Particle-filled polymer derived ceramic coatings on titanium alloy Ti-6Al-4V

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Abstract

Thermodynamic analysis was carried out to predict the phase composition of polysilazane-type polymer derived ceramic coatings on a Ti-6Al-4V titanium alloy by calculating the most probable chemical reactions between the constituents and expected crystalline phases. The feasibility of polysilazane derived coatings on Ti-6Al-4V was proved experimentally. The coatings based on amorphous SiON and SiO_2 and a free Si, which oxidized to SiO_2 during high temperature exposure, enhance the oxidation resistance of Ti-6Al-4V alloy at 800 °C in air up to eight times compared to an uncoated alloy. Copyright © 2018 VBRI Press.

Keywords: Polymer derived ceramics, preceramic polymers, polysilazane, titanium alloys, oxidation barrier coatings.

Introduction

In the modern industry, titanium, as a material with a set of excellent physical and mechanical properties, is widely used in the manufacture of mechanical parts, tools and devices. There is a wide range of use in the most advanced industries due to a high specific strength, high-temperature strength (up to 500 ºC) and corrosion resistance in air, in a variety of salt solutions, in inorganic and in organic acids [**1**]. However, titanium and titanium alloys are characterized by some deficiencies that provide some restrictions in application as construction materials: poor heat resistance at medium and high temperatures and low resistance to high temperature gas corrosion.

Thus, to expand the variety of applications, novel concepts of corrosion and heat resistance increase are necessary. In this respect protective coatings based on components with high reactivity [**2**], in which a passive surface layer is formed, are under discussion, and the concept of polymer derived ceramics (PDCs) might deliver a successful coating strategy [**3, 4**]. PDCs can be obtained, e. g., from polysilazanes by a thermal treatment in nitrogen atmosphere, resulting in a SiOx or SiO(N) ceramic. The formation of elemental Si during thermal treatment facilitates the formation of additional SiO_2, which might act as a passivation layer on Ti and its alloys and provide a thermal stability of up to 1,000 °C and a parabolic oxidation kinetics [**5**]. The use of fillers reduces the shrinkage of the polysilazane precursor during polymer-to-ceramic transformation, which leads to an enhancement of the coating thickness, and it prevents from crack formation as the main drawback of the polymer derived precursor technique. In this work a variety of particulate fillers in a polysilazane derived matrix were investigated in PDC coating systems.

Experimental

In a first part of our investigations thermodynamic possible chemical reactions between polysilazane as a precursor, a pyrolysis gas (here: nitrogen) and constituents of the titanium alloy Ti-6Al-4V were studied. The isobaric-isothermal potential ΔG^o_T of possible phases of Ti, Al, V and Si-N_2-H_2-O_2 was calculated with the software package HSC Chemistry 7.16 (Outotec Oy, Pori, Finland). Based on these data the phase fraction of the most probable composition was calculated as a function of the temperature and the pyrolysis atmosphere.

In the experimental part of this paper titanium alloy Ti-6Al-4V (6 wt.% Al, 4 wt.% V) sheets were cut into samples of 15 mm×20 mm×1.5 mm, ground with SiC paper FEPA P1200 (17.3 µm to 19.3 µm) and cleaned in anacetone (80 %)/ethanol (20%) mixture by ultrasonic treatment and subsequent drying. As the preceramic polymer, a commercially available perhydrydopolysilazane (PHPS NN 120-20, Clariant Advanced Materials GmbH, Sulzbach, Germany,) was chosen. SiC, BN, and $TiSi_2$+B powders (~ 5µm) were mixed with the PHPS precursor in a volume ratio of 60 polymer and40 filler.

A dip coating method was applied for coating with a withdrawal speed of 3 mm/s, and the time of sample holding was 10 s. Coated samples were heated to 110 °C using a slope of 2 K / min^{-1} in air to allow cross-linking for 1 h - 1.5 h. The pyrolysis was conducted in nitrogen atmosphere in a high temperature furnace (HTRRH 70-600/18, Fa.Gero Hochtemperaturöfen GmbH & Co. KG, Neuhausen) at 800 ˚C using a heating and cooling rate of 3 K / min^{-1}; the holding time was 1 h.

