ARCHIVES
of
FOUNDRY ENGINEERING

ISSN (2299-2944)

10.24425/afe.2024.149280

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Analysis of Fragmentation Phenomenon of Composite Layers of Fe-TiC Type Obtained *"in situ"* in Steel Casting

J. Marosz *, S. Sobula
AGH University of Krakow, Poland
* Corresponding author: E-mail address: marosz@agh.edu.pl

Received 12.03.2024; accepted in revised form 06.05.2024; available online 12.06.2024

Abstract

A method for fabrication of a composite layer on the surface of a steel casting using coating containing TiC substrates was presented. The reaction of the synthesis of the ceramic phase was based on the SHS method (Self-propagating High-temperature Synthesis) and was triggered by the heat of molten steel. High hardness titanium carbide ceramic phases were obtained, which strengthened the base material improving its performance properties presented in this article. Microstructural examinations carried out by light microscopy (LM) on the in-situ produced composite layers showed that the layers were the products of reaction of the TiC synthesis – the phenomenon called "*fragmentation"* by the authors of study. The examinations carried out by scanning electron microscopy (SEM) have revealed the presence of spheroidal precipitated and free of impurities. The presence of titanium carbide was twofold increase in hardness in the area of the composite layer as compared to the base alloy which was carbon cast steel.

Keywords: Surface layer, Cast steel, "In situ" composite, MMCs composites, SHSM reaction

1. Introduction

During operation, the working surfaces of crushing machines and devices are exposed to a severe wear and tear process, which is mainly due to the interaction of two friction surfaces leading to abrasive wear. The phenomenon is one of the problems observed in many industries and is responsible for the degradation of the surface of materials. The wear processes on the surface of materials make the repair of equipment necessary and that entails losses, which in developed countries are estimated at 1-4% of the gross national product [1]. The losses related to the process of surface degradation cannot be completely eliminated, but they can be significantly mitigated by modifications introduced to the working surface. There are many processes that increase wear resistance, to mention as an example thermal and thermal-chemical treatment, including laser hardening, carburizing or nitriding [2, 3, 4], application of coatings, including ceramic PVD and CVD layers, another processes [5, 6]. In casting practice, techniques such as production of bimetallic castings, most often provided with an insert made of high-chromium cast iron, are used to increase hardness of the casting surface [7, 8]. Another way is to produce functional layers by coating the mould cavity surface with a mixture of powdered alloying additives or, alternatively, in the full mould technology, by application of the mixture onto the surface of a polystyrene pattern, and then pouring the whole with molten alloy [9, 10]. There are also known methods of producing war-resistant layers by infiltration of a porous, ceramic shaped body [11]. Currently, methods of synthesizing composite layers on the casting surface are gaining popularity, mainly due to the use of the Self-propagating High-temperature Synthesis (SHS). These techniques rely on the SHS reaction taking place between substrates composed of a mixture of metal powders (titanium, tungsten, molybdenum) and non-metals (carbon, boron) [12]. As a result of this reaction, layers composed of hard ceramic particles of carbides or borides are formed [12, 13, 14]. The disadvantage of these methods is porosity and uneven distribution of particles in the alloy matrix. The research conducted by Olejnik et al. [13] has shown that a moderator with the chemical composition similar to that of the base alloy added to the mixture of reagents significantly improves the homogeneous distribution of carbide particles in the composite layer. The SHS method has found application in the technology of producing composite layers from reactive coatings applied onto the mould cavity surface. In his research work [15], Ł. Szymański showed that the phenomena of infiltration and formation of a cohesive bond with the casting take place in the presence of appropriately selected additional filler in the suspension of carboxymethyl cellulose (CMC) and appropriately selected ratio of titanium and carbon powders as components of the SHS reaction. The aim of this study was to upgrade the surface of the steel casting with a layer of an abrasion-resistant metal matrix composite (MMC) and to provide a description of the morphology, microstructure and fragmentation of this layer due to the effect of liquid metal poured into the mould cavity.

2. Research methodology

The research methodology used to carry out the experiment is outlined and described below.

2.1. Fabrication of TiC layer on steel casting

Reactive coatings produced on castings were based on a 2% aqueous solution of carboxymethyl cellulose. For this purpose, carboxymethyl cellulose powder in the form of sodium salt (CMC), known under the trade name of Polofix LV made by CMC S.A., was used. The product characteristics are presented in Table 1.

