Surface modification of molds for titanium casting, and its influence on the allocation of chemical elements in boundary layers of molds

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Abstract. Influence of titanium sputtering on the inner surface of the casting mold on the chemical elements’ allocating in the boundary layers of the mold is considered. It is established that the sputtering of titanium does not exclude the migration of mold’s chemical elements through the titanium to the casting surface.

1. Introduction
One way to reduce the formation of an alpha case during the casting of titanium is the usage of protective technological coatings, for example Al2O3, on the inner surfaces of molds to prevent the formation of an alpha layer. These coatings provide protection against corrosion, decarburization, burnout of alloying elements, surface gas saturation of pieces and stock materials of various configurations and dimensions.

Protective technological coatings allow to save metal up to 8% by eliminating oxide scale and improving the surface quality of parts and semi-finished goods.

Objective: to research boundary layers of the molds used for the casting of titanium, after the deposition of protective coatings on the inner surfaces of the molds.

2. Experimental
We analyzed mold composition: MgO (83.2%), CaO (2.9%), SiO2 (1.9%), Na2O (SiO2) n (12%). The calculated content of chemical elements Mg: O: Si: Ca: Na (at.%) in the form is 41.9 : 50.3 : 2.7 : 1.0 : 4.1. The mold was sintered at a temperature of 1000 ± 50 °C for 6 hours. Casting mold was saturated with carbon dioxide to grasp its components before sintering. Then it’s cooling for 10 hours in the furnace. After excavation from the furnace, a Ti protective layer was applied to the mold by an electric arc method. There were two samples: a form with a deposited Ti (figure 1left) and a form after contact with the casting (figure 1right). Research of the relief, the elemental composition of the mold surface and cross-section were carried out using "EVO 50 XVP" (Carl Zeiss) Scanning Electron Microscope with a probe microanalysis system "INCA Energy-350".

3. Results and discussion
Several surface regions of the form with Ti coating are shown in figure 2 (left) and four cross-section regions are in figure 2 (right). An analysis of the titanium allocating map over the cross-section (figure 2) shows that the thickness of its compact allocation is 200-300 μm. It follows from figure 2 (left) and table 1 that titanium is distributed unequal on the surface. In areas where quantity of titanium is low,
the content of the elements is close to original mold without coating \cite{1}. Nevertheless, where titanium is dominant, there are elements from the original mold, whence it follows, the elements of the form Mg, Ca, Si, Na migrate through the titanium layer to the surface.

![Figure 1](image1.png)

**Figure 1.** Samples of the mold with a Ti layer (left) and after contact with the casting (right).

![Figure 2](image2.png)

**Figure 2.** Images of the investigated regions of the surface (left), the cross section (right) and the Ti allocating map of the Ti layer.

According to the data in Table 1, the oxygen content on the surface of the mold exceeds the required amount for the maximum oxidation of the elements. Perhaps it happens due to the formation of carbonic acid salts, which is formed by the reaction of carbon dioxide with water. In addition, we found a large number of pores located throughout the volume in the sample.

Research of the dependence in the chemical elements profile on the depth of the cross section of the sample (figure 3) and the allocating map of Ti (figure 2) shows that the maximum intussusception
of titanium into the mold reaches 800 μm. At a distance of 1.5 mm from the surface, the elemental composition of the modified mold approximates the composition of the original mold.

Table 1. Element composition (at.%) of the mold surface with Ti coating.

| Elements | Regions of the surface | Original form |
|----------|------------------------|---------------|
|          | Average | 1     | 2     |       |
| O        | 66,17   | 61,80 | 64,76 | 59,3  |
| Mg       | 8,66    | 25,01 | 4,58  | 26,6  |
| Si       | 1,37    | 5,76  | 0,77  | 6,4   |
| Ca       | 0,57    | 1,83  | 0,24  | 3,2   |
| Ti       | 21,93   | 2,06  | 29,03 | -     |
| Na       | 1,30    | 2,90  | 0,61  | 3,5   |
| O*       | 55,83   | 42,28 | 64,42 | 42,6  |

* In case of maximum oxidation of elements.

Figure 3. Profile of the elements content in the depth of the cross section of the mold with Ti coating.

After contact of mold with titanium casting, four regions of the separation surface and 8 sections of the cross section were examined. We found several structures on the surface of the mold detachment (figure 4), despite their difference, as follows from Table 2, the first and second structures are close in composition.

Table 2. Element composition (at.%) of the mold surface with Ti coating after peeling off the casting.

| Elements | Surface | Regions of the surface |       |
|----------|---------|------------------------|-------|
|          |         | 1            | 2    | 3    |
| O        | 62,03   | 64,68        | 65,24| 57,51|
| Mg       | 25,89   | 28,88        | 28,47| 39,44|
| Si       | 1,35    | 1,73         | 1,32 | 1,33 |
| Ca       | 2,61    | 2,81         | 3,16 | 1,40 |
| Ti       | 2,54    | 1,91         | 1,81 | 0,32 |
| O*       | 36,28   | 38,97        | 37,89| 44,14|

* In case of maximum oxidation of elements.
Perhaps this is due to the presence of a similar amount of titanium in both structures. The third structure is close to the composition of the original mold without Ti coating in terms of elemental composition [1]. Study of the cross section showed a pored structure (figure 5 left).

By the content of titanium on the detachment surface (<3%), it can be concluded that separation of the mold from the casting passes along the boundary of sputtered titanium. The homogeneous composition of the form begins at a depth of ~ 800 μm (figure 5 right).

**Figure 4.** Images of surface structures of the mold with titanium coating after peeling off the casting.

**Figure 5.** Image of the cross section (left) and profile of elements content by the depth of section (right) after the mold has been detached from the casting.

4. **Conclusion**
Sputtering of titanium on the surface of the casting mold does not exclude the migration of mold elements through the layer of titanium. After casting, the peeling of the mold from the casting passes along the boundary of sprayed titanium.

5. **References**
[1] Khatmullina A I, Petrov E J and Lyahovich A M 2017 8th Int. Science and Technical
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