Investigations on the sintering response of steel-ceramic composites

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Abstract: Purpose of this article is the evaluation of the influence of sintering parameters on the microstructure evolution and mechanical properties of pressureless sintered metal matrix composites consisting of metastable 16Cr7Mn7Ni-steel with 0 or 5 vol.% magnesia partially stabilized zirconia (Mg-PSZ) particles. The materials were prepared from powder raw materials via extrusion at ambient temperature. Three different temperatures between 1280 °C and 1380 °C and two varying dwell times of 40 min and 120 min at maximum temperature were applied. Both, tensile and compression tests are conducted at quasi-static strain rates for comparison of strength level, deformability and energy absorption capability. The results are discussed with regard to the porosity of the specimens, the interface between steel and ceramic, the Transformation Induced Plasticity (TRIP)-effect occurrence and the failure behavior.

1. Introduction
It is well known that the reinforcement of a ductile and tough metal by stiffer and stronger phases such as ceramics results in a new kind of material with advanced mechanical properties. Considerable are the adjustable high stiffness and specific strength [1, 2] as well as the wear resistance [3, 4] which are not achievable with monolithic alloys. In the past a variety of manufacturing processes have been developed to obtain metal matrix composites (MMC) gaining significant importance for high performance applications in fields of aerospace and transportation industry [5, 6]. A criterion for classification provides the condition of aggregation so that a distinction in liquid, solid and solid-liquid state manufacturing is feasible [7]. The powder metallurgical (PM) processing route belongs to the solid or solid-liquid techniques which depends on the raw materials and the applied temperature regime. Thus, PM possesses numerous advantages compared to casting technologies. A fine and homogenous microstructure is achievable due to the insertion of fine-grained metal and ceramic powders and the lower processing temperatures. Besides, a near-net-shape fabrication becomes possible increasing the material utilization and decreasing the tooling costs which are in case of MMCs and their abrasive reinforcements typically quite high. For exploiting the unique material profile, a fundamental understanding of the influencing process parameters on the microstructure and the mechanical properties is essential for every material system [8, 9].

In the present article the sintering response of a MMC consisting of Cr16Mn7Ni7-steel with 0 or 5 vol.% magnesia partially stabilized zirconia will be analyzed in dependence of the sintering
temperature and dwell time. Additional to the potential strengthening-effect generated by the Mg-PSZ particles, a transformation of the metastable austenitic steel into ferromagnetic α’-martensite or ε-martensite known as the TRansformation Induced Plasticity (TRIP)-effect can contribute to an enhancement of strength during plastic deformation without a loss of ductility [10]. So far, it is not reported in literature which effect both sintering temperature and time have on the occurrence of the TRIP-effect in pressureless sintered MMC-compacts deformed under tensile and compressive load.

2. Materials and methods

The manufacturing process of the investigated TRIP-steel (0Z) and TRIP-matrix-composite (5Z) samples bases on a ceramics-derived cold extrusion process. Therefore, a gas-atomized spherically-shaped steel powder (d<sub>90</sub> < 40 μm) was mixed with 3.3 wt.% magnesia partially stabilized zirconia powder (d<sub>90</sub> value of 30 μm). The chemical composition of the initial powders is revealed in table 1. In a second step, deionized water, plasticizers and binders were added to the steel/ceramic blend. A further mixing process led to a homogenous plastic paste which was subsequently pressed using a de-airing single-screw extruder to obtain strands with a circular cross section of 13.5 mm. All extruded test samples were stepwise dried and cut into 120 mm long rods before debindering at 450 °C for 30 min in air. Afterwards pressureless sintering in a 99.999 % argon-atmosphere at varying temperatures (1280 °C, 1350 °C, 1380 °C) and dwell times (40 min, 120 min) took place. For every condition three strands were produced in order to machine at least two samples for quasi-static compression (cylindrical: 6x6) and tensile (B6x30 DIN 50125) tests as well as microstructure investigations. Compression behavior was investigated according to DIN 50106 using a servohydraulic universal testing machine whereas tensile properties were determined referring to DIN EN ISO 6892-1 using an electronic screw driven testing machine. The microstructure characterization of initial state and deformed samples was realized by light optical microscopy and scanning electron microscopy (SEM) combined with energy and wavelength dispersive X-ray spectroscopy (EDX/WDX). Furthermore, ferromagnetic phase content was determined by the use of a Fluxmeter 480 (Lake Shore) connected with a MSAT-system (Metis Instruments and Equipment NV). Measurements according to Archimedes (DIN EN 993-1) served to determine porosity and the density of the samples.

