Evolution of the phase composition of ZrB_2-$35MoSi_2$-15Al composite coating at annealing

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Evolution of the phase composition of ZrB_2-35$MoSi_2$-15Al composite coating at annealing

I Goncharov[1,2*], M Kovaleva[1], M Yapryntsev[1] and V Sirota[2]

[1]Belgorod State National Research University, Pobeda 85, Belgorod 308015, Russia
[2]Belgorod State Technological University named after V G Shukhov, Kostyukov St, 46, Belgorod, 308012, Russia

E-mail: goncharov@bsu.edu.ru

Abstract. In this article, new composite coatings ZrB_2-35$MoSi_2$-15Al were deposited on the surface of a carbon-carbon composite using a multi-chamber detonation accelerator. The evolution of the phase composition of ZrB_2-35$MoSi_2$-15Al coatings was analyzed with differential scanning calorimeter (DSC) and X-ray diffractometry (in situ HT-XRD) at temperatures from room temperature (~ 25°C) to 1400°C (normal atmosphere and pressure). The coating before annealing according to X-ray diffractometry data is tetragonal (t-ZrO_2) and monocline (m-ZrO_2) zirconium dioxide, monocline silicon oxide (m-SiO_2), hexagonal zirconium diboride (h-ZrB_2), tetragonal molybdenum disilicide (t-$MoSi_2$), cubic aluminum (c-Al) and cubic yttrium oxide (c-Y_2O_3). It was found that the coating crystallizes in m-ZrO_2 at 460ºC, and then mullite with rhombic crystal lattice appears at 960ºC. When the temperature reaches 1050ºC the m-ZrO_2, $ZrSiO_4$, t-ZrO_2, m-SiO_2 and mullite phases formed in the coating. At 1400 ° C, cubic zirconium dioxide appears in the coating. Experimental results can become the basis for the application of ceramic coating ZrB_2-35$MoSi_2$-15Al, which can improve the properties of carbon-carbon composites in an oxygen-containing environment at elevated temperatures.

1. Introduction
Carbon/carbon (C/C) composites materials are considered one of the most promising high-temperature structural materials due to the complex of unique physical-mechanical, thermal, radiation and erosion properties, which allows using them in aircraft and machine building, reactor construction, metallurgy, etc. [1]. The main disadvantage of C/C composites is the low resistance to oxidation at temperatures above 500ºC. Consequently, such materials need to be modified to improve their performance in oxidizing environments, which is a critical limitation preventing their wide application [2]. One method of preventing oxidation at high temperatures is the application of heat resistant coatings [3]. In this paper, ZrB_2-35$MoSi_2$-15Al, obtained using a multi-chamber high-frequency detonation accelerator, is used for the first time as a glass-ceramic heat resistant coating [4-5]. The evolution of phase transformation in ZrB_2-35$MoSi_2$-10Al coating during annealing from room temperature to 1400ºC was investigated.

2. Materials and methods
ZrB_2-35$MoSi_2$-15Al coating was formed using a Robotic complex for detonation spraying of coatings (IntelMashin LLC, Russia) equipped with a multi-chamber detonation accelerator (MCDS) [6]. The coatings were formed on the surface of the carbon-carbon composite substrate without intermediate layers. To increase the wettability of the C/C composites surface, aluminum powder was additionally

added to the initial powder mixture. The evolution of the phase composition was investigated using a combined TGA/DSC/DTA analyzer SDT Q600 (TA Instruments) and a Rigaku SmartLab diffractometer equipped with a Rigaku SHT-1500 high-temperature attachment (in situ HT-XRD). The unit is designed for the study of phase transitions and structural changes at high temperatures (up to 1500 °C). The samples were heated to the target temperature at a rate of 10°C/min, and then the system was thermostated for 30 minutes to stabilize the temperature and course of the processes. The 2θ diffraction angle range was from 20° to 80° with a step width of 0.02°, 2°/min speed, CuKα-radiation, Ni filter. Phase identification was performed using the PDF powder radiographic standards database (JCPDS ICDD), PDF-2. Grating indication was carried out by graphical analysis methods, using PDXL software (RIGAKU).

