The oxidation behavior of classical thermal barrier coatings exposed to extreme temperature

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DOI: 10.13111/2066-8201.2017.9.1.5

Received: 30 January 2017/ Accepted: 23 February 2017/ Published: March 2017
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International Conference of Aerospace Sciences "AEROSPATIAL 2016"
26 - 27 October 2016, Bucharest, Romania, (held at INCAS, B-dul Iuliu Maniu 220, sector 6)
Section 4 – Materials and Structures

Abstract: *Thermal barrier coatings (TBC) are designed to protect metal surfaces from extreme temperatures and improve their resistance to oxidation during service. Currently, the most commonly used systems are those that have the TBC structure bond coat (BC) / top coat (TC) layers. The top coat layer is a ceramic layer.*
Oxidation tests are designed to identify the dynamics of the thermally oxide layer (TGO) growth at the interface of bond coat / top coat layers, delamination mechanism and the TBC structural changes induced by thermal conditions.
This paper is a short study on the evolution of aluminum oxide protective layer along with prolonged exposure to the testing temperature. There have been tested rectangular specimens of metal super alloy with four surfaces coated with a duplex thermal barrier coating system.
The specimens were microscopically and EDAX analyzed before and after the tests. In order to determine the oxide type, the samples were analyzed using X-ray diffraction. The results of the investigation are encouraging for future studies.
The results show a direct relationship between the development of the oxide layer and long exposure to the test temperature. Future research will focus on changing the testing temperature to compare the results.

Key Words: *thermal barrier coating, thermally grown oxide, suspension plasma spray, zirconia stabilized yttria, delamination, layer*

1. INTRODUCTION

Thermal barrier coatings (TBC) are advanced materials typically applied to metal surfaces subjected to extreme temperatures to protect them and increase their lifetime. Gas turbine generators are characterized by extreme high operational conditions.

In literature, it is highlighted a gradual increase of TGO layer thickness. Prescott et al. [1] explain that low growth rate of TGO layer thickness is related to the structure of stoichiometric oxide and high deficiency of band that make electronic conduction difficult. The transport process of Al determines the rate of oxidation, thus affecting material properties by changing creep behavior. Due to their highly reactivity Al and O can be very mobile determining the behavior of an ionic conductor.

Morph structural results support the research literature [1] stating that the Cr existence in this ternary NiCrAlY alloy reduces the Al percentage necessary for development of TGO layer with an increased thickness average of 0.3-0.5 micron.

As seen from the results of the morph structural analysis at 1000^{o}C temperature the oxide containing both α-Al_2O_3 and γ-Al_2O_3. Those oxides are forming in an oxidizing atmosphere. According to research conducted by Wood et al. [2], [3], α-Al_2O_3 has a quite high energy matrix ionic character.

The α-Al_2O_3 is the stable, high-temperature form. Smialek and Gibala [4] have noted that the formation of α-Al_2O_3 on Ni-Cr-Al alloys at 1100^{o}C is preceded by the development of a layer containing γ-Al_2O_3 in the form of sub grains and then will transform slowly to α-Al_2O_3.

1.1 Thermal barrier coatings (TBC) classical structure

Thermal barrier coatings are a widely accepted solution for increasing the life time and other functional performances of some parts of the power generators systems.

The classical structure of the TBC system is:

- the substrate (a metalic super alloy) on which the bond coat is deposited,
- the bond coat (BC) has the form of MeCrAlY,
- the thermally grown oxide (TGO) is formed at high temperature at the BC/TC interface,
- the top coat (TC) is the ceramic layer.

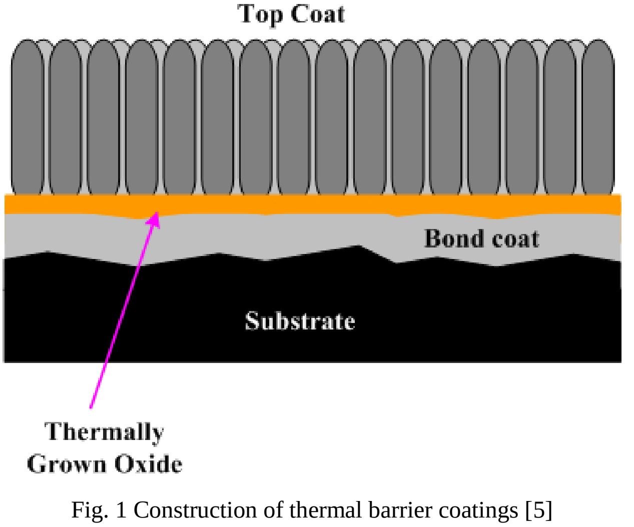


Fig. 1 Construction of thermal barrier coatings [5]