The thermal behavior of the coating slurries was analyzed with a simultaneous thermal analyser (STA 449 F3 Jupiter, Netzsch-Gerätebau GmbH, Selb, Germany) in accordance with the thermal treatment of the coating – in nitrogen atmosphere – at 800 ºC with a heating/cooling rate of 3 K min^{-1}.

The pyrolyzed materials were characterized with respect to their phase composition and microstructure. X-ray diffraction analysis was carried out with a X-ray powder diffractometer (PANalytical GmbH, Kassel) with Cu Kα - radiation (λ = 0,1541 nm) with a standard 2θ arrangement.

Light microscopy (Zeiss, Axiovert 200 M) and scanning electron microscopy (SEM; FEI ESEM XL30 FEG) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector (EDS analysis system DX-4, EDAX Business unit, Ametek GmbH Wiesbaden, Germany) were applied for the investigation of the microstructure and the chemical composition.

Isothermal oxidation tests were conducted in a convection furnace (Model L9/S17, Nabertherm, Lilienthal) at 800 ºC in steps of 8 h, 36 h and 80 h. The specific mass change of the coated samples was carefully measured using an analytical balance with an accuracy of 0.0001 grams. The microstructural features of the oxidized samples were studied by SEM, exemplarily.

Results and discussion

Thermodynamic conditions of the polysilazane deposition on Ti-6Al-4V alloy

To estimate the feasibility of polysilazane coatings on Ti-6Al-4V alloy, the chemical reactions of PHPS with the titanium alloy constituents were analyzed with the help of thermodynamic calculations. The driving force of the reactants' interplay under given conditions is a change of the isobaric-isothermal potential, ΔG^o_T. Under standard conditions, when the initial activity of the *i*-th substance in the equilibrium is $a_i^\circ = 1$ or gas P_i° = 101,325 Pa, the value of ΔG^o_T is associated with equation (1.1) [**6**]:

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ \quad (1.1)$$

where ΔH_T° is the standard enthalpy change (heat of reaction) and ΔS_T° is the standard entropy change.

In a result of the polysilazane interaction with the titanium matrix the formation of Si_3N_4 is possible according to the following reaction equation:

$$3Si+3H_2(g)+3N_2(g)=Si_3N_4+2NH_3(g) \quad (1.2)$$

In the presence of oxygen as a component of air, which is incorporated during cross-linking of the polymer precursor, the formation of other silicon phases, Si_2N_2O and SiO_2 may occur (eqns. (1.3 and 1.4):

$$4Si+3H_2(g)+3N_2(g)+O_2(g)=2Si_2N_2O+2NH_3(g) \quad (1.3)$$
$$Si+3H_2(g)+N_2(g)+O_2(g)=SiO_2+2NH_3(g) \quad (1.4),$$

where the formation of Si_2N_2O is thermodynamically more possible than the formation of SiO_2, but to a smaller extent as of Si_3N_4. This is explained by a higher chemical affinity of silicon to nitrogen than to oxygen, [**7**]. In turn, Ti is characterized by a strong chemical affinity to oxygen, higher to that of nitrogen [8, 9], the standard electrode potential is in a range of -1.2 to -2.0 V for the Ti ↔ Ti^{3+} electrode reactions [**9**], that points out the formation of a TiO_2 (rutile) layer on the surface of titanium alloys even at room temperature. Experimentally it was found that a strongly adherent rutile film accrued after 1–2 hours in the presence of oxygen, when titanium alloy was exposed to air [**8**]. Therefore, the presence of oxygen should be taken into account in thermodynamic calculations of polysilazane and titanium alloy interplay.