Table 1. Chemical composition of steel and ceramic powder at initial state in wt.%.

| steel     | Cr   | Mn   | Ni   | C   | Si  | S    | N    | Mo  | Nb |
|-----------|------|------|------|-----|-----|------|------|-----|----|
| initial state | 16.30 | 7.20 | 6.60 | 0.03 | 1.00 | 0.007 | 0.088 | 0.007 | 0.001 |
| ceramic   | ZrO<sub>2</sub> | HfO<sub>2</sub> | MgO | SiO<sub>2</sub> | Al<sub>2</sub>O<sub>3</sub> | CaO | TiO<sub>2</sub> | Fe<sub>2</sub>O<sub>3</sub> | Y<sub>2</sub>O<sub>3</sub> |
| initial state | 92.88 | 1.85 | 3.25 | 0.10 | 1.58 | 0.060 | 0.130 | 0.019 | 0.130 |

3. Results and discussion

In order to assess the influence of the varying process parameters on the microstructure evolution, characteristic light optical micrographs of the unreinforced samples are depicted in figure 1. Principally, the increase of dwell time from 40 min to 120 min at a constant temperature level causes a decrease of closed porosity, as exemplary shown for 1280 °C in figure 1 a/b). The Archimedes-measurements for evaluation of total porosity confirm these observations. The results reveal an average difference of 3.5 % for short and long time sintering at 1280 °C. Comparable results are recordable at 1350 °C where the porosity decreases from 14.4 ± 0.7 % to 10.4 ± 0.7 %. Nevertheless, the reduction from 11.1 ± 0.4 % to 10.3 ± 0.6 % at 1380 °C is less pronounced. Under consideration of pore quantity evolution for a constant dwell time, an increase of temperature effects a decrease of porosity. The described tendencies are also valid for the composite samples. However, the absolute porosity values range for the low and medium temperature levels above those of the corresponding 0 vol.% Mg-PSZ samples. Only after sintering at 1380 °C the composite porosity amounts 10.6 ± 0.7 % (40 min)/9 ± 0.3 % (120 min) and is therefore comparable with the unreinforced compacts.
Essentially, sintering is a diffusion controlled mechanism where the reduction of free surface operates as driving force. Material transfer processes from the particles center to the points of contact introduce the initial stage of sintering denoted as neck formation. In the following intermediate stage an interconnection of the interstices takes place so that a great amount of densification can be achieved. The curve progress of relative density as a function of sintering follows a logarithmic shape. For this reason, relative long sintering times in comparison to the other stages become necessary to remove the isolated pores in the third sintering interval [11, 12]. Through the microstructure images of 1280 °C samples (figure 1 a/b) it is apparent that an insufficient diffusion for both 40 min and 120 min sintering occurred due to the low process temperature. The shape of the former steel particle boundaries are still apparent and narrow sinter necks have formed indicating sintering stage one. At 1350 °C and 1380 °C the selected time of 120 min (figure 1 c/d)) is sufficient to reach mechanism stage three. For obtaining a dense microstructure without any porosity sintering times much longer than 120 min have to be chosen. However, grain growth would start being adverse for the strength properties. Besides, further temperature increase will lead to the melting of the steel particles which is not desirable in terms of the compacts form stability. The presence of Mg-PSZ seems to constrain the densification process for temperatures of 1280 °C and 1350 °C. Rahimian et al. [13] explain this phenomenon with the reduction of compressibility at initial state as well as the inhibiting effect of the reinforcement in the rearrangement of the particles during sintering.

![Microstructure images](image1.png)

**Figure 1.** Microstructure evolution as a function of sintering temperature and dwell time.

In figure 2 the true stress-strain-curves of the composites recorded under tensile load are displayed. It becomes obvious that the increase of process temperature and time results in an increase of yield strength as well as fracture strain and thus leads to a higher energy absorption capability. Besides, a
change of curve progress appears from an almost linear to a sigmoidal shape at 1380 °C/120 min indicating the formation of deformation induced martensite (TRIP-effect) [14].

Figure 2. Influence of sintering temperature and time on tensile properties of 16Cr7Mn7Ni-steel reinforced with 5 vol.% Mg-PSZ (5Z) and comparison with unreinforced state (0Z).

Important for the uniform distribution of stress and thus isotropic mechanical properties is the homogeneous dispersion of the reinforcements. This requirement was confirmed by optical microscopy for the investigated compacts. Reason for the low load bearing capacity and deformability of the samples manufactured at low and medium temperatures is rather the already mentioned porosity. The load transfer from one particle to the other one is limited due to the weak sinter necks promoting an easy pore coalescence and crack initiation along the previous interfaces of steel/steel or steel/ceramic particles. Besides, a high number of pores exhibit an edged shape leading to stress concentration fields. Under consideration of the fracture surfaces depicted in figure 03 which are also representative for the 40 min sintered samples, an intergranular failure mechanism can be confirmed for 1280 °C and 1350 °C.

