RESEARCH ARTICLE | OCTOBER 06 2023

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AIP Conf. Proc. 2815, 160002 (2023)
https://doi.org/10.1063/5.0150215

Evaluation of Ceramic Proppants as Heat Transfer and Storage Medium

Gözde Alkan[1,a)], Peter Mechnich[1,b)], Hicham Barbri[2,c)], Ferdinand Flucht[1,d)], Johannes Pernpeintner[3,e)], Dmitry Sergeev[4,f)], Michael Müller[4,g)]

[1]*German Aerospace Center (DLR) Institute of Materials Research, 51147 Köln, Germany*
[2] *German Aerospace Center (DLR) Institute of Solar Research, 70569 Stuttgart, Germany*
[3] *German Aerospace Center (DLR) Institute of Solar Research, 51147 Köln, Germany*
[4]*Forschungszentrum Jülich, Institute of Energy and Climate Research, IEK-2, 52425 Jülich, Germany*

[a)] Corresponding author: goezde.alkan@dlr.de
[b)] peter.mechnich@dlr.de
[c)] hicham.barbri@dlr.de
[d)] ferdinand.flucht@dlr.de
[e)] johannes.pernpeinter@dlr.de
[f)] d.sergeev@fz-juelich.de
[g)] mic.mueller@fz-juelich.de

Abstract Various commercial proppants originally produced for fracking industry were examined as candidate materials to be used in concentrating solar power (CSP) plants as heat transfer and storage medium. Material properties as well as application related functional properties have been elucidated in a comparative manner. Despite their similar chemical composition, varying microstructures resulted in distinct application related functional properties. Carboceramics proppants are determined as the most promising candidate with highest viscous flow temperature, heat capacity, solar absorptance after thermal aging and abrasion resistance owing to well crystallized microstructure without glassy components. Moreover, the importance of the microstructure to achieve desired application related properties is revealed, in the scope of this study.

INTRODUCTION

Concentrating solar power (CSP) plants with thermal energy storage (TES) systems are one of the most promising renewable energy technologies with enhanced solar to electricity yield ratios [1,2] The need of higher operation temperatures than the current state-of-the-art solar salt technology induced the development of solar particle receiver systems. Ceramic particles enable higher peak operation temperatures and wide temperature ranges, owing to their high temperature stability up to 1100 ˚C [3]. The utilization of those materials as absorber, heat transfer, and storage medium in solar particle receivers promises high energy storage densities and low storage costs. Among various ceramic materials, commercial proppants originally used in the fracking industry are considered as promising candidates, owing to their good sphericity, solar absorbance and thermal shock resistance [4]. However, beyond those properties, for particle receiver applications the structural and mechanical stability at elevated temperatures, abrasion resistance, and heat capacity are also crucial for highly efficient solar heat absorbtion and storage [5]. In this study, four different proppants produced by Wanli Group Co. Ltd., Seppe Technologies, Carboceramics and Saint-Gobain have been investigated in terms of their material properties such as microstructure, chemical composition, and phase content. Furthermore, the application relevant functional properties such as abrasion resistance, softening temperature, structural endurance (mechanical durability?) at elevated temperature, heat capacity, angle of repose, flowability and

SolarPACES: Solar Power & Chemical Energy Systems
AIP Conf. Proc. 2815, 160002-1–160002-8; https://doi.org/10.1063/5.0150215
Published by AIP Publishing. 978-0-7354-4623-6/$30.00

solar absorbance were elucidated. The relation between functional properties and material properties and the required microstructure of the ceramic proppants for solar energy applications are discussed.

EXPERIMENTAL PROCEDURE

Commercial proppants produced by four different companies; Wanli Group Co (China), Seppe Technologies (China), Carboceramics (USA) and Saint-Gobain (France) were investigated. Microstructure and chemical analysis was performed by scanning electron microscopy (SEM; Ultra 55, Zeiss, Germany) and energy-dispersive spectroscopy (EDS; UltiMate, Oxford, UK. Phase components in initial condition and after thermal treatment were monitored by X-ray- powder diffraction (XRD; D8 Advance, Bruker AXS, Germany). Optical properties and absorptance of the proppants were measured by Perkin Elmer Lambda 950 Spectrometer according to the method described by Gobereit et al. [6]. Evaluation and solar weighting (ASTM 173d) were performed in the range of wavelengths from 320 nm to 2500 nm. Heat capacity of the proppants were determined by an mHTC 96 Setaram drop calorimeter with DSC sample carrier under inert atmosphere (He) with a heating rate of 4 K/min. Mass of measured samples was around 1000 mg. The reference material used (α-Al_2O_3, NIST Standard Reference Material SRM 720, with purity 99.95%) had a similar mass as the samples. Calibration and baseline measurements were performed before and after each sample. The uncertainty of obtained heat capacity values by this methodology is 5%.