Among others, TiN and $TiSi_2$ phases have a high thermodynamic probability of formation, please see eqns. (1.5) and (1.6):

$$6Si(g) + 3N_2(g) + 3H_2(g) + Ti + O_2(g) = Si_3N_4 + TiSi_2 + SiO_2 + 2NH_3(g) \quad (1.5)$$

$$4Si + 4N_2(g) + 3H_2(g) + 2Ti + O_2(g) = Si_3N_4 + 2TiN + SiO_2 + 2NH_3(g) \quad (1.6)$$

Taking into account 6.18 wt.% of Al and 4.76 wt.% of V within the Ti-6Al-4V alloy, VSi_2, VO_2, V_2O_3, V_3O_5, VN and AlN, Al_2SiO_5, Al_2O_3 might be present in the system. According to our calculations, vanadium primarily react with silicon to form VSi_2, while aluminum reacts with N_2 forming AlN. The formation of VO_2 or VN has 7mostly equal thermodynamic chances, (eqns. (1.7 and 1.8):

$$8Si(g) + 3N_2(g) + Al + V + 2Ti + O_2(g) = 2Si_2N_2O + TiSi_2 + TiN + VSi_2 + AlN \quad (1.7)$$

$$5Si(g) + 2N_2(g) + 2Al + V + 2Ti + 3O_2(g) = Si_2N_2O + TiSi_2 + TiN + VN + Al_2SiO_5 \quad (1.8)$$

In a further step the equilibrium of expected phases of the reaction medium in a closed system with maximum entropy was calculated between 200 °C and 1000 ºC for a system that includes Si, N_2, H_2, Ti, Al, V; the presence of oxygen was considered, please see table.1. For all systems studied the calculations were carried out under nitrogen atmosphere.

Table 1. Molar concentration of the constituents and temperature range for the system (Si-N_2-H_2-Ti-Al-V).

Process parameters:	
Temperature range	200-1000 ºC
Components amount	mol
N_2	0.152
H_2	0.024
Si	0.213
Ti	0.050
Al	0.0006
V	0.0004
O_2	0.001-0.010

According to the above calculations of the equilibrium of the expected phases in the systems Si-N_2-H_2-Ti-Al-V and Si-N_2-H_2-O_2-Ti-Al-V, the thermodynamically most probable combinations of chemical compositions are: (Si_3N_4 + TiN + $TiSi_2$), (Si_3N_4 + TiN + Si_2N_2O), (Si_2N_2O+$TiSi_2$+TiN) and (Si_2N_2O+$TiSi_2$+SiO_2). The quantitative phase compositions are shown in, **Fig. 1, 2.**

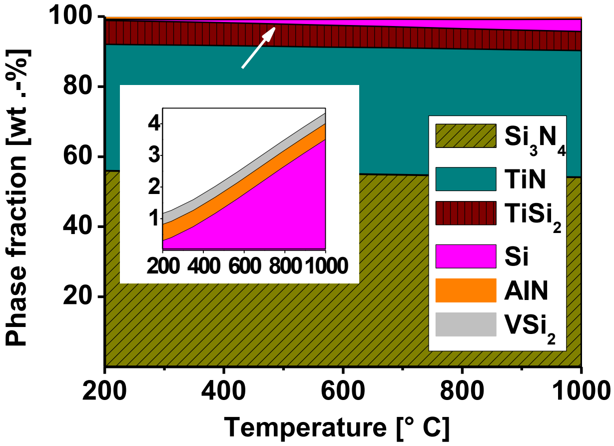

Fig. 1. Phase equilibrium of the system Si-N_2-H_2-Ti-Al-V=(0.213-0.152-0.024-0.050-0.0006-0.0004) mol.

The amount of the Si_3N_4 phase remained high (45.5-55.5 wt.%) over the entire temperature range. The TiN amount remained stable at 37.5 wt.% throughout the temperature range studied. In the presence of oxygen (0.01 mol) in the Si-N_2-H_2-Ti-Al-V system 13.5-14.0 wt.% of silicon oxynitride (Si_2N_2O) and 1.8 wt.% of silica (SiO_2) occurred, please see eqns. (1.5) -(1.8). The SiO_2 phase has a high thermodynamic stability up to 1725 °C, [**10**], and the diffusion coefficient of oxygen in silica is quite low, [**11**]. As a part of the coatings system, SiO_2 provides a high oxidation resistance, and its growth obeys a parabolic rate law when formed by the oxidation of silicon [**12**]:

$$x\,dx = k'\,dt \tag{1.9}$$

where x is the oxide thickness, t is the time and k' is the parabolic rate constant for oxidation.