1.2 Suspension plasma spray (SPS) deposition method [6]

The suspension plasma spray is a plasma spraying deposition method which consists in injecting a suspension of nanoparticles in the plasma jet. The suspension of nanoparticles is the only way to inject such small particles with the suitable momentum. After being transferred to the plasma jet, the solid particles are melted and projected onto the prepared surface deposition (metallic substrate).

The SPS method presents the following advantages:

- a good control of the coating porosity by adjusting the experimental parameters,
- it enables multi-layer deposition gradient properties (composition, porosity etc.) using one or more suspensions,
- it works in ambient air with minor modifications of conventional plasma spraying system.

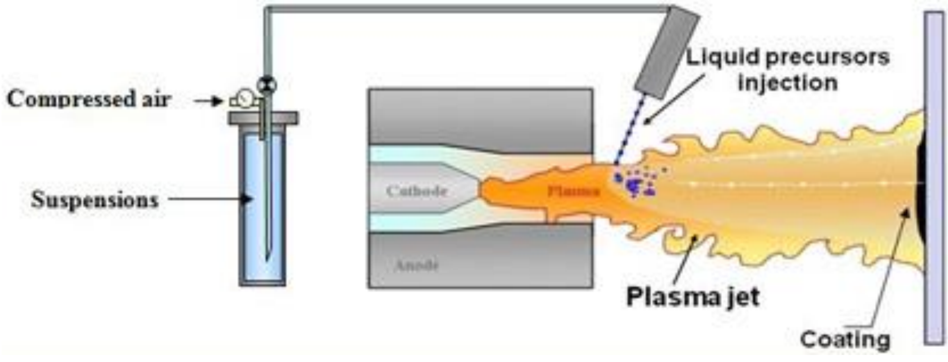


Fig. 2 Suspension plasma spray deposition [6]

The paper describes the oxidation long term testing of the classical type of thermal barrier coatings used to protect a super alloy. Oxidation tests are designed to identify the dynamics of the thermally oxide layer (TGO) growth at the interface of bond coat / top coat layers, delamination mechanism and the TBC structural changes induced by thermal conditions.

The test is used to ilustrate the transformations that occur in the structure of materials under different testing conditions (extreme temperature) of materials used in aeronautical aplications. The aim of this paper is to identify the formation dynamics of TGO and its role to the delamination and spallation mechanisms of the protection layers and endurance by analyzing the structural changes induced by extreme thermal stress.

2. EXPERIMENTAL METHOD

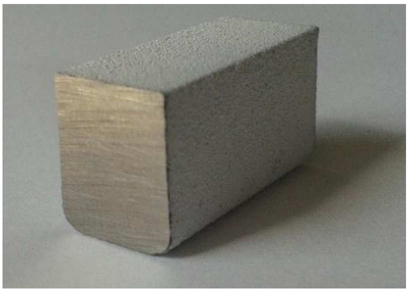
2.1 Samples for oxidation testing

The isothermal long term tests were performed on rectangular samples coated on 4 sides by SPS method, provided by MIRTEC [7]. The samples are made of Nimonic substrate with YSZ top coat.

The structure of SPS samples:

- Super alloy: MeCrAlY,
- Bond Coat: NiCoCrAlY,
- Top Coat: YSZ (yttria stabilized zirconia); Chemical composition of the top coat: $ZrO_2 8\% Y_2O_3$.

a) lateral image



b) 3D image

Fig. 3 Specimen 1 prepared for the first test at 1000°C

2.2 Testing method

The isothermal long term tests were performed on the rectangular SPS coated samples. The samples are made of Nimonic substrate with YSZ top coat.

Isothermal testing long term protocol used for this kind of tests is described below. Oxidation testing parametres were established by INCAS:

- Temperatures: 1000°C,
- Heating time: 2h,
- Dwell time: 25 hours,
- Cooling time: 29 min in air.

