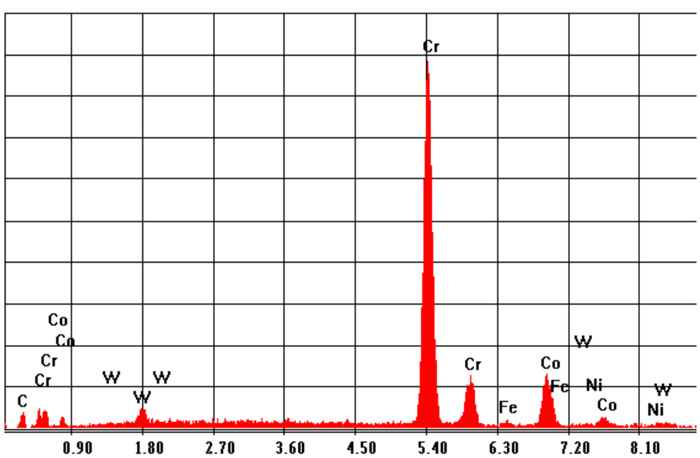


Element	[%] weight
C K	16.62
CrK	56.08
FeK	1.29
CoK	18.69
NiK	1.28
W L	6.04
Total	100

Fig. 8. a) EDS for phase 2 in Stellite 6 layer submitted to quick thermal shock at 950°C

Fig. 8. b) Quantitative analysis for phase 2

Phase 2' in Figure 4



Element	[%] weight
C K	16.2
CrK	60.32
FeK	1.22
CoK	15.36
NiK	0.98
W L	5.92
Total	100

Fig. 9. a) EDS for phase 2' in Stellite 6 layer submitted to quick thermal shock at 950°C

Fig. 9. b) Quantitative analysis for phase 2'

Following to quick thermal shock, a rise of the cobalt content in the solid solution together with a depletion of the latter in alloying elements (Cr, W) can be seen (Figure 5 vs. Figure 6).

On the other hand, in the sample submitted to thermal shock at 950°C, *phases 2 and 2'* contain a large amount of tungsten, close to that of the Stellite 6 alloy (about 5%), amount that is not to be found in the composition of *the phase 2* in the MS 10 sample. This fact is in full accordance with the qualitative phase analysis made by X-ray diffraction which reveals tungsten carbides only in MS 14 sample. In MS 10 sample, tungsten was found only dissolved in the solid solution (*phase 1* analyzed by spectrometry, Figure 5).

Because blast tuyeres protection layers require, besides a thermal shock erosion resistance, also a great hardness and wear resistance, tests of Vickers HV10 hardness were made (10kgf, respectively 98,07N) on MS 10 and MS 14 samples. The results are presented in Table 3.

Table 3

Layer hardness of MS 10 and MS 14 samples

Sample	Hardness HV10			
	Test 1	Test 2	Test 3	Average
MS 10 layer	432	427	443	434
MS 14 layer	433	425	441	433

4. Discussion and Conclusions

- The qualitative phase analysis made by indexing the X-ray diffraction pattern of the MS 10 sample revealed the following phase composition: cobalt - based solid solution having a face-centered cubic (FCC) crystal lattice containing chromium carbides Cr_7C_3 and possibly $M_{23}C_6$ – type carbides $((Cr_{0,77}Co_{0,15}Mo_{0,08})_{23}C_6)$.
- The FCC crystal lattice of the cobalt - based solid solution is cubic and not hexagonal even if low temperature cobalt's allotropic modification (stable up to 417°C) has a hexagonal lattice; this is due on one hand to a high cooling and solidification rate of the Stellite 6 coating and on the other hand to elements such as nickel, iron and carbon which stabilize the FCC structure by allotropic transformation suppression [5].
- The quick thermal shock determined the partial transformation of Cr_7C_3 carbides in chromium richer carbides of the $Cr_{23}C_6$ type. The mechanism of this transformation consists in chromium atoms migration from the solid solution towards the carbides. The reaction describing chromium carbides transformation $3Cr_7C_3 + 2Cr = Cr_{23}C_6 + 3C$ [6] and the decrease in tungsten content of the solid solution for the MS 14 sample's layer confirms the appearance in it of the tungsten carbide. Tungsten is the most carbide forming chemical element in

Stellite 6 and obviously it will form tungsten carbide and excess carbon according to the previous reaction.

- The alloying elements content decrease in the solid solution, the appearance of chromium richer carbides together with tungsten carbide have been confirmed by X-ray diffraction analysis and energy dispersive X-ray spectroscopy (EDS).
- Despite the fact that $Cr_{23}C_6$ hardness is lower than that of Cr_7C_3, the protection layer's hardness as a whole did not decrease (see Table 3) due to the appearance in the MS 14 sample's structure of the tungsten carbide. Therefore it can be stated that even though quick thermal shock leads to structural changes, these facts do not affect the coating behaviour on abrupt temperature variations. For this purpose it can be concluded that a Stellite 6 protection layer is an advantageous solution in order to rise the durability of the blast-furnace tuyeres.

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