3. Results and discussions

In the process of coating with detonation spraying in an air atmosphere there is local heating of the applied materials to temperatures over 2000ºC [7]. ZrB_2-35$MoSi_2$-15Al coating before annealing according to X-ray diffractometry data is tetragonal (t-ZrO_2) and monocline (m-ZrO_2) zirconium dioxide, monocline silicon oxide (m-SiO_2), hexagonal zirconium diboride (h-ZrB_2), tetragonal molybdenum disilicide (t-$MoSi_2$), cubic aluminum (c-Al) and cubic yttrium oxide (c-Y_2O_3) (Figure 1).

The temperature program for oxidative annealing was formed taking into account the data obtained using a combined TGA/DSC/DTA analyzer SDT Q600 (TA Instruments) (Figure 2).
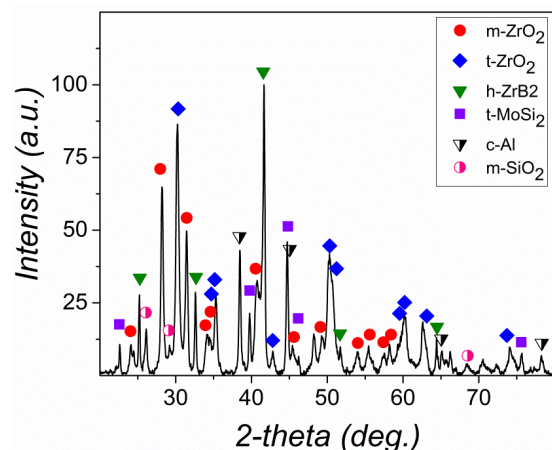

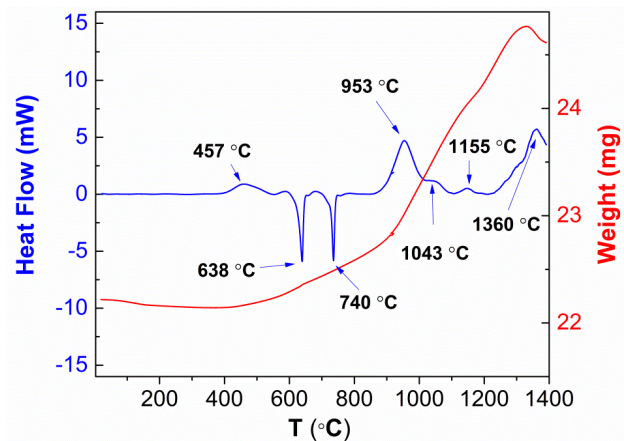**Figure 1.** XRD pattern of the ZrB_2-35$MoSi_2$-15Al coatings before annealing.

Figure 2. TGA-DSC curves of coatings ZrB_2-35$MoSi_2$-15Al during annealing from at room temperature to 1400°C at a heating rate of 10º/min.

