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Multi Component Powder Injection Moulding of Metal-Ceramic-Composites

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Abstract

Two-component powder injection moulding is a new processing route in powder technology that can be used for the manufacturing of complex shaped metal-ceramic composites in large scale. The following work presents two process variants known from polymer injection moulding (multi component injection moulding and inmould labeling) to achieve a co-sintered metal-ceramic component containing steel 17-4PH and yttria stabilized ZrO_2. The chemistry of the metal-ceramic interface is determined by x-ray analysis and electron microscopy respectively. The strength of the joining zone is determined by tensile test. The composition of the metal and the ceramic material was systematically modified to achieve an adjusted sintering shrinkage and a chemical compatibility between both materials respectively.

1. Introduction

Metal-ceramic material compounds combine the ductility of metal components with the high strength and temperature resistance of ceramic materials. The combination of both materials in just one component leads to a higher functional density and can be seen in relation to the miniaturization of the component. Both aspects secure the economical relevance of multifunctional metal-ceramic-components in terms of a compulsive developing criterion. The profile of requirements towards the metal-ceramic component is complex and determines its design as well as the available manufacturing technology. The two process variants multi component injection moulding (2C-PIM, figure 1) and inmould labelling (figure 2), established in polymer shaping, are used in the following work for manufacturing of metal-ceramic material compounds starting from powder materials.

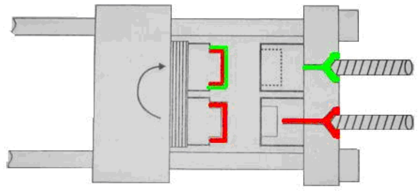


Figure 1 - 2C-PIM via rotating mould tool

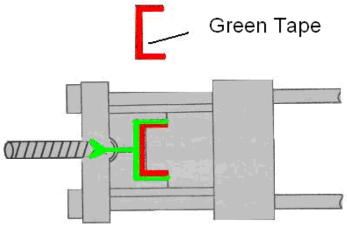


Figure 2 - Inmould labeling

Contrary to the 2C-PIM where two thermoplastic feedstocks are combined with each other in inmould labelling the first material component is inserted into the mould cavity as a powder technological semi finished part (green tape) whereas the feedstock is injected afterwards. The process variant inmould labelling widens the possibilities of multi component powder injection moulding by two appreciable degrees of freedom. Thus, the thin (50µm up to 1mm) green tapes allow the realization of aspect ratios which cannot be reached in regular powder injection moulding, because of the limitation of the feedstock flowability. Furthermore, the semi finished product “green tape” can be modified in its composition layer by layer so that a tailoring of a gradient between metal and ceramic powders becomes possible. If the development of green tapes would allow to deep draw and die cut them, they could be inserted in a three dimensional shaped mould cavity. Thus, a green tape can be used as functional surface or as an intermediated bonding layer. The principal feasibility of metal-ceramic material compounds has to be considered always from two points of view, the material system and the available manufacturing technology (figure 3). The cardinal question is the durability of the adhesion between two materials with metallic bindings on the one side and ionic/covalent bindings at the other side, especially how to reach a chemical adhesion. There are works known in basic material research that describe the properties and boundary conditions of metal ceramic compounds via ab initio calculations [1]. However, in this case the technological development also depends from empirical value. With historical evidence the expression functional gradient materials (FGM) subsumes a group of defined, tailor made, powder technological metal ceramic compounds for the first time [2]. The so called active brazing has to be mentioned here as the process in terms of the state of the art for joining metals with ceramics [3]. The concept for the manufacturing of metal-ceramic compounds presented in this contribution is absolutely new and combines the aspects of shaping and joining in just one processing step.