Table 1.
Properties of Polofix LV carboxymethyl cellulose (CMC) [15]

Appearance/ colour	**White to light cream colour powder**
Active substance content in terms of dry matter	59
Degree of substitution	0.6
pH of 2% aqueous solution	7.0-9.0
Moisture content [%]	8-10
Water solubility	YES

The mixture of substrates necessary for the in-situ generation of a ceramic phase in the form of TiC was prepared in the atomic ratio of 55% Ti: 45% C. The specification of titanium and graphite powders is presented in Table 2.

Table 2.
Specification of titanium and graphite powders

No.	Material	Purity, %	Grain size, µm
1	titanium	99.95	44
2	graphite	96.40	<5

The weighed samples of substrates were mixed for two hours without access of air. The process of producing reactive coatings on castings consisted in combining the previously prepared aqueous CMC solution with a mixture of titanium and graphite powders in a 2:1 weight ratio. Figures 1 and 2 show, respectively, a cross-section of the mould (Fig.1) and the surface of a mould cavity with the applied reactive coating (Fig.2).

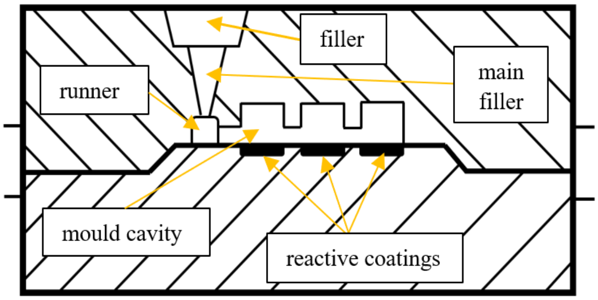

Fig. 1. Schematic diagram of the experimental mould

The foundry mould onto the surface of which the reagents were applied was made of silica sand with water glass binder. The properly prepared mould cavities were covered with reactive coatings forming circular patterns (Fig.2).

Fig. 2. View of the mould surface, with areas of reactive coating

Moulds prepared in this way were dried at 100^{o}C to evaporate water and were next poured with carbon steel at a temperature of 1550^{o}C. In this way, a circular layer composed of TiC cast steel matrix. The chemical composition of the alloy is presented in Table 3.

Table 3.
Chemical composition of the base alloy (carbon cast steel)

Chemical composition, % wt.						
Fe	C	Si	Mn	Cr	S	P
97.22	0.25	0.83	1.30	0.35	0.03	0.02

2.2. Microscopic examinations and heat treatment

Samples for microstructural examinations were cut out in a direction perpendicular to the casting surface. Images of microstructures and studies fraction of the carbide particles on the examined surface were made with a Keyence VHX-7000 digital microscope and SEM scanning microscope to carry out the quantitative analysis and confirm the synthesis of titanium carbides, showing also their morphology. The morphology of the composite layer was investigated in both as-cast condition and after heat treatment. The samples were austenitized at 1050ºC for one hour and then cooled in air. The next step was tempering at 600ºC for thirty minutes.

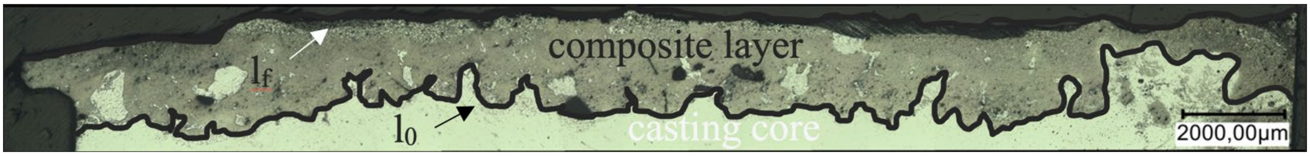

Fig. 3. Microstructure of carbon cast steel before heat treatment (S1)

Fig. 4. Microstructure of carbon cast steel after heat treatment (S2)

2.3. Measurements of the number and size of carbides

The volume fraction of titanium carbide particles was calculated by the microscope software used for the image examination and registration. Measurements were carried out in 20 randomly selected areas. The size of the equivalent diameters of the obtained carbides (d_{ekw}) was estimated by the analytical method. First, the area occupied by titanium carbides was taken into account, and then the area of a single precipitate of the TiC phase, producing the quotient of the total area occupied by the particles and their number. Both the surface contribution and equivalent diameter were measured using a Keyence VHX-7000 confocal microscope.