The isothermal long term tests were performed in air, in a Nabertherm furnace (fig. 4), the cooling taking place outside the furnace.

Fig. 4 Nabertherm furnace

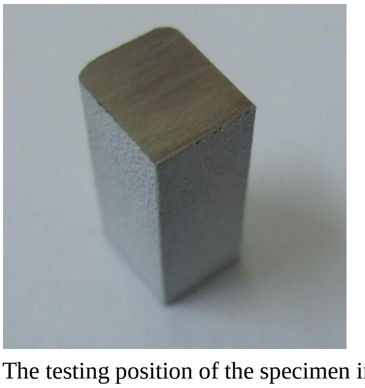


Fig. 5 The testing position of the specimen in the furnace

Fig. 6 Removing the sample from the furnace

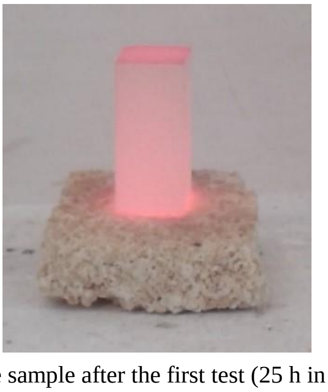


Fig. 7 The sample after the first test (25 h in furnace)

The first sample was introduced manually with pliers in the preheated furnace at 1000 °C and was held at this temperature for 25 hours.

Then the sample was manually removed from the furnace (fig.6) and allowed to cool in air for 27 minutes (fig. 7).

Tests continued until the maximum number of cycles/ time is achieved or until the spallation reached 10-20% of the TBC area.

In this case, the tests continued for 11 cycles (275 h) without deboning.

3. RESULTS AND DISCUTIONS

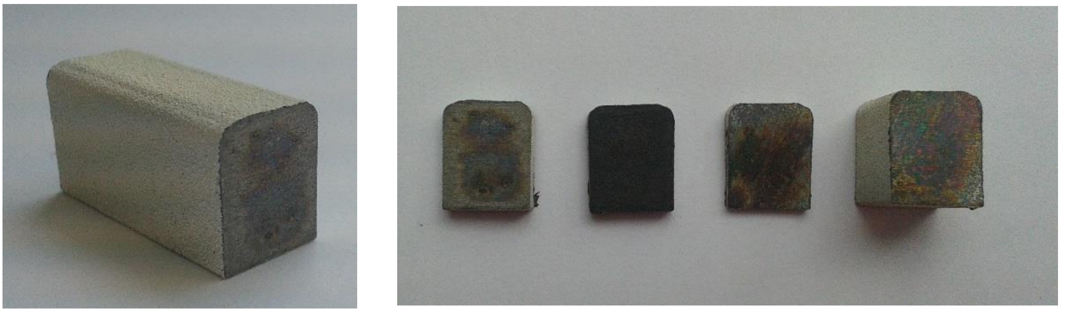
3.1 Inspection of the tested samples

For carrying out the tests, a number of three specimens with the above-mentioned specifications was used.

The samples were introduced into the furnace simultaneously, and after each test cycle, a specimen was removed in order to cut a sample piece from it.

That specimen was cooled in air according to the protocol mentioned above, then a part of it was cut for morphs structural analysis while the rest of the specimen was reintroduced into the furnace.

From each specimen, it resulted 4 parts that were used to analyze the changes of TGO layer. Finally, 11 pieces resulted, that cumulated 275 hours of testing without delamination of the ceramic layer.



a) after 1 testing cycle b) after 4 cycles (100 h) all cut pieces

Fig. 8 Specimen 1 prepared for the first test at 1000°C

3.2 Morphological analysis of TGO

The micrographs image, highlights the uniform structures of the ceramic layer with 35 microns average thickness.

At TC/BC interface it can be seen the presence of an oxide layer. The EDAX results confirm the Al_2O_3 existence which was formed by the migration of Al from BC and elemental oxidation reactivity.

The Al transport process at 1000°C led to the formation of the oxide layer into strips indicating a constant reactivity of the element.

The phase transition at this temperature can be deduced from the laminar arrangement of the oxide.

The thickness of the oxide layer varies according to the temperature and dwell time, with an average between 1,5 and 3 microns.

