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Selection of protective coatings obtained by plasma-spraying method for foundry industry

Dobór powłok ochronnych otrzymanych metodą natrysku plazmowego do zastosowania w przemyśle odlewniczym

Abstract
This article presents results from the studies of protective coatings applied to industrial graphite molds used for the casting of non-ferrous metals. The selection of coatings was based on the results of measurements of surface wettability by liquid copper and microstructure examinations. The study involved industrial graphite molds with single-layer protective coatings of Al_2O_3 + 30%C and ZrO_2-Y_2O_3 + 30%C as well as two-layer protective coatings of Al_2O_3 + 30%C /glassy carbon and ZrO_2-Y_2O_3 + 30%C /glassy carbon.

Key words: plasma spraying, foundry industry, microstructure, wettability

Streszczenie
W artykule przedstawiono wyniki badań powłok ochronnych przeznaczonych do ochrony grafitowych krystalizatorów stosowanych w przemyśle odlewniczym. Dobór powłok nastąpił na podstawie wyników badań mikrostruktury i pomiarów zwilżalności powierzchni przez ciekłą miedź. Badaniami objęto grafitowe krystalizatory z naniesionymi powłokami ochronnymi: jednowarstwowymi Al_2O_3 + 30%C i ZrO_2-Y_2O_3 + 30%C oraz dwuwarstwowymi Al_2O_3 + 30%C /węgiel szklisty i ZrO_2-Y_2O_3 + 30%C /węgiel szklisty.

Słowa kluczowe: natrysk plazmowy, przemysł odlewniczy, mikrostruktura, zwilżalność

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1. Introduction

One of the problems emerging in the industry is the surface degradation of molds used for the manufacture of products from non-ferrous metals (copper, in particular). The benefits offered by graphite as a material for molds include high thermal conductivity, resistance to high temperatures, and low wettability by liquid copper [1]. However, there are also some disadvantages, such as high porosity, lack of homogeneity, and easy oxidation even at low temperatures. The consequence is the sticking of liquid metal to the mold working surfaces during casting, which causes surface degradation and a need for mold replacement [2]. An innovative approach leading to mold improvement and longer service life consists of surface modification through the use of coatings with suitable properties, which keeps liquid metal from sticking to the mold surface. The presence of this coating prolongs the performance life of molds with an obvious benefit: a more-efficient casting process [3].

The studies carried out by the authors have indicated the possibility of using coatings based on zirconium oxide and aluminium oxide [4, 5]. The ceramic coatings of Al_2O_3 and Zr_2O_3-Y_2O_3 applied by plasma spraying are characterized by low wettability in contact with liquid copper, micrometer thickness, and good abrasion resistance. In spite of all of these benefits, the low thermal conductivity [6, 7] can result in coating detachment from molds during casting. A solution to this problem is introducing a large amount of graphite to the coating composition or applying an outer layer of glassy carbon, which also shows a low degree of wettability by liquid copper [5, 8].

This paper presents results from the studies of coatings produced by plasma spraying, designed to protect the surface of graphite molds used in the non-ferrous metal industry.

2. Test materials and methods

Ceramic coatings of ZrO_2-Y_2O_3 + 30% C and Al_2O_3 + 30% C were deposited on a graphite substrate by plasma spraying in an MIM-40 device. The process was based on the use of ZrO_2-Y_2O_3 and Al_2O_3 powders with properties as specified in Table 1 as well as plasma-forming gases (i.e., argon and hydrogen). Details of the injection process parameters are summarized in Table 2. In order to increase the conductivity of the coatings, the first batch of samples was enriched with a 30% graphite addition.

Table 1. The type and chemical composition of powders

Type of powder	Chemical composition	Gradation [μm]	Shape of powder
Amperit 821.084	ZrO_2-Y_2O_3 80/20	55–75	irregular
Metco 105NS	Al_2O_3	30–45	irregular

Table 2. Parameters of the plasma spraying process

Distance [mm]	Linear velocity [m/min]	Pitch [mm]	Plasma-forming gases [l/h]		Plasma voltage [V]	Plasma current [A]	Powder carrier gas N_2 [l/h]
			Ar	H_2			
80	30	2	2500	160	58	450	900

Measurements of the critical contact angle of coatings wetted by liquid copper were made by the sessile drop method using a Ziehm Exposcop 8000 (X-ray unit). The sample with the test material on the surface was placed in a furnace and heated to a temperature of 1100 ± 1°C in an atmosphere of argon. After reaching the required temperature, X-ray images of the sample were taken, and the critical contact angle was measured. Increasing the critical contact angle decreases the wettability.