2.4. Methodology of hardness measurements

Hardness measurements were made under a load of 10kG (dwelling time 10s) with a hardness tester designed by Micro Vickers Hardness Tester BeiJing United Test Co., Ltd. The results are summarized in Table 7.

2.5. Fragmentation coefficient

To determine the homogeneity of the layer, we propose to calculate the fragmentation coefficient W_f. It can be calculated in accordance with formula (1):

$$W_f = \frac{l_f}{l_0} \quad (1)$$

where:
W_f - fragmentation coefficient, -,
l_f - total length of the layer, μm,
l_0 - length of the layer – substrate interface, μm.

3. Research results

Figures 3 and 4 show images of the microstructure obtained in a composite layer. A fairly high degree of development of the surface layer – cast steel core interface is visible, indicating the phenomenon of fragmentation. It is important to note that the application of heat treatment had a positive effect on the reduction of this area (Fig.4). In the examined composite area, places with porosity are also visible. The results of studies of the composite layer before heat treatment – S1 (Fig.5) and after heat treatment – S2 (Fig.6) are presented below.

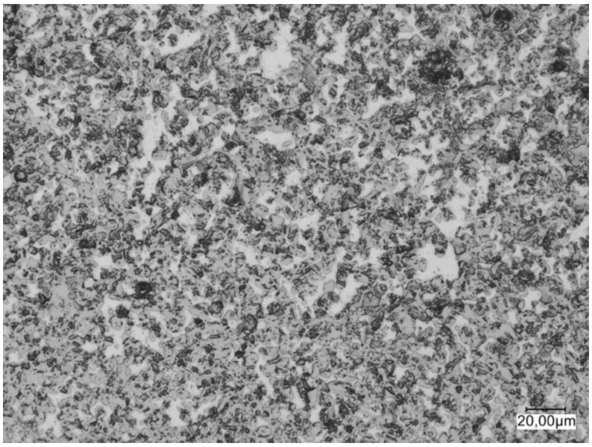

Fig. 5. Microstructure of composite layer for carbon cast steel before heat treatment (S1)

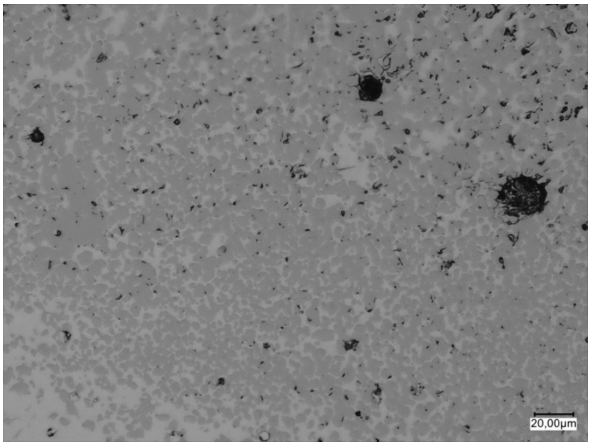

Fig. 6. Microstructure of composite layer for carbon cast steel after heat treatment (S2)

From the microstructure images in Figures 7 and 8 it follows that the examined layer is characterized by the presence of carbides of a spherical or dendritic shape. The content of carbides in the examined layer is 32-60% (Table 4). The size of carbides in the examined samples ranges from 1.28-1.94 µm (Table 5).

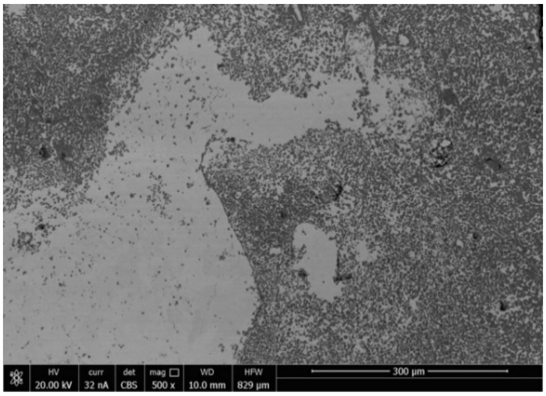

Fig. 7. Microstructure of examined layer

Table 4.
Surface fraction of TiC layers on carbon cast steel (S1, S2)

Sample type	Surface fraction, %
Cast steel before heat treatment (S1)	31.95
Cast steel after heat treatment (S2)	59.82

Table 5.
Equivalent diameters and fragmentation coefficient of examined samples (S1, S2)