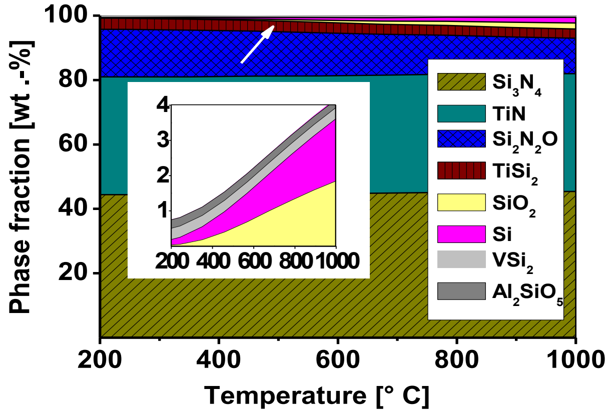

Fig. 2. Phase equilibrium of the system Si-N_2-H_2-O_2-Ti-Al-V = (0.213-0.152-0.024-0.010-0.050-0.0006-0.0004) mol.

Also, the free silicon of the PHPS precursor [**5**] will react with O_2 during to form a glassy layer which may have self-healing properties.

Phase composition of the coating layers

The use of BN, Si_3N_4, SiC, and ZrO_2 agents as passive fillers in a PDC matrix was demonstrated for mild (1.0037) and stainless steels (AISI 304, AISI 430) as coating systems [**13**], [**14**]. Dierdorf *et al.* [**13**] and Kraus *et al.* [**14**] figured out, that BN flakes lead to a coating thickness of 5 µm to 20 µm depending on the dip-coating speed and the particle suspension concentration within the suspension. The obtained composite coatings with a filler content of 40 vol.% reduced crack formation in the coating layers, and they showed a parabolic oxidation kinetics at 500 °C up to 100 h. Less successful were zirconia-filled coatings due to inhomogeneities caused by a particle settlement; this results in very thin coatings [**13**].

The use of filler in this work was predetermined by the refractory properties of the materials and limited data in the literature of their application on titanium substrate.

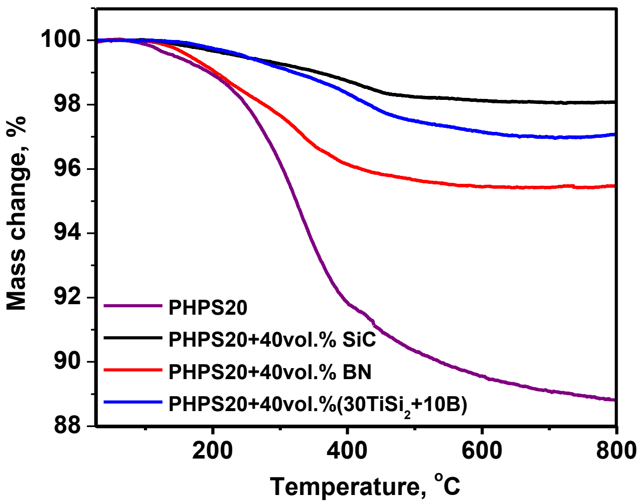

Fig. 3. TGA measurements of plain PHPS and PHPS/40 filler vol.%. powders (SiC, BN, $TiSi_2$+B) in nitrogen atmosphere.

To obtain information about the polymer-to-ceramic transformation, the PHPS/fillers mixtures were characterized with thermal analysis (TGA). TGA measurements, see **Fig. 3,** of the pyrolysis behavior of plain PHPS and with SiC, BN, and $TiSi_2$+B (40 vol.%) fine powders were carried out in N_2 atmosphere at 800 °C.

According to TGA, the cross-linking of the PHPS continues up to 150 °C, some mass change was detected at this temperature. In the temperature range between 150 °C – 700 °C, a significant weight loss for PHPS was observed that reflects a pyrolysis. For PHPS + 40 vol.% SiC and BN powders the cross-linking process occurs approximately at 180 °C – 220 °C, and pyrolysis takes place up to 600 °C. These results coincide well with those of Günthner *et al.* [**3, 5**] for thermo-gravimetric analyses of PHPS fine powder pyrolyzed in nitrogen at 1000 °C. They also detected a mass loss of PHPS in the temperature range from 200 °C – 700 °C.

