

TRIBOLOGICAL ANALYSES OF COMPOSITE MULTILAYER COATINGS APPLIED FOR MOLDS IN TIRE PRODUCTION

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Abstract. The goal of this work is to determine the suitability of cobalt-based powder used in coating aluminum forms, using atmospheric plasma spraying. The experimental part is focused on evaluation of the performed analyses and practical tests to determine the suitability of the coating in practice. The goal of the experimental part of this work was to evaluate the applicability of coating aluminum molds used for vulcanization of tires. Cobalt-based powder was used for coating. Firstly, by itself, secondly, together with a NiAl intermediate layer. Both layers were applied using the method of atmospheric plasma spraying. The desired result of these coats was to increase their lifespan, increased amount of work cycles between necessary cleaning of the mold and simplification of maintenance. The NiAl intermediate layer used along cobalt - based powder in coating resulted in more equally distributed elements in deposited layers, especially cobalt and molybdenum, and near complete reduction in chrome agglomeration. Furthermore, layer adherence was improved due to the creation of heat bridge in-between aluminum and powder, resulting in form lifespan improvements and reduced wear and tear. The usage of the NiAl interlayer did not however improve the mechanical properties of coatings; the test results show small if any improvements. During the process of spraying, uneven coating and coat thickness fluctuation took place. The results of the practical test, however, did not seem to be the influence by this occurrence.

Keywords: atmospheric plasma spraying, coatings, molds, deposited coatings, practical coating tests.

Introduction

The aim of the research was to test and evaluate the properties of coated aluminum molds intended for vulcanizing rubber tires and to evaluate their possible usability in practice with the aim of extending the life of molds in tire production. The research work was commissioned by MoldCast s.r.o. and the coating was carried out by Czech companies – S.A.M. Společnost Holding s.r.o. The molds are coated by atmospheric plasma spraying (APS) with a powder based on Co47Mo33Cr18Si2 with an intermediate NiAl layer, which is on the surface of the base material and Co47Mo33Cr18Si2 is applied to the layer.

Materials and methods

Atmospheric plasma spray (APS) technology is a method of thermal coating of the entire spectrum of metallic materials (metals or alloys) by depositing molten or partially molten surface shells of metal and non-metal particles. The use of a plasma beam, created in a torch from a gas ionized by an electric arc between an anode and a cathode with a direct voltage, allows the use of even difficult-to-melt metals for coating. Metal and non-metal particles melted at high temperatures are accelerated by a plasma stream and deposited on the surface of the base metal material, where they adhere to its surface mainly due to mechanical anchoring and form lamellae creating coating layers [1-3].

During the experiment, it was first necessary to prepare samples for coating. These were prepared either in the form of discs for tribological tests, spectrometric analysis and EDS analysis. In addition, specially developed prototype segments were used. In both cases, the same aluminum alloy AlSi10CuNiMn0.3 was used, as is used in real conditions for certain types of vulcanization molds. The actual composition of this alloy is in Table I, which was measured on a Q4 TASMEN optical emission spectrometer. This alloy is used for low-pressure casting, and its advantage is the possibility of use even at higher temperatures up to 150-200 °C, where it exhibits stable mechanical properties.

Table 1

Base material of the samples

Element	Si	Cu	Ni	Mn	Mg	Sr
Representation, %	100.7	10.02	00.98	00.31	00.56	00.032

Characterization of the properties of the applied powders and the structure of the coatings

The powder of the applied material is melted by the plasma and accelerated towards the deposited surface of the base metal material. Due to the spraying parameters, a greater or lesser number of not

completely melted particles are formed, which fall on the surface. These particles then form the surface of the coating together with the properly melted particles. Insufficiently melted particles then deteriorate the mechanical properties of the coating and its adhesion to the base surface or to the intermediate layer. The particles falling on the surface create lamellae, from which the individual layers of the coating are formed. The thickness of the lamellae is influenced by the size and speed of the falling particles. Outside the layers, porosity arises as a result of irregular impacts of the particles, cooling of the surfaces and contact with the surrounding atmosphere, and partial oxidation of the particles occurs [2; 4]. The main tool for assessing the quality of deposited surfaces is linear, area or point EDS analyses performed on a scanning electron microscope. Its use allows obtaining information not only about the structure of the deposited layer but also about its microchemical composition. The coating was performed with a powder with the composition $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$. The melting point of the powder stated by the manufacturer is $1600\text{ }^\circ\text{C}$. The powder was subjected to XRD analysis before its use. The powder also contains trace amounts of aluminum, iron and nickel. The coated samples were divided into two groups. One group of the base aluminum alloy was coated only with $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ powder, and in the second group, a NiAl layer was applied to the base aluminum alloy (as an intermediate layer) and then a $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ coating layer was applied on top of it. Linear EDS analysis of the $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ coating (Fig. 1) provides information on the distribution of individual elements throughout the depth of the deposited layer down to the base material. The content of individual elements is relatively constant, without sudden changes, except for chromium. It has a slightly inhomogeneous distribution, creating concentration peaks from the otherwise relatively uniform distribution of other elements in the material. The presence of oxygen is also evident, and its concentration also in the transition between the base material and the deposited layer. However, in certain areas the thickness of the coating reaches only 30 to 60 μm , while in the rest of the coating it is up to 100 μm . These changes in the thickness of the coating are accompanied by obvious depressions in the base material and microcracks are visible at the interface between the base material and the coating.