The surface mass loss was evaluated as a preliminary assessment of long-term abrasion-resistance of particles [6]. In a typical experiment, 20 g of proppants were filled into 0.1 L polymer bottles and agitated in a 3D Turbula mixer (WAB Group, Switzerland) in order to stimulate intensive particle-particle collisions for up to 24 hours. Subsequently, particles were washed with DI (de-ionized) water and kept at ultrasonic bath for 30 min to remove the sticking dust from the particle surface. After drying at 80 ˚C for 1 hour, the weight of dried proppants was measured to record the time-dependent mass loss. Viscous flow temperature of the proppants were measured under uniaxial mechanical load by a universal testing system (UTS, Zwick-Roell, Germany). Moreover, the proppants were subjected to thermal aging at 1000 ˚C for one week with subsequent phase microstructure and absorptance analysis to reveal their stability at elevated temperatures. A DN80 pipe with a 60 mm orifice and 45 inclination was used to evaluate the mass flow rate of the particles. Each test was carried out using 20 kg of particles. The average value of 5 experiments was calculated. The tilting box method was used to measure angle of repose. The particles are shaken out of a funnel with an opening of 3 cm. Images are made when particles started to form a tilt. Afterwards, the angles on both sides were determined by a measures+ program.

RESULTS AND DICSUSSION

The phase components of the proppants in as received condition and after 1-week thermal aging at 1000 ˚C evaluated by XRD diffraction is given in Fig. 1.

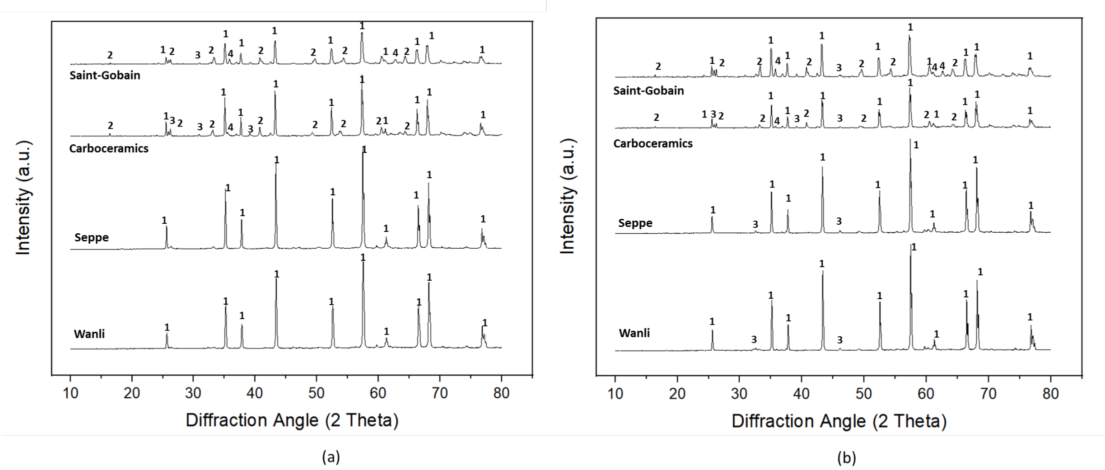
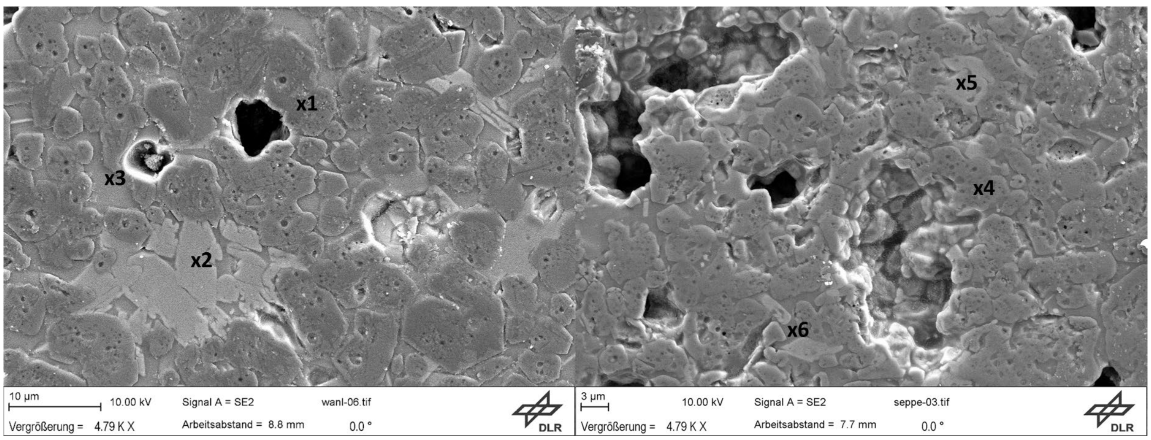