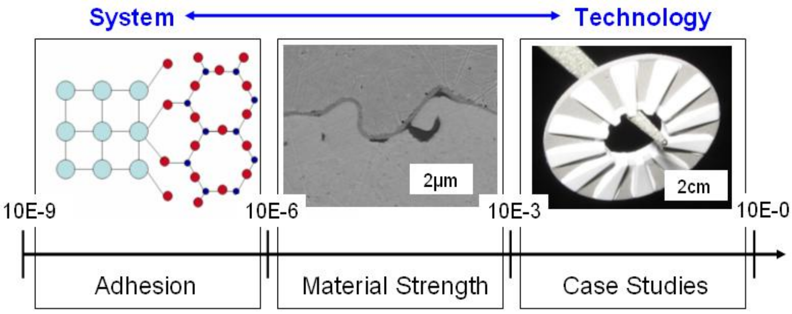


Figure 3 - Aspect levels of metal-ceramic material compound

2. Material and processing

2.1 Material specification

Prerequisite for obtaining a metal-ceramic compound by powder technology is the successful co-sintering of the chosen powder materials. This has to be realized for both material partners under identical temperature conditions and kiln atmosphere. Considering the thermal shock resistance it is necessary that the thermal expansion coefficients of both materials are quite similar. The chosen system stainless steel 17-4PH and yttria stabilized ZrO_2 meets this conditions. Both materials have got a thermal expansion coefficient between 11 x 10^{-6} K^{-1} and 12 x 10^{-6} K^{-1}. The results in this contribution were strictly done in the system 17-4PH (Sandvik Osprey; 80 % < 22 µm) and ZrO_2 (Tosoh Ltd.; TZ-3Y-E and Unitec Ceramics Ltd.; Y5-5). To modify the reference steel alloy (17-4PH) and initiate a better adhesion between metallic and ceramic material 2 % titanium powder (< 45 µm) were mixed to the 17-4PH powder. The adjusted sintering shrinkage in the 17-4PH green tape, the 17-4PH feedstock and the ZrO_2 feedstock were approx. 15 % in linear (figure 4). To obtain a green density of 60 vol % in the ZrO_2-feedstock it was necessary to use a mixture of fine TZ-3Y-E and coarse Y5-5 powder (1 : 3 wt %).

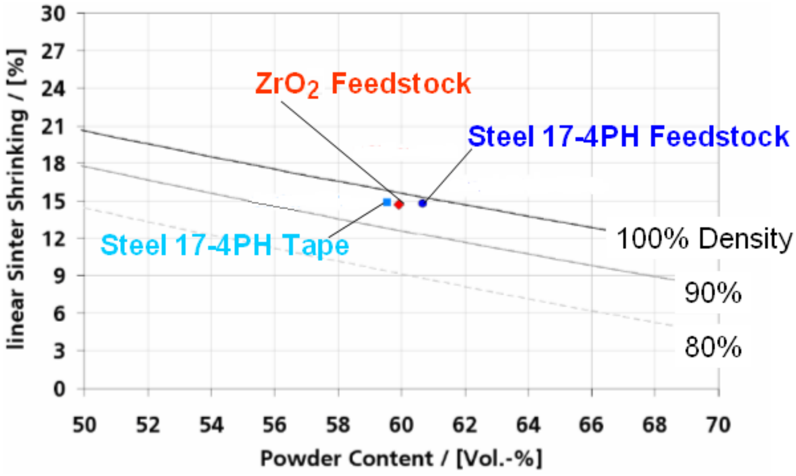


Figure 4 - Material specification

2.2 Material preparation

For the feedstock preparation the powders are mixed with a thermoplastic binder (based on polyamide) at temperatures up to 150 °C in a sigma kneader for 3 h. Afterwards the premix is put on a shear roll extruder for homogenisation and granulation. The obtained feedstock is applied to the process of PIM. For the preparation of green tapes a slurry based on water and PVA is used. The dispersion is mixed and homogenised by means of a ball mill. Green tapes are fabricated by the doctor blade method. After drying the green tape is die cut and applied to the mould cavity for inmould labeling. For PIM a 2C-PIM machine from Arburg GmbH & Co. KG (Allrounder 320S 500-60) was used.

2.3 Sample processing and characterisation

All samples were debinded by extraction in acetone (Δm ca. 45 %) for 30 h at 50 °C. Afterwards they were debinded by thermal heat treatment during the co-firing step that was carried out under hydrogen atmosphere at 600°C. The co-sintering took place at 1350 °C under hydrogen atmosphere using a vacuum gas sinter kiln from Heidorn Engineering GmbH. The co-sintered material compounds (tensile specimens) were determined by electron microscopy, x-ray diffractometry and tensile tests. The process feasibility is proven by two case studies.