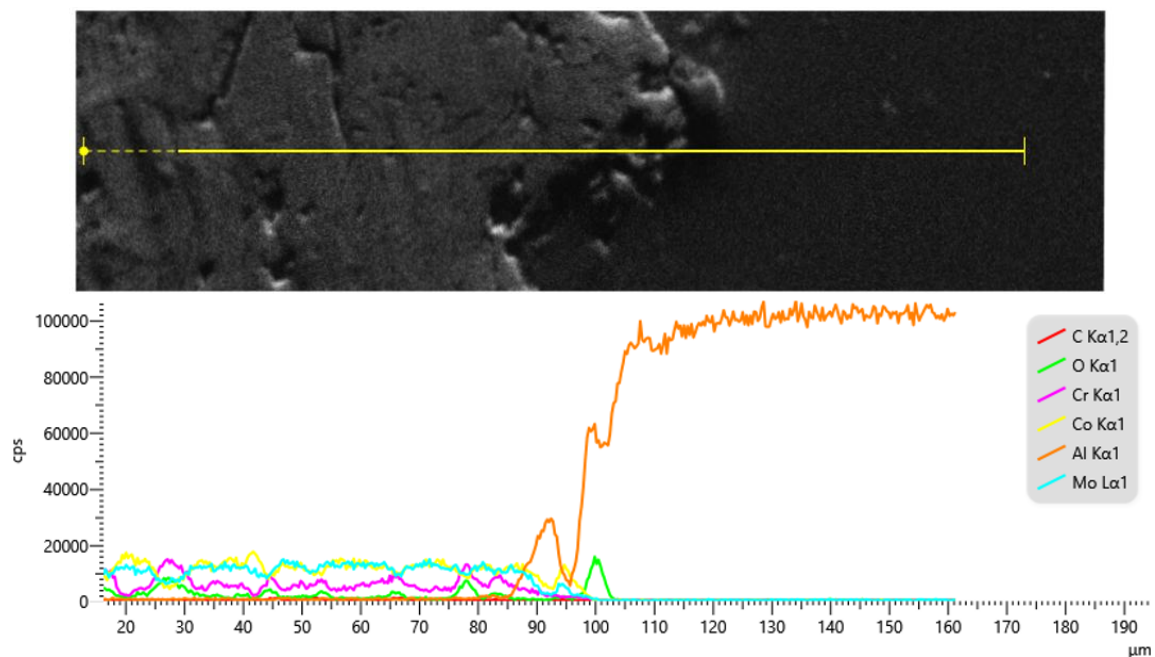


Fig. 1. Linear EDS analysis of $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ coating

Linear analysis of $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2 + \text{NiAl}$ (Fig. 2) provides information on the distribution of elements depending on the depth of the coating. It is evident that the NiAl interlayer becomes approximately 30 μm thick, and the total thickness of the coating increases. The only exception to the relatively homogeneous representation of elements in the section is chromium, which still agglomerates from an otherwise evenly balanced composition. However, this phenomenon is manifested to a much lesser extent than in the coating itself.