According to the results of thermogravimetric analysis TGA (red line) (Figure 2) there is an increase in weight by 11% due to oxidation of the initial substances. On the DSC curve (blue line) the first phase transformation is observed at temperature ~ 460º C. At this temperature (Figure 3b) zirconium dioxide (m-ZrO_2) monocline phase crystallization occurs. This is evidenced by the increase in the relative intensity of reflexes corresponding to this phase (Figure 6).
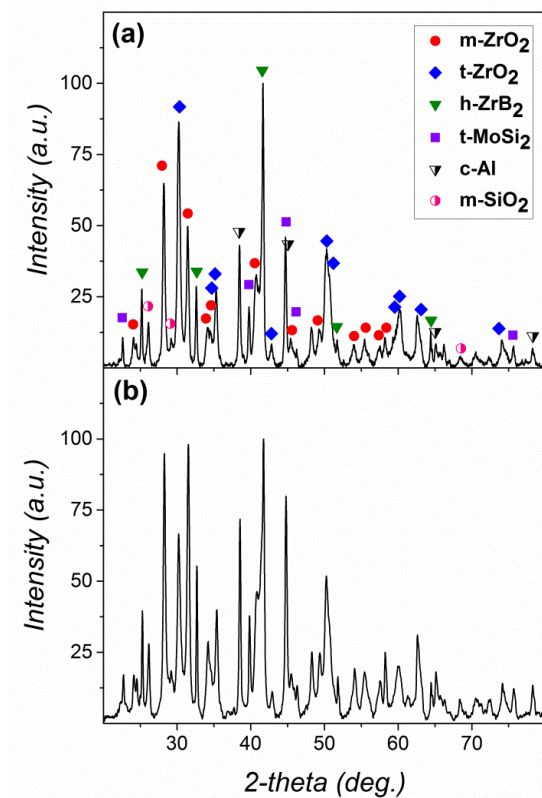
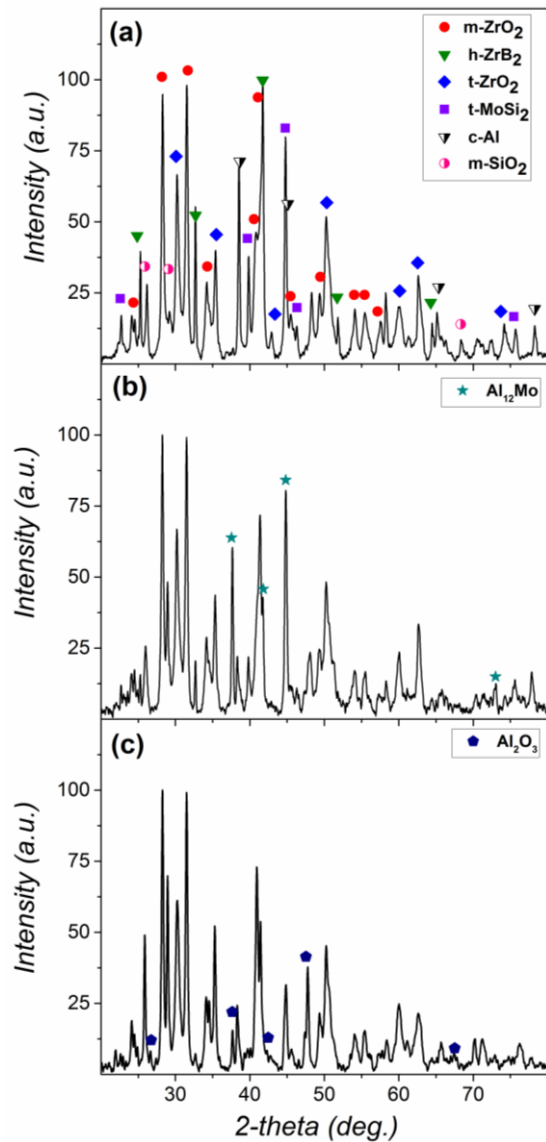**Figure 3.** XRD pattern of ZrB$_2$-35MoSi$_2$-15Al coating before (a) and after annealing at 457ºC (b).

Figure 4. XRD pattern of ZrB$_2$-35MoSi$_2$-15Al coating after annealing at 638ºC (a), 740ºC (b) and 953ºC (c)

Phase transformation at ~ 640ºC (Figure 4a) is caused by the formation of Al$_{12}$Mo phase with cubic crystal lattice. According to the Al-Mo phase diagram [8, 9] and literature data [10] the formation of Al$_{12}$Mo phase is thermodynamically possible at this temperature. At the moment of MoSi$_2$ oxidation, nanosized reaction products are formed, which are capable of forming Al$_{12}$Mo phase by mutual diffusion of aluminum and molybdenum at the interface below the melting point of aluminum [11]. Silicon is released in the form of silicon oxide (m-SiO$_2$), as evidenced by the increase in the intensity of reflexes corresponding to this phase with increasing annealing temperature (Figure 6). Evaporation of molybdenum oxide at this temperature is not observed, which is confirmed by the mass increase on the TGA curve in the 638ºC area. Complete destruction of molybdenum disilicide does not occur at this temperature.

Then the annealing temperature was increased to ~ 740ºC, according to the DSC data. The endothermic effect on the DSC curve at this temperature is due to the oxidation of zirconium diboride. Despite the high melting point of ZrB$_2$ (~3000º C), the destruction of zirconium diboride-based materials

starts at lower temperatures due to oxidation of components by air oxygen. Also the temperature ~740º C is characterized by the increase of monoclinic silicon oxide and aluminum oxide formation (Figure 4b).