3. Results and discussion

3.1 Analysis of the interface in the metal-ceramic compound

Microscopic images of the interface between the co-sintered material compound containing steel 17-4PH and ZrO_2 and 17-4PH + 2 % Ti and ZrO_2 show the structures in figure 5. While the metal component in the reference system 17-4PH becomes dense the modified system 17-4PH (+2% Ti) shows some macro pores as a result of the added titanium powder. Both material systems show a defect-free interface. By increasing the resolution of the sample interface considering the reference system 17-4PH and ZrO_2 in figure 6 a ca. 0.1 µm thin interlayer can be seen. X-ray analysis proof that the alloying elements of steel 17-4PH, chromium, and silicon diffuse into the interface, forming an oxide layer and resulting in a chemical adhesion between metal and ceramic component during co-sintering. Driving force for the diffusion of these elements is the high affinity to the oxygen of the zirconia ceramic. This notice leads to the cognition that elements with high affinity to oxygen especially refractory metals can be used as adhesive agents. Either they are part of the metal alloy, or they can be added to the metal powder as powder material [4]. The subsequent co-sintering step under reducing atmosphere forces the diffusion of these elements into the interface, and an adhesive interlayer of metal oxides is formed.

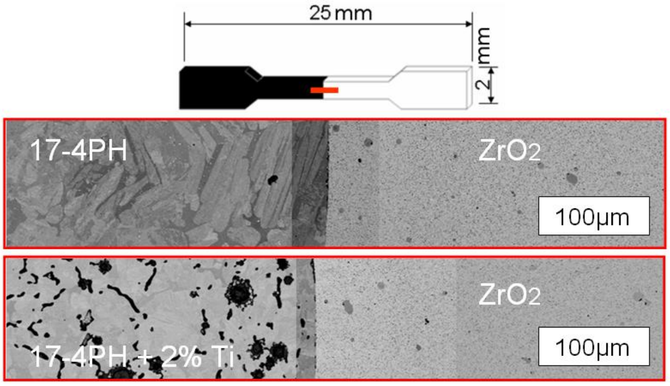


Figure 5 - Metal-ceramic interface from co-sintered test specimens considering the reference system 17-4PH and ZrO_2 (above) and the modified system 17-4PH + 2% Ti and ZrO_2 (below)

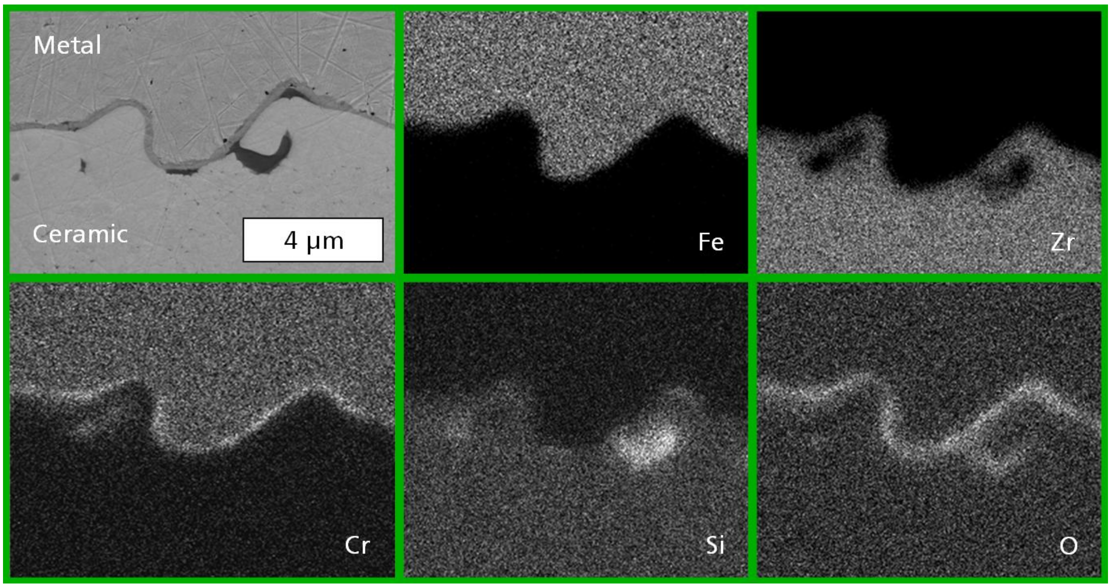
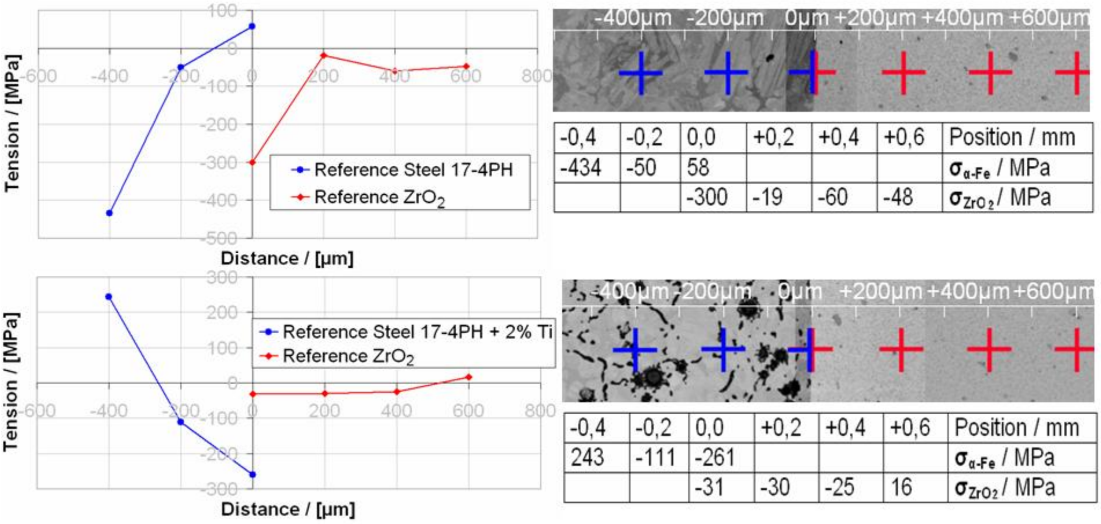