Figure 3. Fracture surfaces of 5 vol.% reinforced 16Cr7Mn7Ni steel samples sintered at varying temperatures for 120 min.

In contrast to this, the SEM-image of the 1380 °C sample displays a dimpled surface indicating a ductile failure mechanism. Through the centered position of the Mg-PSZ within the dimples, it can be concluded that during deformation the failure starts with the detachment of the steel matrix from the Mg-PSZ followed by the consolidation of cavities. Thereby, a better load transfer is possible and more
energy is needed to initiate the described processes leading to an increase of energy absorption capability.

However, noticeable is the distinct higher strength and ductility level of the 1380 °C/120 min composites despite that after 40 min and 120 min sintering a similar porosity is measurable. Although the applied sintering process belongs to the solid-state processes where often the absence of an extensive reaction is mentioned as an advantage, an interfacial layer between steel and Mg-PSZ is visible for the samples sintered at 1350 °C and 1380 °C (see figure 4). The WDX-profiles show that the formed phases which are located at the interfaces steel/ceramic and ceramic/ceramic mainly consist of oxygen, manganese, magnesium and silicon. It is comprehensible that the formation of this layer is also diffusion controlled so that a longer sintering time at a constant temperature leads to an enhanced formation. Obviously, the greater layer thickness implies a better connection to the steel matrix and thus contributes advantageously to a higher tensile strength and deformability.

![Figure 4. WDX-profiles of Mg-PSZ particles surrounded by 16Cr7Mn7Ni steel matrix sintered for 120 min at varying temperatures.](image)

The results of MSAT-measurements included in figure 2 clarify that in every composite sample a deformation induced transformation from paramagnetic austenite into ferromagnetic α'-martensite occurred indicating the TRIP-effect. Furthermore, the amount of ferromagnetic phase fraction increases with increasing sintering temperature and time. In summary it is concluded, that the high strength and ductility at 1380 °C arise from a lower porosity as well as a superior connection to the steel matrix (interfacial layer) inducing a better load transfer and thus providing an greater amount of mechanical work for the phase transformation of the TRIP-effect.

Under consideration of tensile properties (figure 2), the proof stress of the composite sintered at 1380 °C/120 min exceeds the value of the unreinforced state whereas the tensile strength and the fracture strain are comparable. For lower process temperatures the performance of the steel samples is distinct superior. By comparing the present results with the tensile properties of particulate reinforced samples reported in literature, it becomes obvious that the achieved strength and failure strains of the investigated TRIP-matrix-composites are unobtainable with these ferritic steel and aluminum MMC systems [8, 15].
Figure 5 reveals the stress-strain behavior of the 5 vol.% Mg-PSZ samples under compressive load. Consistent with the tensile flow curves, the yield strength increases with increasing sintering temperature and time. However, appropriate to the strength differential (S-D) effect reported in literature for metallic materials [16] a higher stress level for all investigated samples is visible under compression. Furthermore, the shape of the curves changes from linear at 1280 °C to a parabolic progress at 1380 °C. As under tensile load, the 1280 °C samples provide a low resistance against plastic deformation due to the high porosity values. The mechanical densification of the vacancies contribute a high amount of deformation to the overall compression strain so that minor stresses are generated in the steel particles and a lower strain hardening takes place. Therefore, the TRIP-effect is less pronounced as indicated by lower ferromagnetic phase fractions after deformation. The almost similar ferromagnetic contents of the samples sintered at 1350 °C and 1380 °C can be explained by exceeding the saturation value which is dependent on the chemical composition, test temperature and strain rate. Nevertheless, through the strong connection of the steel matrix and the Mg-PSZ generated by the interfacial layer (figure 4) a better load transfer becomes possible so that also under compressive load the mechanical properties of the 1380 °C composite samples are preferable to the 0 vol.% Mg-PSZ samples (figure 5).

4. Conclusion
The microstructural investigations as well as mechanical testing on TRIP-steel and TRIP-matrix-composites manufactured by pressureless sintering with varying process parameters led to the following findings:

- An increase of sintering temperature and time results in an enhancement of strength under tensile and compressive load.
- In all samples the deformation induced transition from paramagnetic austenite into ferromagnetic martensite is recordable indicating the occurrence of the TRIP-effect.
- Under tensile deformation the amount of ferromagnetic phase increased with increasing processing temperature and time whereas under compressive deformation a comparable amount (saturation value) for 1350 °C and 1380 °C samples could be measured.
- WDX-investigations reveal the formation of an interfacial layer during sintering which contributes to a better connection between steel and Mg-PSZ.
By comparing un- and reinforced state, the composite samples manufactured at 1380 °C/120 min exceed the mechanical properties of the 0 vol.% Mg-PSZ samples and thus possess a greater energy absorption capability.

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