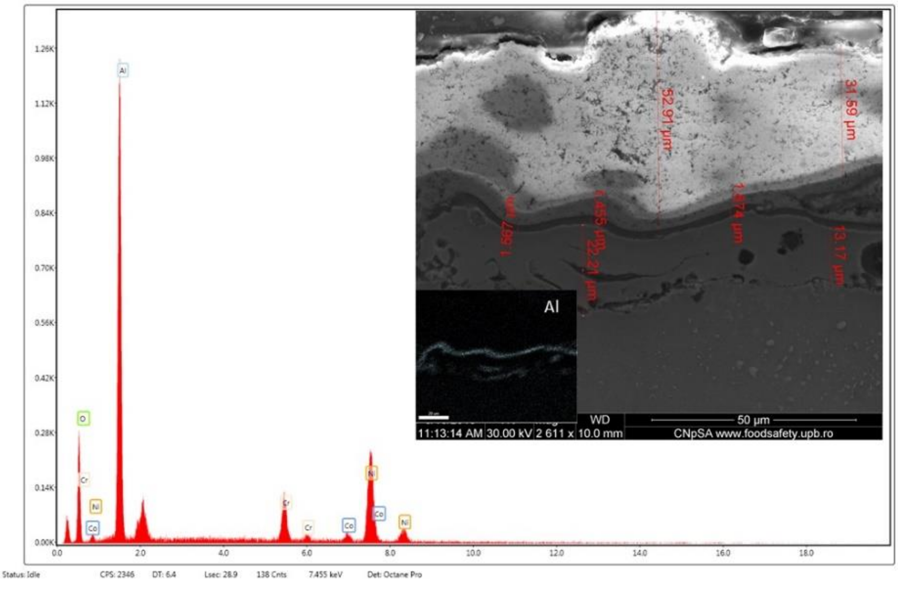


Fig. 9 Specimen microstructure after 25 h of testing (1 cycle)

It can be noticed a very good adhesion to the substrate of the layer BC, and a good adhesion at the interface of the two layers TC and BC. TGO layer is continuous and relatively evenly distributed. TC thickness shows differences of about 20 microns. Inside the BC layer aluminum oxide inclusions can be seen, which affect the layer characteristics.

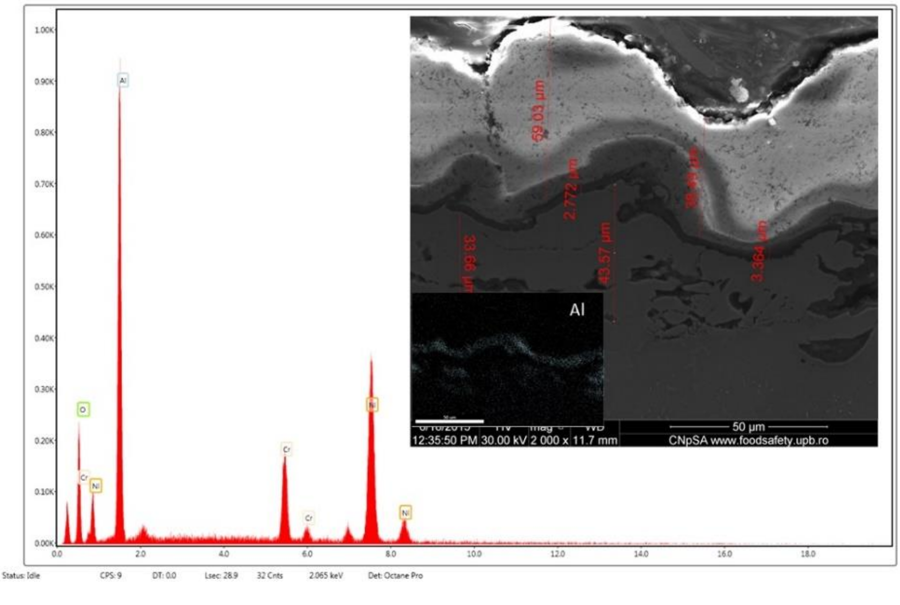


Fig. 10 Specimen microstructure after 100 h of testing (4 cycles)

From the morph-graphical image it can be observed that in some places the TC layer diminishes its thickness following exposure to the temperature. It shows a very good adhesion to the substrate layer BC interface and a good grip TC / BC. After morphological and structural analysis of the oxide layer, it can be observed that its stability is remarkable and that it is coherent and adherent.