Parameter	Sample S1	Sample S2
d_{ekw}	1.942	1.284
W_f	1.68	1.45

Table 6.
Hardness measurement results (HV10) for cast steel samples before heat treatment (S1) and after heat treatment (S2)

No.	Cast steel sample S1		Cast steel sample S2	
	Base	Composite	Base	Composite
1	405	988	503	1097.5
2	397.5	946	503	946
3	397.5	974	503	988
4	405	946	503	974
5	405	946	503	960
Mean	402	960	503	993
Standard deviation σ	3.67	17.1	0	54.04

Table 7.
EDS analysis of examined phases

Spot	%C	%Ti	%Fe	%Cr	%Mn	%Si
1	26.4	72.6	1.0	-	-	-
2	-	3.8	93.9	0.3	1.4	0.6
3	-	24.9	67.9	0.3	1.1	5.8

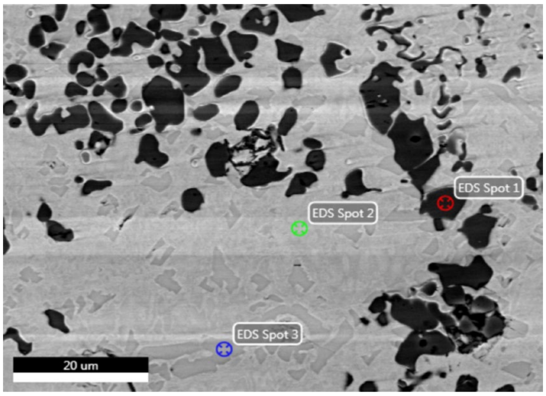

Fig. 8. Microstructure of examined layer

4. Discussion of results

In the presented research, various properties of composite layers were investigated, including fragmentation, hardness, size of carbides and fragmentation coefficient obtained for the composite layers produced in-situ by SHSM method on surface of carbon steel castings. As a result of the SHS reaction initiated by the high temperature of molten alloy in a suspension applied onto the mould cavity surface, titanium carbide was formed and hardened the upper layer of castings.

The layer formed on the surface of the cast steel sample had a total thickness of about 2000 μm. It was characterized by a diversified structure consisting of a homogeneous area, the thickness of which was approximately 1000 μm, and the remaining area adjacent to the substrate, folded, undulating and heterogeneous. This was due to the turbulent flow of the liquid alloy during mould pouring.

When the layer described above was undergoing the process of synthesis and the crystallization front was moving along, the mixture of TiC ceramic particles and base metal became a thixotropic mixture with low fluidity. Titanium carbides has a spherical shape, which is very advantageous for the casting surfaces exposed to abrasion process, as the "notch effect" breaking the hard phases is not operating any longer. To better characterize the quality of the produced layers, the fragmentation coefficient was used.

This coefficient enabled numerical determination of the ratio of the interface length to the interface length represented as a straight line. For the areas studied, the fragmentation coefficient decreased after heat treatment from 1.68 to 1.45 μm (Table 6). Szymanski's research [16-18], on reactive coatings is described in detail in the papers, in this article the authors have paid special attention to the nature of the resulting steel-based layer and focused on its qualitative and quantitative description. The main and most important parameter is the fragmentation factor, named by the authors

5. Conclusions

The described method of hardening composite castings guarantees obtaining titanium carbide layers with a thickness form 1000 μm to 2500 μm. The SHSM method ensures an average content of titanium carbide in the layer of up to 50%. The heat treatment carried out on cast steel had no major effect on the size of titanium carbide precipitates. Locally coagulating precipitates of titanium carbide particles were observed to form in a steel casting under the effect of heat treatment. The hardness measurements carried out on the layers produced by the SHSM method showed an over twofold increase in hardness (Table 7) compared to the base metal. This proves that the described technology of producing carbide zones can effectively upgrades the surface of castings exposed to abrasive wear.

References

[1] Swain, B., Bhuyan, S., Behera, R., Mohapatra, S., Behera, A. (2020). Wear: a serious problem in industry. In Patnaik, A., Singh, T., & Kukshal, V. (Eds.), *Tribology in Materials and Manufacturing-Wear, Friction and Lubrication* (pp. 279-298). DOI: 10.5772/intechopen.94211.

[2] Nowotyńska, I., Kut, S. & Kogut, K. (2018). Laser hardening of tools with the use of the beam. *Autobusy.* 19(6), 636-639. DOI: 10.24136/atest.2018.147. (in Polish).