FIGURE 1. XRD Diffractograms of commercial proppants (a) as received condition (b) after thermal aging at 1000 ˚C for 1 week, where 1: corundum (ICDD #46-1212), 2: mullite (ICDD #79-1275), 3: pseudobrookite (ICDD #73-1631), 4: hematite (ICDD #13-0534)

XRD results in Fig. 1a depicts that Wanli and Seppe proppants exhibit a very similar composition, enriched in terms of corundum (Al_2O_3). On the other hand, Carboceramics and Saint-Gobain proppants contain a significant amount of mullite ($Al_6Si_2O_{13}$) accompanying corundum. Moreover, both exhibit pseudobrookite (Fe_2TiO_5) and hematite (Fe_2O_3) peaks indicating the better crystallization of colour giving elements when compared with Wanli and Seppe proppants. It is also worth to mention that the presence of hematite is more dominant in Saint-Gobain proppants.

The XRD patterns of proppants after heat treatment is represented in Fig. 1b to elucidate their high temperature structural stability. The appearance of corresponding pseudobrookite peaks indicated the crystallization of iron rich constituents upon thermal aging also in the case of Wanli and Seppe proppants. Beside this crystallization, phase composition remained unchanged. Carboceramics has not experienced a significant phase transformation, indicating it´s high temperature stability. Similarly, Saint-Gobain proppants were also stable but a slight increase in the intensity of hematite peaks have been observed, which is attributed to an oxidation of present Fe^{2+} to Fe^{3+} occurring at elevated temperatures, see below.

In order to gain insight into the details of the microstructure and chemistry of the components, polished cross sections of all proppants have been analysed by SEM/EDS. The microstructures of Wanli and Seppe with corresponding EDS analysis are given in Fig. 2 and Table 1; respectively.



(a) (b)

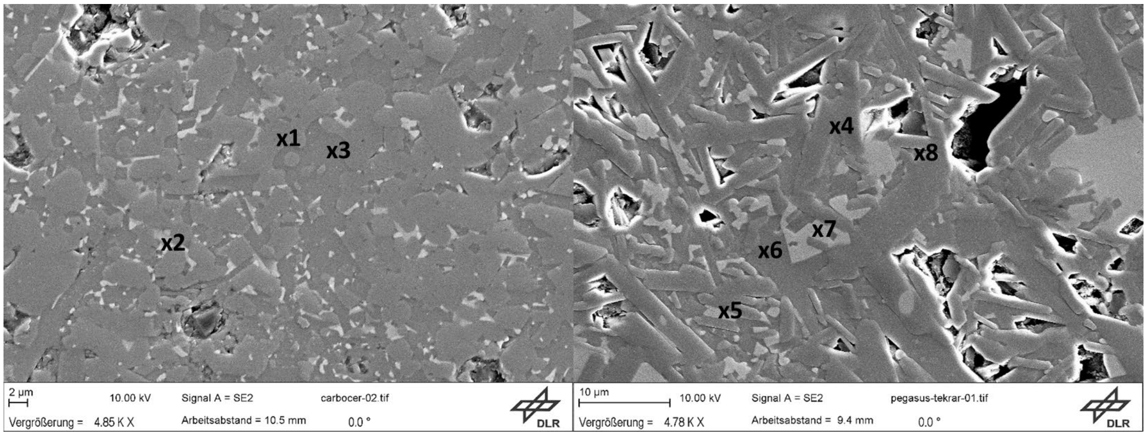
FIGURE 2. SEM micrographs of (a) Wanli (b) Seppe proppants

TABLE 1. Point EDS analysis of the corresponding phase components labelled in Fig. 2.