Figure 6 - EDX analysis of co-sintered interface of the reference system

3.2 Tensions in the injection moulded metal-ceramic compound

X-ray diffractometry considering the iron lattice in metal component and the ZrO_2 lattice in ceramic component of both co-sintered material systems allow to detect the material tensions shown in figure 7. Six measuring points with a diameter of 100 µm were taken within a distance of 200 µm from each other crossing the interface. Material tensions could be detected in the iron lattice mainly. The reference sample containing 17-4PH and ZrO_2 is characterised by compressive stress with values up to 434 MPa at a distance from 400 µm from interface in the iron lattice. The metal component in the modified system 17-4PH + 2 % Ti and ZrO_2 shows tensile stress with values up to 243 MPa at a distance from 400 µm that is turning into compressive stress with values up to 261MPa directly in the interface. In the modified system the metal component does not become fully dense as can be seen in the microscopic image at figure 7 (below). This seems to be correlated with the difference of tension measured in iron lattice and ZrO_2 lattice at the intact interface. While the reference system 17-4PH and ZrO_2 which becomes dense in both components shows a difference from 358 MPa, the modified system 17-4PH + 2 % Ti and ZrO_2, those metal component has got some macro pores, only shows a difference from 230 MPa at the interface. Furthermore, it is shown that the ZrO_2 lattice is influenced by tensions near the interface, when the corresponding metal component is completely densified during co-sintering (figure 7 above). If not, the ZrO_2 lattice is free of tensions and the zero crossing from tensile stress into compressive stress in the metal component takes place at a farer distance from interface as it is shown in figure 7 below.



-0,4	-0,2	0,0	+0,2	+0,4	+0,6	Position / mm
-434	-50	58				$\sigma_{\alpha\text{-}Fe}$ / MPa
		-300	-19	-60	-48	σ_{ZrO_2} / MPa