The mass loss of plain PHPS caused by pyrolysis is 11.5%, which is at least four times higher than that of PHPS with fillers. The ceramic yield of PHPS with 40 vol.% BN after thermal treatment at 800 °C is 95.8 wt.%, PHPS + 40 vol.% SiC – 98.8 wt.% and PHPS + 40 vol.% $TiSi_2$+B – 97.4 wt.%. Thus, less shrinkage of the coatings with fillers is expected, as well as higher thickness and more stable oxidation properties in comparison to samples with plain PHPS.

Phase analysis was carried out with X-ray powder diffractometry after pyrolysis at 800 °C in nitrogen atmosphere.

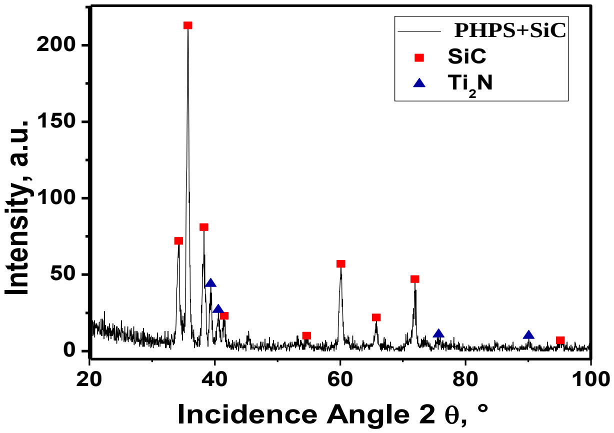

Fig. 4. XRD analysis of PHPS + 40 vol.% SiC coatings on titanium alloy substate.

XRD powder patterns, **Fig. 4, Fig. 5,** of PHPS + 40 vol.% SiC and PHPS + 40 vol.% BN demonstrate crystalline fillers and Ti_2N phase formation in the coating layer. The occurrence of other phases including Si_2N_2O, Si_3N_4, SiO_2, that were found in thermodynamic calculations were not detected by XRD. However, according to the EDS investigations of the coatings, an increased amount of Si 8.5-10.6 wt.%, O_2 6.6-10.4 wt.% and N_2 9.6-10.8 wt.% in the distance of 23,0-26,0 µm from the surface of the sample was observed. The formation of amorphous SiON and SiO_2 phases was deduced, embeddedat the interface coating/substrate. Also, the content of 40.0-41.5 wt. % Ti and a high amount of N_2 gives evidence for Ti_2N formation at the interface.

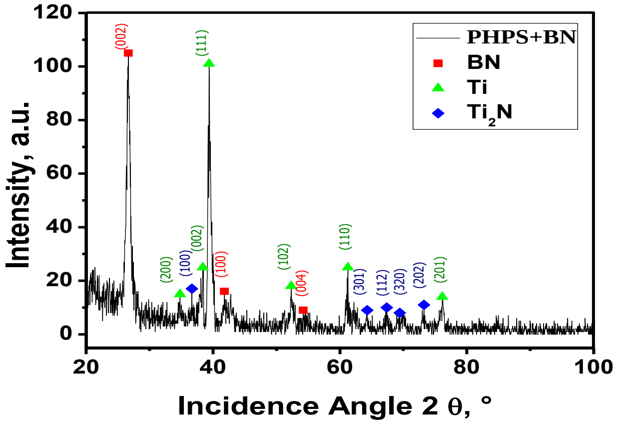

Fig. 5. XRD analysis of PHPS + 40 vol.% BN coatings on titanium alloy substate.

The microstructuree of the coatingsis shown in **Fig. 6.** The interface layers appear in a light-gray line having athickness of 3.0 µm – 5.0 µm.

The interlayer is formed over the entire cross section of the samples. The total thickness of the coatings is 20.0 µm – 25.0 µm, and is characterized by continuity along the length of the speciments without any phase segregation.