Element (at.%)	O	Al	Si	Fe	Ti	Mn	K	Mg	Ca	
1	63.2	36.8	-	-	-	-	-	-	-	Corundum
2	63.8	16.7	0.3	7.5	10.4	1.3	-	-	-	Fe bearing ox.
3	63.9	10	15.8	-	0.5	7.3	1.8	0.7	-	Glass phase
4	61.5	37.2	0.4	0.9	-	-	-	-	-	Corundum
5	60.7	6.7	0.5	11.2	13.5	6	-	1.4	-	Fe bearing ox.
6	66.5	6.7	22.2	-	-	1.6	2.5	-	0.5	Glass phase

Typical granular particle morphology, where primary particles coalescence and form the final spherical like product with certain amount of porosities, was observed as given in Figure 2 [7]. Wanli and Seppe proppants exhibit very similar microstructures, where the main component are corundum particles labelled as 1 and 4, consistent with the XRD findings. Moreover, relatively light-gray parts are corresponding to iron bearing oxides with poor crystallinity marked as 2 and 5. SEM/EDS results reveal the presence of poorly crystallized glassy matrix surrounding the corundum particles. The glassy phases labelled as 3 and 6 are enriched in terms of Si and hold certain amount of Al, K, Mg ad Ca as presented in Table 1.

Figure 3 displays SEM micrographs of Carboceramics and Saint-Gobain proppants, where corresponding EDS analyses are listed in Table 2



(a) (b)

FIGURE 3. SEM micrographs of (a) Carboceramics (b) Saint-Gobain proppants

TABLE 2. Point EDS analysis of the corresponding phase components labelled in Fig. 3

Element (at.%)	O	Al	Si	Fe	Ti	K	Mg	Na	Ca	
1	60.8	34.9	-	4.3	-	-	-	-	-	Corundum
2	57.6	12.2	1.7	26.1	2.4	-	-	-	-	Pseudobrookite
3	62.9	25.8	7.7	3.2	0.4	-	-	-	-	Mullite
4	59.6	36.8	-	3.6	-	-	-	-	-	Corundum
5	58.7	5.9	-	32	3.5	-	-	-	-	Hematite
6	61.4	29.1	5.9	3.7	-	-	-	-	-	Mullite
7	59.9	5.8	-	23	11.2	-	1.4	-	-	Pseudobrookite.
8	61.2	19.1	12.8	3.5	-	0.5		0.7	2.2	Glass phase

Carboceramics proppants exhibit a well crystallized microstructure consistent with the XRD findings, i.e. corundum, iron titanium oxide and mullite could be detected by EDS, labelled as 1, 2 and 3 in the Table 2. It is worth to highlight that no glassy phase was found in these proppants. As can be seen in Fig 3 b, Saint-Gobain proppants exhibited corundum particles in rod-like morphology, in contrast to the other three proppants. The presence of hematite solid solution, listed as 4 in Table 2, in parallel with XRD findings, have been also confirmed by EDS analysis. Similar to the Carboceramics, the presence of mullite and iron titanium oxide has been confirmed, listed as 6 and 7. In addition to these four crystalline components, a negligible amount of glassy phase is also detected in Saint-Gobain proppants, which is marked as 8.

The microstructure of the thermally aged samples with point EDS analysis are given in Figure 4 and Table 3; respectively. After thermal aging, the formation of iron titanium oxide was also confirmed by EDS analysis for Wanli and Seppe proppants. The post thermal aging SEM microstructure of Carboceramics is almost identical to the initial condition, which shows its high microstructural endurance at elevated temperatures. However, EDS analysis of iron titanium oxide particle indicated slight oxidation upon thermal aging, as can be seen in Table 3. In the case of Saint-Gobain, the elimination of sharp edges of corundum particles was observed through the thermal aging, whereas the rest of the microstructure remained stable. In parallel with XRD findings, EDS analysis also indicated an oxidation-related transformation to hematite for Saint-Gobain proppants.