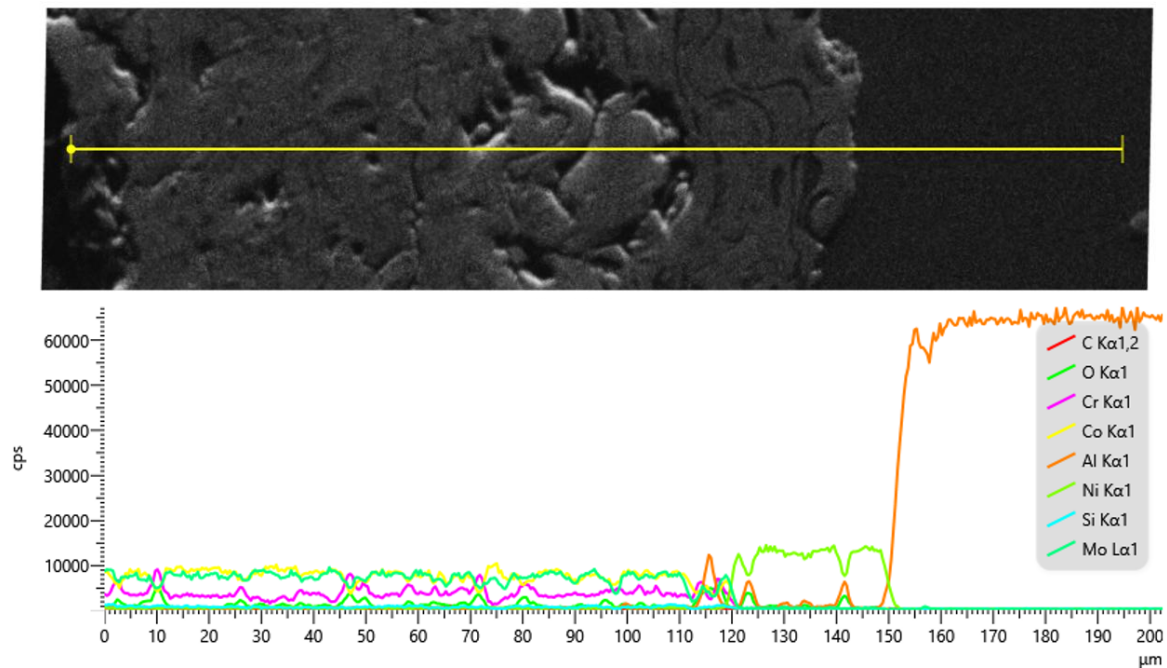


Fig. 2. Linear EDS analysis of Co47Mo33Cr18Si2 + NiAl surface

Tribological analyses

Friction tests were performed using the Pin-on-Disc method, according to the standard (ISO 14830-1). This is a process of pressing a test body, in this case a sapphire ball, into the surface of the test body. The ball performs a rotational movement around the circumference of the test sample. The test leaves traces on the sample after the test body was rolled. Basic aluminum alloys with a diameter of 49.5 mm and a thickness of 10 mm were used as samples. Each of the samples was used for 4 independent tests. The tests were performed at room temperature under the following constant conditions: test duration: 120 s; test body pressure force: 30 N; body speed 10 RPM; test body - sapphire ball. The Bruker UMT TriboLab machine was used for the tests. Not only the values of the friction coefficient were obtained but also records of the course of individual tests. The result of each measurement was the measured COF. Each test on the same sample was carried out at a different distance from the centre. The reason is the effort to minimize the difference in the applied coating in different places of the sample and to use the average resulting values. The results are shown in Table 2.

Table 2

Tribological testing of both types of coatings

Test No.	Type of coating	Specific deviation	\varnothing COF
Test 1	Co47Mo33Cr18Si	0.0180	0.1663
Test 2	Co47Mo33Cr18Si2 + NiAl	0.0159	0.1661

Course of friction tests. The values changed drastically at the beginning of the tests and stabilized only after about 10 seconds of the test. This running-in phase can be attributed to the increasing load until the stabilized test value and the unevenness of the surface that the test specimen first encounters at the start of the test.

Applied tribological testing

Practical, applied tests monitored the behaviour of coated prototypes under repeated loading by rubber vulcanization. The mold sample corresponds to the final sample for tire production, but the shape of the prototypes was adapted to the test conditions. The test prototypes contain buffers that serve to define the test area and are not found on real molds. Defects arising in this area are not indicative of the expected behaviour of the coating during real use in production. The first group of prototypes was coated with Co47Mo33Cr18Si2 powder, the second group contains a Co47Mo33Cr18Si2 coating together with a NiAl intermediate layer. Both coatings were applied to prototypes with summer and winter tread

patterns (with Fe lamellas). The shape of the winter tread pattern is identical to the summer tread pattern, with the exception of the inserted steel lamellas. The material of the lamellas from the basic mold then creates space for the formation of unexpected defects. Unlike the test samples, the coating was carried out manually. The reason is mainly the complex shape of the prototype, which greatly complicates the placement of the deposited layer evenly on all surfaces and edges of the tread. For this reason, it is possible to assume the occurrence of defects caused by the human factor during coating. The molds shown in Fig. 3 were clamped into the platform after coating, where the test with vulcanized rubber was carried out. 200 tests were carried out, the condition of the rubbers was monitored after every ten tests, a total of 21 rubbers were examined, together with the very first sample. The rubber heated to the working temperature was pressed into the molds, which it filled, and the excess material caused the individual molds to connect with each other.