The ready coatings were applied onto the industrial graphite molds. Sequentially, they were subjected to laboratory tests, which consisted of the repeated casting of tin bronze. The Foundry Research Institute, a special facility located in Krakow, was used for this process. The melted alloy was B8 bronze with the following chemical composition: Sn 8.55%, Zn 0.15% Pb 0.02%, and W 0.01%. The composition was determined on as-cast samples. The temperature of the metal in the furnace before pouring was 1250°C, while the mold temperature during the first pouring was 200°C: this increased in subsequent cycles due to the heating of the mold by liquid metal (Tab. 3). Each mold was poured six times; the only exception was the mold with the ZrO_2-Y_2O_3 + 30% C coating (it was poured only four times because of metal solidification in the fourth pouring). After the casting process, macro photos of each mold surface were taken. Then, from the area where fragments of the coating were sticking to the mold surface, a specimen was cut out for examinations to be made on a cross-section with a Hitachii SU-70 scanning electron microscope. EDS analysis was also performed to check the chemical composition of the coating and residual metal remaining after the casting process.

Table 3. Mold temperature during successive pourings (T1 – temperature of the first pouring, T2 – temperature of the second pouring, etc.)

T1	T2	T3	T4	T5	T6
200°C	320°C	400°C	450°C	530°C	580°C

3. Results and discussion

Figure 1 shows the X-ray images of specimens taken out of the apparatus for wettability measurements. All coatings are characterized by similar critical contact angles, which assume the following values: for ZrO_2-Y_2O_3 + 30% C – 121°; for Al_2O_3 + 30% C – 125°;

for ZrO_2-Y_2O_3 + 30% C/glassy carbon – 131°; and for Al_2O_3 + 30% C/glassy carbon – 133°. These values represent the poor wettability of the coating by liquid copper, which was a prerequisite for the use of coatings in the foundry industry.

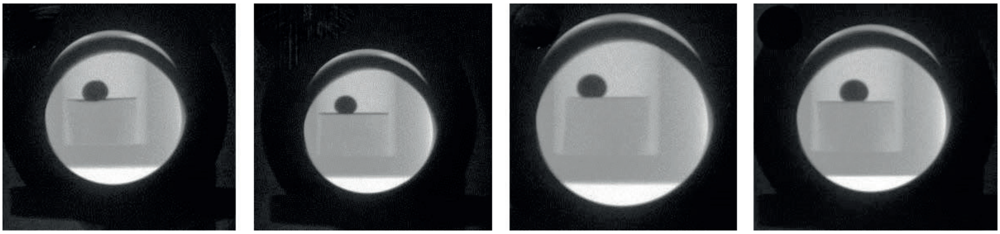

Fig. 1. The results of wettability measurements taken for liquid copper and samples coated with: a) ZrO_2-Y_2O_3 + 30% C; b) Al_2O_3 + 30% C; c) ZrO_2-Y_2O_3/glassy carbon; d) Al_2O_3/glassy carbon

Figure 2 shows the macro photos of molds with various coatings after the test casting of tin bronze in the laboratory. In the case of molds coated with ZrO_2-Y_2O_3 + 30% C (Fig. 2a) and Al_2O_3 + 30% C (Fig. 2b), a large part of the coating was observed to detach from the mold surface. Locally, drops of the cast alloy were sticking to the surfaces (both coated and uncoated). In molds where the outer surface was coated with a layer of glassy carbon (Figs. 2c and 2d), the coatings were not detached and suffered only minor local surface damage. In terms of quality, it was the mold with ZrO_2-Y_2O_3 + 30%/glassy carbon coating that remained in the best condition (Fig. 2c).