When the annealing temperature increases above ~ 960ºC (Figure 4c), the complete oxidation of the initial substances occurs. At this temperature mullite with rhombic crystal lattice of $Al_{2.35}Si_{0.64}O_{4.82}$. composition begins to form in the coating. The free $m-SiO_2$ phase is preserved. The main phases at this temperature are $m-SiO_2$ and $m-ZrO_2$. The zirconium orthosilicate phase (zircon - $ZrSiO_4$) is also formed in the sample. In accordance with the ZrO_2-SiO_2 system state diagram [12], the formation of $ZrSiO_4$ with an impurity of oxides (ZrO_2 or SiO_2 depending on the initial material composition) is possible in this temperature range. The cubic zirconium oxide ($c-ZrO_2$) and corundum ($h-Al_2O_3$) phases are also formed at 953º C in the studied sample. The reflexes corresponding to $h-Al_2O_3$ have low intensity that can be connected with the formation of X-ray amorphous aluminosilicates. The qualitative phase composition at increasing temperature from 953 to 1155º C remains constant, but the quantitative ratio of the phases changes. The content of $ZrSiO_4$ and ZrO_2 increases, and the content of SiO_2 decreases. Temperature 1155º C is close to phase transition temperature of $m-ZrO_2$ to $t-ZrO_2$, but the formation of $t-ZrO_2$ phase does not occur. From the analysis of intensity distribution of reflexes corresponding SiO_2 it can be seen that when reaching 1155º C there is a sharp decrease of monoclinic silicon dioxide content (Figure 5).
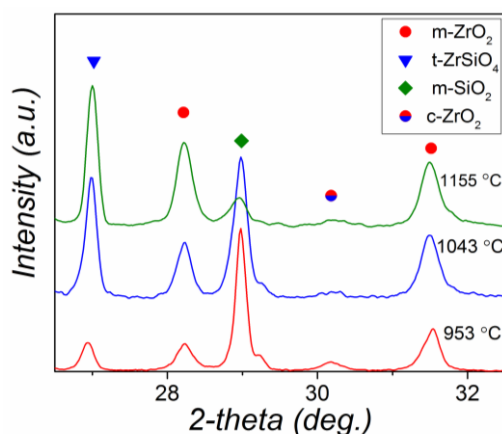

Figure 5. Change of relative intensity of diffraction peaks of $m-ZrO_2$, $t-ZriO_4$, $m-SiO_2$ and $c-ZrO_2$ in the temperature range 953 - 1155ºC.

When reaching the hyperthermal oxidation temperature of ~ 1050º C the coating has the following composition: $m-ZrO_2$, $ZrSiO_4$, $t-ZrO_2$, $m-SiO_2$ and mullite (Figure 7). The mullite content according to the X-ray phase analysis is close to the detection limit (the intensity of reflexes corresponding to mullite is close to the background value of intensity).

The endothermic effects on the DSC curve at temperatures ~ 1050ºC and ~ 1160ºC correspond to the formation of zircon. The qualitative phase composition remains constant as the temperature increases from ~ 960 to ~ 1160ºC (Fig. 7).

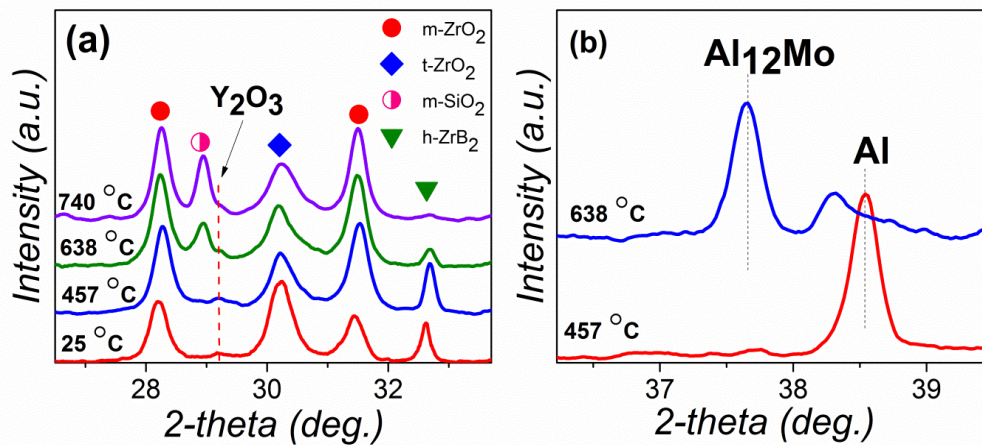**Figure 6.** Change of relative intensity of diffraction peaks:
(a) the m-ZrO$_2$, t-ZrO$_2$, m-SiO$_2$, and h-ZrB$_2$ phases in the temperature range 25 - 740 ºC;
(b) Al and Al$_{12}$Mo phases at increasing temperature from 457ºC to 638ºC.