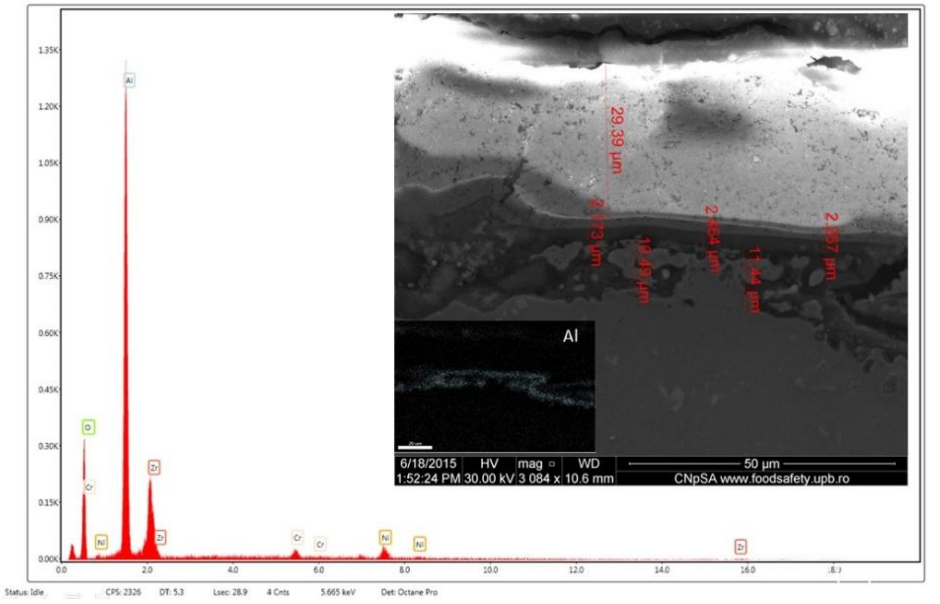


Fig. 11 Specimen microstructure after 200 h of testing (8 cycles)

EDAX image highlights the concentration of the oxide layer at the interface BC / TC. It can be noticed a very good adhesion to the substrate of the BC layer and a good adhesion at the interface of the two layers TC and BC. The TGO layer average thickness variation is around 0.3 microns, and the BC thickness varies between 11.5 and 10.5 µm.

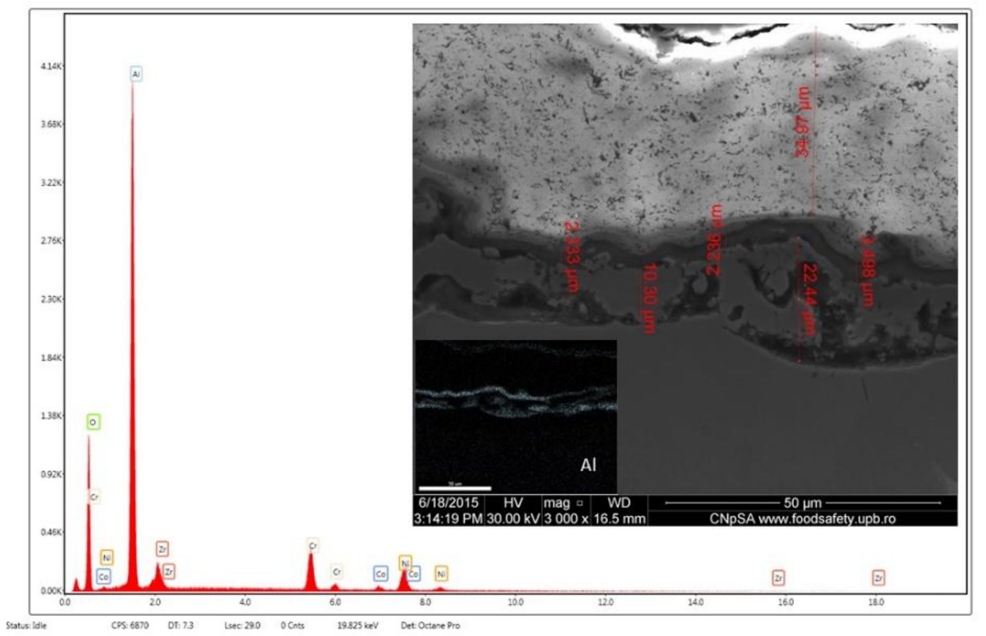


Fig. 12 Specimen microstructure after 250 h of testing (10 cycles)

To highlight the oxide formation at this temperature it is recommended that the results of the SEM microscopy to be corroborated with X-ray diffraction for phase transition.