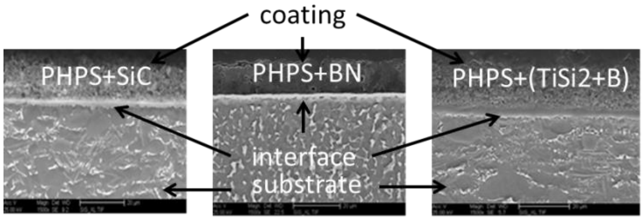

Fig. 6. SEM images of PHPS+40 vol.% filler (left: SiC; middle: BN; right: $TiSi_2$ + B) coatings on Ti-6Al-4V titanium alloy.

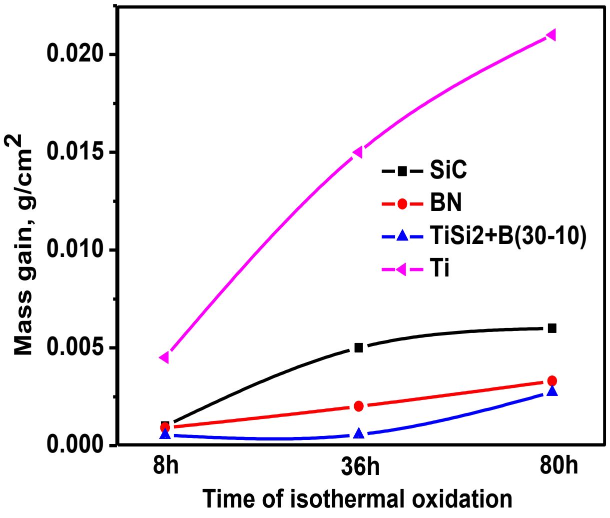

Fig. 7. Mass gain of PHPS coated samples and pure Ti-6Al-4V titanium alloy.

Oxidation behavior of PHPS coatings

Isothermal oxidation tests were conducted with a plain and with PDCs coated Ti-6Al-4V. The influence of the coatings on the weight change of the samples in the air atmosphere at the temperature of 800 ºC during 80 hours was investigated. Five parallel tests were performed for each holding time, for which the average rate of oxidation index Km, g/(sm^{2}·h) was calculated, **Fig. 7.** The experimental data show an exponential growth of the weight gain of the samples as a function of time of exposure.

The coatings provide a significant oxidation protecting effect on the Ti-6Al-4V substrate: oxidation of the PHPS coated samples practically does not occur up to 80 h of exposure. The mass gain of the coated samples does not exceed 0.003 g/sm^2 after 80 hours of isothermal hold, when for uncoated sample it equals to 0.023 g/sm^2. Therefore, the coating layer formation at the surface of the titanium alloy Ti-6Al-4V promotes its oxidation resistance with an increase by the factor eight in times.

The order of the oxidation rate of the Ti-6Al-4V alloy is caused by formation of a brittle rutile TiO_2 layer on the surface of the samples. This layer is not attached to the basic alloy, thus it is easily destroyed in the temperature range from 400 °C - 800 °C [**15**], and this facilitates access of oxygen to the alloy matrix. According to macroscopic investigations of the samples without coatings oxidized at 800 ºC during 80 h, they had dark red color that is typical for rutile film [**15**], while the PHPS-coated samples remained light gray. A spalling off of the coatings on the Ti alloy in the all-time of exposure experiments was not observed.

Conclusion

In the present study thermodynamic conditions of the polysilazane-type PDC coatings deposition on titanium alloy Ti-6Al-4V were studied. Based on Free Gibbs Energy calculations of the most probable chemical reactions, which occur between the precursor and the titanium matrix, and the equilibrium content of active gas and condensed phases of Si-N_2-H_2-Ti-Al-V and Si-N_2-H_2-O_2-Ti-Al-V systems, a phase composition of the coatings was predicted and proven experimentally. A significant difference in theoretical and resulting phase composition of the coatings was observed. The reason for this deviation is that reactions might occur only in surface-near regions and the reaction rate is affected by the diffusion of reactants throughout the already formed layers. However, these coatings enhance the oxidation resistance of the Ti-6Al-4V alloy at 800 ºC by eight times due to amorphous SiON and SiO_2 layer formation. Additionally, elemental Si, formed from polysilazanes by a thermal treatment, facilitates SiO_2 formation to form a passivation layer, and acts as a promising oxidation resistant barrier coating at high temperatures for titanium alloys.

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