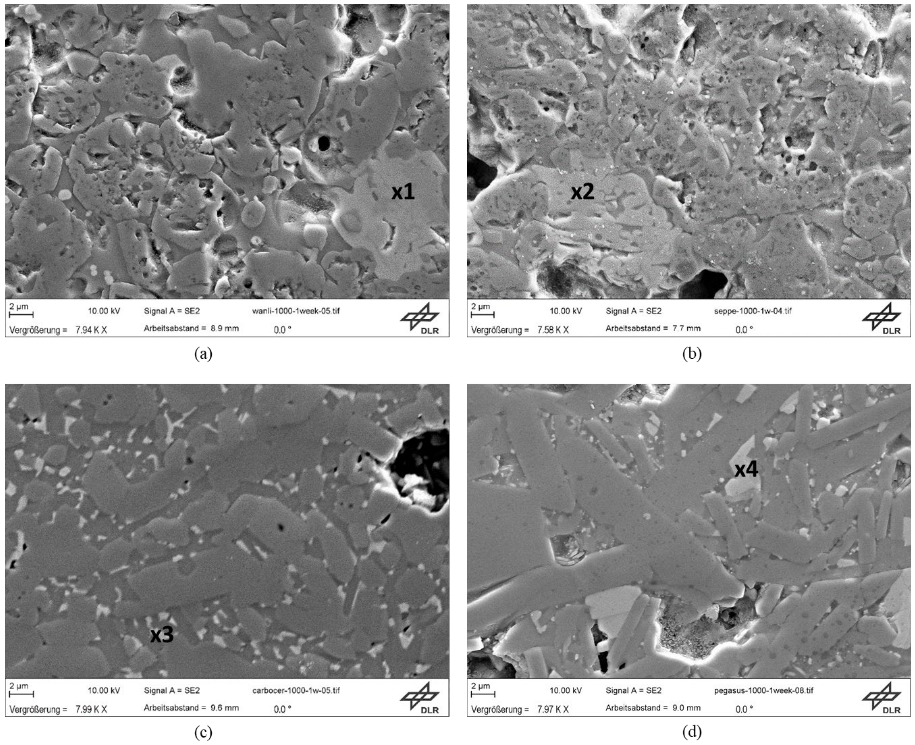


FIGURE 4. SEM micrographs of the thermally aged proppants (a) Wanli (b) Seppe (c) Carboceramics (d) Saint-Gobain

TABLE 3. Point EDS analysis of the corresponding phase components labelled in Fig. 7.

Element (at.%)	O	Al	Si	Fe	Ti	Mn	Mg
Wanli	64.3	17.8	-	6.2	11.3	-	0.4
Seppe	60.7	5.4	0.4	11.4	13.2	7.6	1.3
Carboceramics	62.7	7.3	2.8	18.9	8.2	-	-
Saint-Gobain	60	8.8	4.3	25.8	1.1	-	-

Considering XRD and SEM/EDS findings, it can be said that Wanli and Seppe proppants are very similar, where the major phase component corundum is surrounded by a substantial amount of glassy phase and poorly crystallized oxides bearing color giving elements. On the other hand, Saint-Gobain and Carboceramics proppants exhibit better crystallized microstructures, where color giving elements are also bound in crystals. Whereas the former still contains a low amount of glassy phase, the latter is completely and well crystalized, which promotes high structural stability at elevated temperatures.

In order to evaluate the viscous flow temperature, the high-temperature compression behavior of single particles was tested. For this purpose, a uniaxial controlled force of 30 N was applied to the particles and the temperature dependent displacement of cross-head was recorded. A comparison of the viscous flow temperatures of the investigated proppants is given in Fig. 5