[3] Wołowiec-Korecka, E., Korecki, M., Klimek, L. (2022). Influence of flow and pressure of carburising mixture on low-pressure carburising process efficiency. *Coatings*. 12(3), 337, 1-7. https://doi.org/10.3390/coatings12030337.

[4] Jhao-Yo Guo, Yu-Lin Kuo, Hsien-Po Wang, (2021). A facile nitriding approach for improved impact wear of martensitic cold-work stell using H2/N2 mixture gas in an ac pulsed atmospheric plasma jet. *Coatings*. 11(9), 1119, 1-15. https://doi.org/10.3390/coatings11091119.

[5] Sedov, V., Martyanov, A., Altakhov, A. (2022). Effect of substrate holder design on stress and uniformity of large-area polycrystalline diamond films grown by microwave plasma-assisted CVD. *Coatings.* 10(10), 939, 1-10. DOI:10.3390/coatings10100939

[6] Bitay, E., Tóth, L., Kovacs, T.A., Nyikes, Z. & Gergely, A.L. (2021). Experimental study on the influence of TiN/AlTiN PVD layer on the surface characteristics of hot work toll steel. *Applied Sciences.* 11(19), 9309, 1-12. https://doi.org/10.3390/app11199309.

[7] Zhu, Yc., Wei, Zj., Rong, Sf., Wang, H. & Zou, C. (2016). Formation mechanism of bimetal composite layer between LCS and HCCI. *China Foundry.* 13, 396-401. https://doi.org/10.1007/s41230-016-5021-2.

[8] Szajnar, J. & Wróbel, T. (2015). Bimetallic casting: ferritic stainless steel – grey cast iron. *Archives of Metallurgy and Materials*. 60(3), 2361-2365. DOI: 10.1515/amm-2015-0385. ISSN 1733-3490.

[9] Wang, F., Xu, L., Wei, S. et al. (2021). Preparation and wear properties of high-vanadium alloy composite layer. *Friction*. 10, 1166-1179. https://doi.org/10.1007/s40544-021-0515-3.

[10] Ovcharenko, P.G., Leshchev, A.Y., Tarasov, V.V. et al. (2021). Effect of alloyed coating composition on composite casting surface layer properties. *Metallurgist*. 64, 1208-1213. https://doi.org/10.1007/s11015-021-01106-z

[11] Studnicki, A., Dulska, A. & Szajnar, J. (2017). Reinforcing cast iron with composite insert. *Archives of Metallurgy and Materials*. 62(1), 355-357, DOI: 10.1515/amm-2017-0054.

[12] Fraś, E., Olejnik, E., Janas, A. & Kolbus, A. (2009). FGMs generated method SHSM. *Archives of Foundry Engineering* 9(2), 123-128. ISSN (1897-3310).

[13] Olejnik, E., Janas, A., Kolbus, A. & Grabowska, B. (2011) Composite layer fabricated by in situ technique in iron castings. *Composites (Kompozyty).* 11(2), 120-124.

[14] Szymański, Ł., Olejnik, E., Tokarski, T., Kurtyka, P., Drożyński, D. & Żymankowska-Kumon S. (2018) Reactive casting coatings for obtaining in situ composite layers based on Fe alloys. 350, 346-358. https://doi.org/10.1016/j.surfcoat.2018.06.085.

[15] Szymański, Ł. (2020*). Composite layers produced in situ in castings based on Fe alloys*. PhD thesis. AGH, Kraków.

[16] Szymański, Ł., Sobczak, J.J., Peddeti. K. (2024). Production of metal matrix composite reinforced by TiC by reactive infiltration of cast iron into Ti + C preforms. *Ceramic international*. 50(10), 17452-17464. https://doi.org/10.1016/j.ceramint.2024.02.233.

[17] Szymański, Ł., Olejnik, E. & Sobczak, J.J. (2022). Dry sliding, slurry abrasion and cavitation erosion of composite layers reinforced by TiC fabricated in situ cast steel and gray cast iron. Elsevier. *Journal of Materials Processing Technology*. 308, 117688, 1-15. https://doi.org/10.1016/j.jmatprotec.2022.117688.

[18] Szymański, Ł., Olejnik, E., Sobczak, J.J. (2022). Improvement of TiC/Fe in situ composite layer formation on surface of Fe-based castings. *Materials Letters.* 309, 131399, 1-5. DOI: https://doi.org/10.1016/j.matlet.2021.131399.