During the isothermal test the TGO thickness is growing.

Table 1. Variation of TGO layer

Testing time, [h]	Average of TGO layer thickness, [μm]
25 (1 cycle)	1.565
100 (4 cycles)	3.068
200 (8 cycles)	2.301
250 (10 cycles)	2.689

3.3 X-Ray Diffraction

The diffraction chart of TBC layers MeCrAlY / $ZrO_2$8% Y_2O_3 (fig. 13) outlines the formation of the tetragonal γ-Al_2O_3, by recrystallization at high temperature, due to the surface diffusion of Al, and the oxidation reaction. This phase begins to form at 1000°C.

In this phase the peak at (002) is reflected with 100% intensity. The result showed well defined peaks at (004), (220), (327) and (2212).

It is found ZrO_2 orthorhombic structure having 100% intensity peak (111) observed in 2Theta = 30^o.

It can also be observed characteristic peaks for ZrO_2 structure (200), (220) and (311) having 35%, 50% and 59% peak intensity.

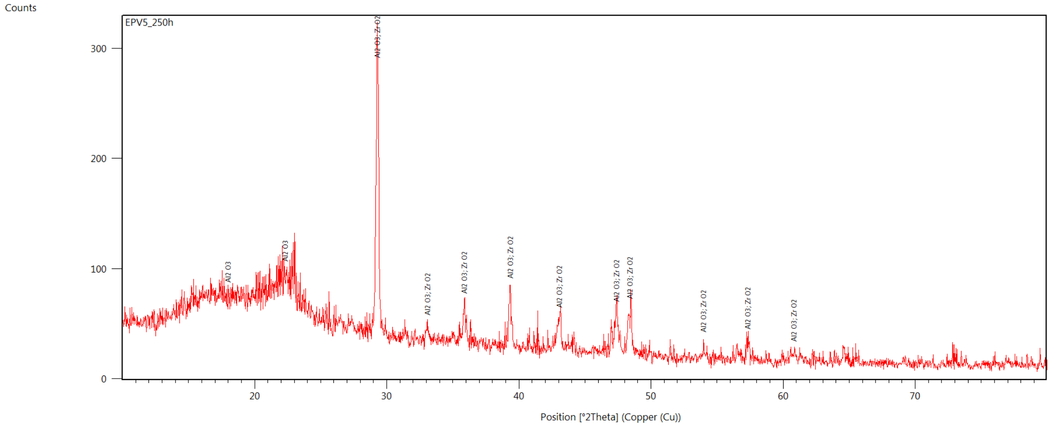


Fig. 13 X-Ray Diffraction of thermal barrier coating MeCrAlY / ZrO28%Y2O3 of sample after 250 h testing (10 cycles) at 1000°C

4. CONCLUSIONS

At 1000°C degree, the samples resisted up to 11 cycles (275 h of testing) without debonding. During the isothermal test the TGO has a variation of thickness increase.

The morphological structure highlights a good adhesion between bond coat and top coat layers. It can be concluded an even distribution of TGO layer, but it is distinguished the impoverishment of the BC layer. After morphological and structural analysis of the oxide layer, it can be observed that its stability is remarkable and that it is coherent and adherent.

The diffraction chart outlines the formation of the tetragonal γ-Al_2O_3, by recrystallization at high temperature, due to the surface diffusion and oxidation of Al. This phase begins to form at 1000°C.

The next step for future research in this direction is performing testing campaigns at higher temperatures (1100°C and 1200°C) to compare the results and structural modifications in the TGO.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the TheBarCode (Grant Agreement no. 310750/10.12.2012) FP 7 [7] project partners for their technical support in performing the samples. We also give thanks for the technical support to the "POLITEHNICA" University of Bucharest for morphological analysis and X-ray diffraction investigations. Also, we would like to express our thanks to our colleague Gherghina PANA, technician within the Materials Compartment of INCAS, for the technical support in performing the tests.

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