There is a broad exothermic peak corresponding to the mullite formation (r-Al$_{2.35}$Si$_{0.64}$O$_{4.82}$) and simultaneous destruction of zircon (t-ZrSiO$_4$) in the temperature range 1220-1400ºC by DSC analysis of ZrB$_2$-35MoSi$_2$-15Al coating. Also, when the maximum temperature is reached, cubic zirconium dioxide (c-ZrO$_2$) is formed in the system (Figure 8).

In the composition of the coating ZrB$_2$-35MoSi$_2$-15Al studied by high-temperature XRA at the maximum temperature phases m-ZrO$_2$ and t-ZrSiO$_4$ remain, which can be explained by the insufficient time of annealing process under the conditions of this analysis.

On the TGA curves, the beginning of the weight loss effect is observed. This behavior of the TGA curve is due to the evaporation of molybdenum oxide. The absence of reflexes on the X-ray diffractograms can be explained by the formation of a solid solution with the coating components. The content of free molybdenum oxide in the form of X-ray amorphous phase is excluded, due to the fact that the boiling point of MoO$_3$ is 1155ºC, but at this temperature no weight loss was recorded. An increase in the annealing temperature does not lead to a change in the phase composition. A broad exothermic peak in the temperature range of 1220-1400ºC on the DTA curves corresponds to the final formation of the coating structure.
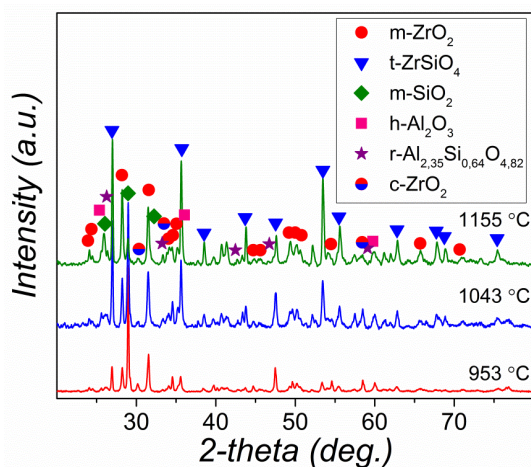

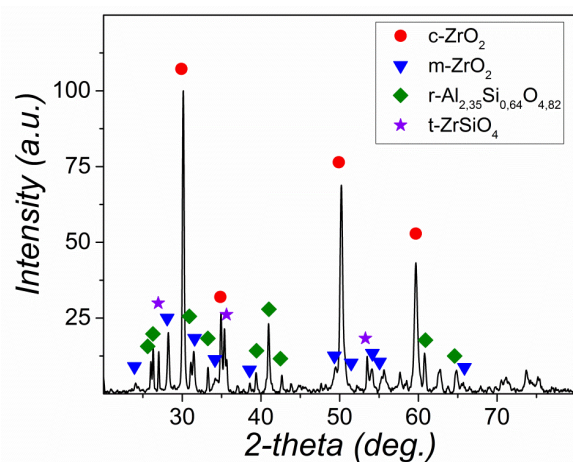**Figure 7.** XRD pattern of ZrB$_2$-35MoSi$_2$-15Al coatings after annealing at 953, 1043 and 1155°C.

Figure 8. XRD pattern of ZrB$_2$-35MoSi$_2$-15Al coatings after annealing at 1360ºC.

4. Summary

The phase transformations of composite coating ZrB_2-35$MoSi_2$-15Al obtained by multi-chamber detonation accelerator after annealing from 25 to 1400ºC were analyzed. It was found that at 460ºC crystallization of zirconium dioxide monocline phase (m-ZrO_2) occurs in the coating, at 640ºC $Al_{12}Mo$ and silicon oxide (m-SiO_2) is formed, at 740ºC aluminum oxide is formed. At annealing temperature of 960ºC there is a complete oxidation of the initial substances and the formation of mullite with rhombic crystal lattice. Zircon $ZrSiO_4$ is formed in the coating when the temperature reaches 1050ºC. Zircon (t-$ZrSiO_4$) decomposes at 1220-1400ºC.

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Acknowledgments