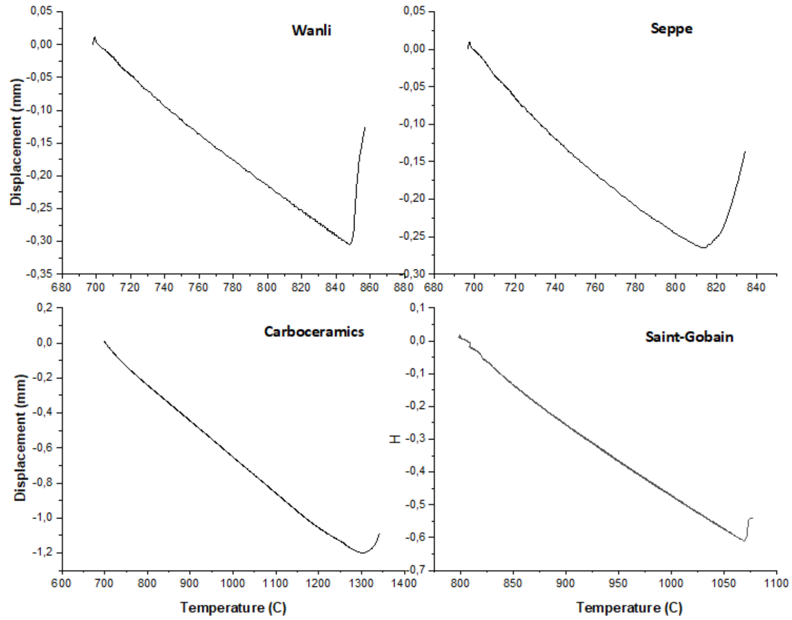


FIGURE 5. Viscous flow temperature of the proppants

All proppants exhibit initially a linear displacement with increasing temperature, which is originated by thermal expansion. Note that the testing system is recording expansion as negative with respect to the zero-starting value. The sudden drop in the displacement curves indicate the mechanical destabilization due the viscous flow of the proppants. Viscous flow temperatures were determined as 850 ˚C, 810 ˚C, 1070 ˚C, and 1310 ˚C for Wanli, Seppe, Saint-Gobain and Carboceramics; respectively. Those results are in line with SEM/EDX findings and indicate that viscous flow temperatures are correlated to better crystallization of components and minimized glassy phase content. Carboceramics proppants exhibit a very high viscous flow temperature, which is highly promising for the envisaged high temperature solar thermal applications.

Figure 6 illustrates the time-dependent abrasion mass loss induced by particle-particle friction in the Turbula mixer.

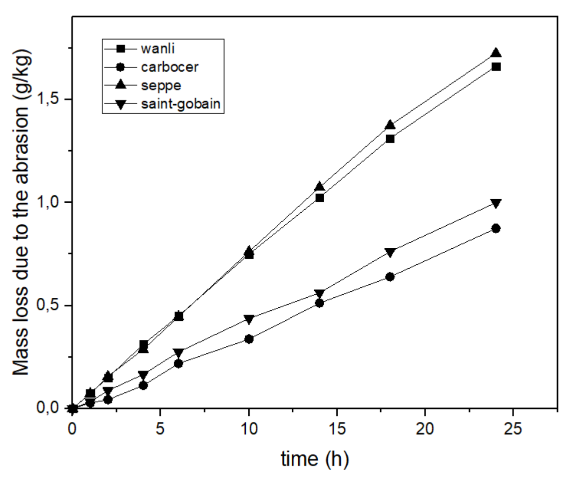


FIGURE 6. Mass loss per kg due to abrasion as a function of time

An almost linear trend in the mass loss is observed for the all proppants. However, Wanli and Seppe proppants suffer of almost 2 times more mass losses due the abrasion when compared with Carboceramics and Saint-Gobain proppants. This distinct behavior can be also explained by the presence of a glassy phase component, which is softer than crystallized compounds and therefore, leads to less abrasion resistance. It can be concluded that, a well crystallized microstructure promotes also higher abrasion resistance.

The heat capacities of the investigated proppants as a function of temperature are given in Fig. 7.