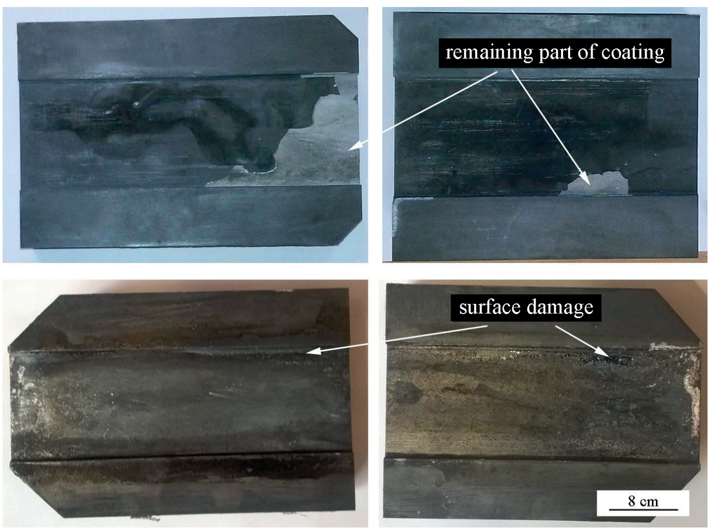

Fig. 2. The inner surface of mold coated with: a) ZrO_2-Y_2O_3 + 30% C; b) Al_2O_3 + 30% C; c) ZrO_2-Y_2O_3/glassy carbon; d) Al_2O_3/glassy carbon

Figure 3 shows the results of studies carried out on samples taken from the molds with an outer layer made of glassy carbon. Sticking fragments of the cast metal are locally observed on the surface of the glassy carbon layer (Fig. 3a, combined with metal penetration into the affected portion of the coating, Fig. 3b).

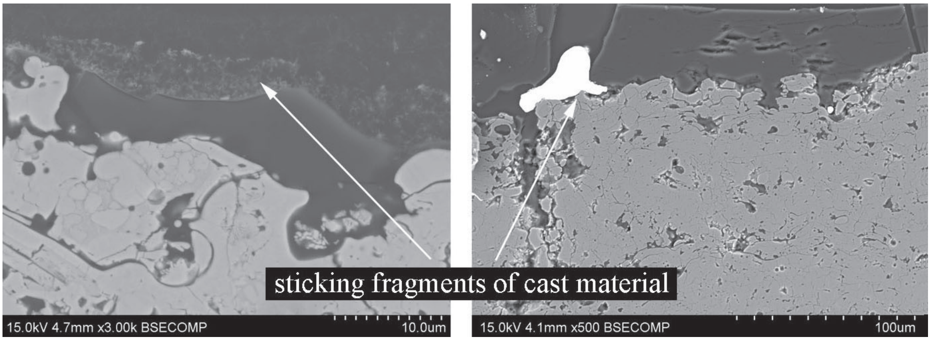

Fig. 3. Cross-section of mold coated with: a) ZrO_2-Y_2O_3/glassy carbon; b) Al_2O_3/glassy carbon

Figure 4 shows the results of EDS spot analysis of chemical composition carried out on the cross-section of a specimen of the ZrO_2-Y_2O_3/glassy carbon coating, with small fragments of the alloy adhering to its surface. The presence of Zr, Y, and O was identified in the interlayer, and carbon was found in the outer layer of the coating (thus confirming the assumptions made previously). The sticking alloy contained Fe, Cu, Sn, and O.

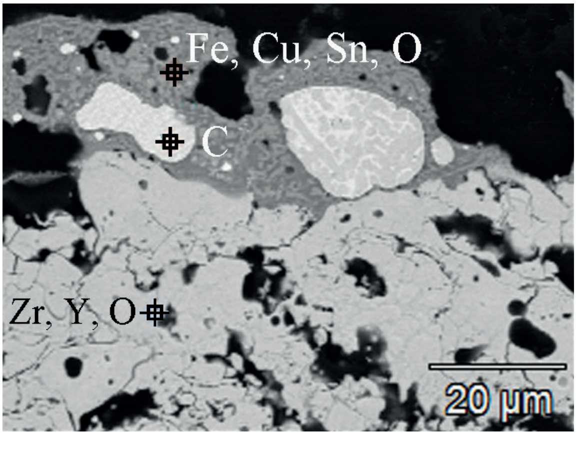

Fig. 4. EDS spot analysis of mold surface with ZrO_2-Y_2O_3/glassy carbon coating after performance tests

4. Conclusions

The test results enabled us to draw the conclusion that, among various plasma-sprayed coatings, it is the double-layer ZrO_2-Y_2O_3/glassy carbon coating that gives the best protection to industrial graphite molds. It should be noted, however, that the addition of carbon to both coatings (i.e., to Y_2O_3-ZrO_2 and Al_2O_3) failed to give the expected effect of improving the coating's thermal conductivity to such an extent that it would prevent its detachment from the substrate. This goal was achieved through the application of an outer layer made of glassy carbon. The use of this particular material not only prevented the coating from detaching from mold, but it also conferred a smooth surface to the mold after casting, with only scarce traces of the poured metal.

Acknowledgements

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