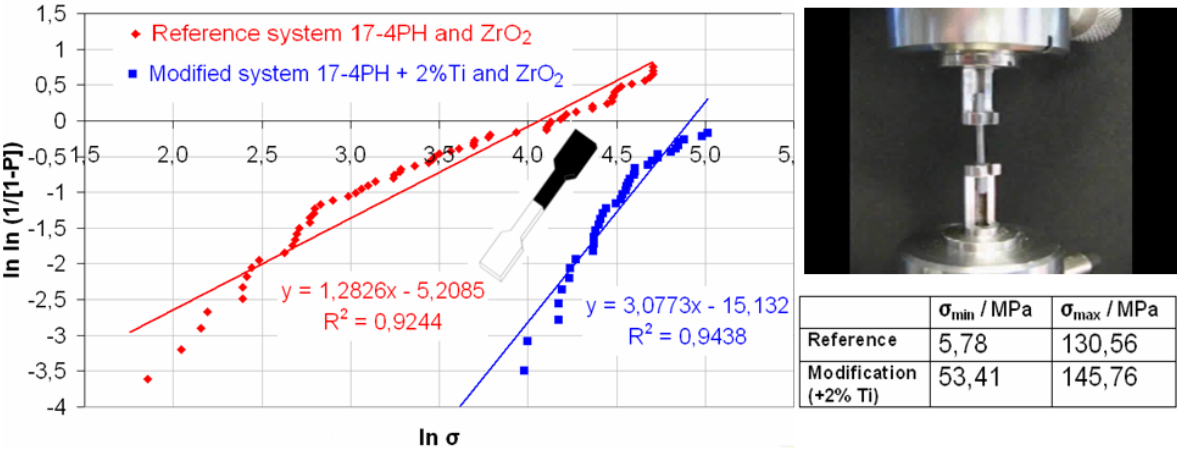
-0,4	-0,2	0,0	+0,2	+0,4	+0,6	Position / mm
243	-111	-261				$\sigma_{\alpha\text{-}Fe}$ / MPa
		-31	-30	-25	16	σ_{ZrO_2} / MPa

Figure 7 - Material tensions determined by x-ray diffractometry

3.3 Mechanical strength of sintered metal-ceramic compounds

To get to reliable characteristics of the strength of the metal ceramic compounds which are not influenced by defects coming from the obligatory technological process management (e.g. airpockets) the sample geometry was minimized up to micro tensile specimens with an interface in the green body of just $1mm^2$. This leads also to the exclusion of the risk of delaminations arising during the co-firing step caused by mismatches in thermal expansion or in sinter shrinking which still can occure in macroscopic components even when the green densities and the absolute values of sinter shrinking are well adjusted as it is shown in chapter 2.1. This procedure ensures that the material strength in the metal-ceramic compound which was achieved during co-sintering is not influenced by defects from the manufacturing process. The applied mechanism for initiating a chemical adhesion between metal and ceramic component during the subsequently co-sintering step is reported in [4]. Figure 8 shows the Weibull distributions of the tensile strengths determined for the reference system 17-4PH and ZrO_2 such as for the modified system 17-4PH + 2 % Ti and ZrO_2. Considering the measurements in the reference system 17-4PH and ZrO_2 63 % of the sample specimens broke at tensions up to 53 MPa (m = 1,3). The measurements in the modified system 17-4PH + 2% Ti and ZrO_2 however shows tensile strengths from up to 146

MPa (m = 3,1). The results prove in principle that the initiation of a chemical adhesion between stainless steel (17-4PH) and ZrO_2 by the use of the multi component powder injection moulding and subsequently co-sintering is possible. Furthermore it has been proven that the material strength of the metal-ceramic compound can be significantly increased by the use of refractory metals (e.g. titanium) which were added to the metal alloy.



	σ_{min} / MPa	σ_{max} / MPa
Reference	5,78	130,56
Modification (+2% Ti)	53,41	145,76

Figure 8 - Mechanical tensile strengths of micro tensile samples

3.4 Case studies

The process variants 2C-PIM and inmould labelling which are described above have got a high potential in industry for the economical production of microscopic and macroscopic metal-ceramic material compounds. It was shown that the manufacturing of specified co-sintered microscopic metal-ceramic (tensile-) specimens in large scale is feasible under statistically safe conditions. First-time the process capability was demonstrated by the following case studies. Figure 9 shows a gear wheel (designed by Robert Bosch GmbH within the European Project CarCIM) with an outer ring made of steel 17-4PH and a concentric inner ring that is made of wear protecting ZrO_2-ceramic. This component was manufactured by combining a metal and ceramic feedstock in the 2C-PIM process. Figure 10 shows a thread guide for textile machinery (designed by Rauschert Heinersdorf-Pressig GmbH) which was manufactured by the inmould labelling process. Therefore a green tape of steel 17-4PH powder was die cut and inserted into the mould cavity before a ZrO_2-feedstock was injected. Both case studies are applications for dynamic systems which will be stressed by rotation force and wear mechanisms. The necessary condition for the functionality of these components containing a metal-ceramic material compound is given by the results of the material development and characterization described above and is supported by the concentric design of the material interface.