Fig. 3. Mold stored in the machine ready to be pressed with material

Implementation and evaluation of applied tribological testing

The rubber vulcanization was carried out on molds coated with $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ METCO powder simultaneously with $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2 + \text{NiAl}$ molds. All test conditions were the same for both coatings. In the prototypes coated with pure $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ powder, two significant defects occurred in particular.

- Peeling of the $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ coating. These areas are marked in green in Fig. 4. These defects occurred already during the first vulcanization.
- Surface wear, visible in the marked areas of the mold ribs.



Fig. 4. Prototype with $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ coating with summer tread pattern after rubber vulcanization test

On the first rubber vulcanized in the prototype with deposited $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ powder, particles of the peeled coating stuck, see Fig. 5. On the other samples, peeling no longer occurred.

The prototypes with the $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2$ coating with the winter tread performed similarly, with a similar level of peeling of the deposited layer and surface wear. Rubber islands continued to form on the vulcanized rubbers, filling the peeled layers of the coating. However, the coating shows almost no tendency to peel or other defects in the area of the steel lamellae. The summer prototype coated with the $\text{Co}_47\text{Mo}_33\text{Cr}_18\text{Si}_2 + \text{NiAl}$ powder showed almost no peeling of the coating. Surface wear was also

minimal. The vulcanized rubbers with the $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2 + \text{NiAl}$ prototypes showed no defects until the end of the test.



Fig. 5. Stains on vulcanized rubber caused by previous peeling of the coating first vulcanized rubber in summer form coated with $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ powder

Conclusions

1. The results of EDS analyses indicate a lower content of all metals, especially molybdenum, compared to the values determined by XRD powder analysis. The reason may be their evaporation during deposition, especially for silicon and cobalt with a lower melting point.
2. The content of metals is further reduced by the content of oxygen and carbon, which entered the layers through environmental contamination.
3. For cobalt and molybdenum, their increased concentration is evident closer to the base material. The application of the NiAl interlayer almost completely prevented this phenomenon, which indicates the ability of the interlayer to support a uniform distribution of elements in the structure and achieve better heat flows during solidification of the spray.
4. EDS mapping of the $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ coating revealed the tendency of chromium to form clusters in which its concentration increases significantly. When applying the NiAl interlayer, these areas almost completely disappear. The NiAl interlayer thus achieved a reduction of chromium agglomeration to a minimum.
5. The use of the SEM microscope further revealed changes in the thickness of the deposited coatings. Changes in the thickness of the coating can be caused by the treatment of the material before coating or the coating parameters.
6. When using the NiAl interlayer, the average measured microhardness increased slightly. This fact can be attributed to a better distribution of elements in the coating due to the NiAl interlayer.
7. The friction coefficient tests show almost identical average values. However, individual measurements achieved a slightly more uniform development of the coefficient when using the NiAl interlayer.
8. The last step in investigating the behaviour of the deposited coatings was practical tests. Prototype molds with the desired pattern were coated and subjected to test rubber vulcanization.
9. Already during the first rubber vulcanization, the coating separated from the mold in the mold with the coating. During the test, the mold surfaces were obviously worn out.
10. The mold with the coating and the NiAl intermediate layer demonstrated much higher layer cohesion and a drastic reduction in coating peeling compared to the pure coating. At the same time, there was a significantly lower degree of mold surface wear.
11. In both cases, there were no expected defects in the area of the lamellas of the winter molds. This indicates the ability of the coating to adhere to other base materials.

The use of the NiAl intermediate layer when coating with $\text{Co}_{47}\text{Mo}_{33}\text{Cr}_{18}\text{Si}_2$ powder resulted in a more even distribution of elements in the structure, especially cobalt and molybdenum, and an almost complete reduction in chromium agglomeration. Furthermore, better cohesion between the individual layers was achieved thanks to the creation of a temperature bridge between the base material. There was a significant improvement in the mold life and a reduction in its wear.

Despite the shortcomings that the coatings showed during the investigation, based on the tests performed, the use of the METCO + NiAl coating can be recommended for application to vulcanizing molds in production.

Author contributions

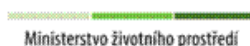
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