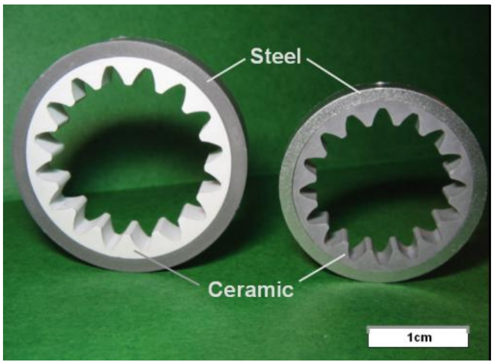


Figure 9 - Case study gear wheel, (green and as fired) manufactured by regular 2C-PIM - Design by Robert Bosch GmbH (diameter 24mm)

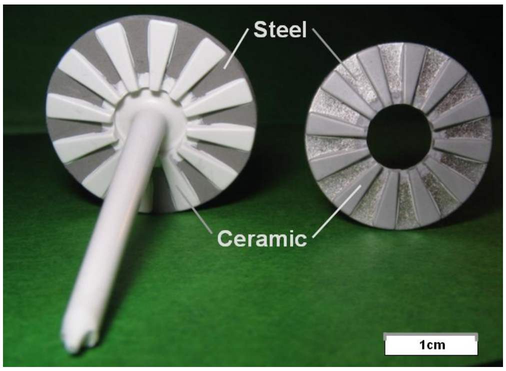


Figure 10 - Case study thread guide, (green and as fired) manufactured by inmould labeling - Design by Rauschert-Heinersdorf Pressig GmbH (diameter 20mm)

4. Conclusions

Starting with powder selection and characterization the feasibility of multi component powder injection moulding and co-firing the material compound, considering the system 17-4PH and ZrO_2, has been shown. By using the two process variants 2C-PIM and inmould labeling it was possible to manufacture testing samples containing a ceramic and a metallic component which were co-sintered under hydrogen atmosphere at 1350 °C with an adjusted sinter shrinking of 15 % (linear) leading to densities of at least 95 % (ZrO_2) and 97% (17-4PH) respectively. The combination metal-ceramic has been achieved with two material systems considering the combination of regular 17-4PH and ZrO_2 as well as modified 17-4PH with 2 % titanium powder and ZrO_2 respectively. For characterizing the chosen material systems injection moulded tensile specimens with an interface area of $1mm^2$ were used. The metal-ceramic interface was analyzed by electron microscopy and x-ray diffractometry. It could be observed that a ca. 0.1 µm (in some cases up to 10 µm) thick interlayer containing metal oxides (chromium oxide and silica) as well as intermetallic phases were formed during the co-sintering step in the interface of the material compound. Material tensions were measured by x-ray diffractometry considering the iron and the ZrO_2 lattice by using the reflexes 311 for iron and 313 and 331 for the ZrO_2. It was shown that lattice distortions only could be detected in the metallic component of the compound. The reference samples containing 17-4PH and ZrO_2 showed a compressive stress of 434 MPa in the metallic component whereas the modified sample containing 17-4PH + 2%Ti and ZrO_2 showed a tension stress of 243 MPa in the metallic component. The difference in stresses measured at iron and ZrO_2-lattice at the interface is 358 MPa for the reference system containing 17-4PH and ZrO_2 and 230 MPa for the modified system containing 17-4PH + 2%Ti and ZrO_2 respectively. The tensile strength which was determined in both material systems showed values between 6 MPa and 131 MPa for the reference system containing 17-4PH and ZrO_2 and values between 54 MPa and 146 MPa for the modified system containing 17-4PH + 2 %Ti and ZrO_2. The differences in the stresses seem to be in correlation with the tensile strengths. The higher the difference of material stress at the interface of the co-sintered material compound the lower the tensile strength. Furthermore, it could be shown that the addition of 2 % titanium powder to the steel 17-4PH powder leads to a higher tensile strength. This effect is due to the high affinity of titanium to the oxygen of the zirconia ceramic which becomes reduced during the co-sintering step by the titanium at the interface. The feasibility of the 2C-PIM process for manufacturing of metal-ceramic-compounds using the determined material system has been shown by two case studies - a metal-ceramic thread guide for textile machines (BMWi project GreenTaPIM) and a gear wheel with a ceramic insert for automotive applications (EU project CarCIM).

Acknowledgement

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