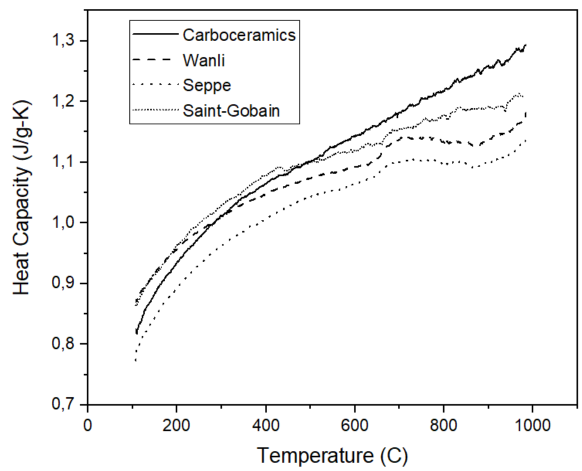


FIGURE 7. Heat capacity of the proppants as a function of temperature

In order to ensure sufficiently high energy storage densities, a minimum of 1 J/g-K heat capacity is generally required in the application temperature range. As can be seen in Fig. 7, all proppants meet this criterion at elevated temperatures. However, Carboceramics proppants exhibit the highest value with 1.3 J/g-K around 1000 ˚C, which evidently qualifies it as an excellent candidate. On the other hand, heat capacity curves of Saint-Gobain and Seppe proppants show some evidence for continuous solid-solid transition in the temperature range of 650°C to 850 °C, which can have a negative influence on the long-term stability of the proppants during continuous thermal cycling.

The solar weighted absorbance of the proppants as determined according to ASTM 173 standards are shown in as received condition and after 1 day and 1-week thermal aging at 1000 ˚C in Fig. 8.

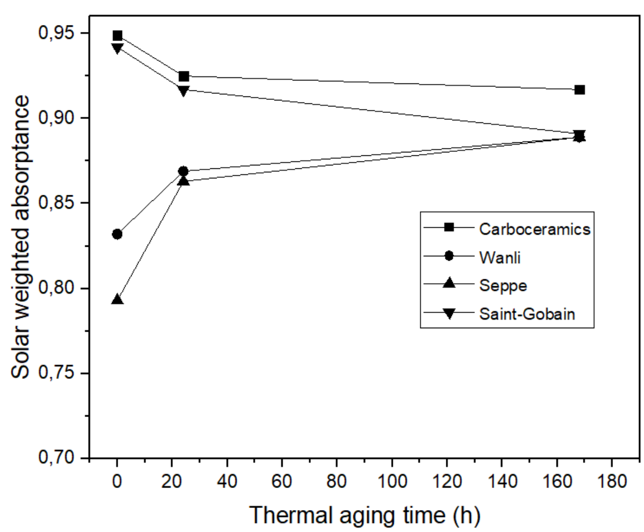


FIGURE 8. Solar absorbance of the as received and thermally aged proppants

Carboceramics as well as Saint-Gobain proppants have high initial absorbances around 0.95, owing to the crystallized color giving elements in as received condition (see previous results). In contrast, Wanli and Seppe proppants with poorly crystallized oxides bearing color giving elements exhibit lower absorbances around 0.8, emphasizing the importance of well-crystallized microstructures. After thermal aging, an increased solar absorbance was revealed for both Wanli and Seppe proppants. Thermal aging at 1000 ˚C provided enough energy and time for sufficient diffusion of species, which results in crystallization of color giving element bearing oxides and therefore enhanced absorbance. Carboceramics and Saint-Gobain proppants experienced a slight decrease in their absorbance through aging, which is explained by the partial oxidation of Fe^{2+} to Fe^{3+}, also supported by the SEM/EDS findings. Despite this decrease, especially for the Carboceramics proppants absorbance remains still higher than 0.9 after 1 week aging, which is very promising for long-term operation.

The measured mass flow rates through the DN80 test pipe and the angle of repose values are listed in Table 4 for all proppants.

TABLE 4. Mass flow rate and angle of repose of the proppants

	Mass flow rate (kg/s)	**Angle of repose (°)**
Wanli	3.01	29.6
Seppe	2.25	32.3
Carboceramics	3.30	34.3
Saint-Gobain	3.32	32.5

In order to achieve a sufficiently good flowability of the particles in the receiver, the particles must be able to achieve a minimum mass flow of 3 kg/s. All proppants except of Seppe meet this criterion, where Saint-Gobain and Carboceramics yield the highest values. Considering the inclination of the piping and particle film properties, an angle of repose around 30 is required, which is also met by all proppants as can be seen in Table 4.

CONCLUSIONS

Four different commercial proppants were evaluated as heat transfer and storage medium candidate materials. All proppants with similar chemistry had distinct functional properties originating from their different microstructures. Microstructural analyses combined with application-specific thermal-physical characterizations revealed that well crystallized microstructures with minimized glassy phase components are most favorable for application in solar thermal receiver applications. Considering the mechanical and structural endurance at elevated temperatures, heat capacity and solar absorptance, proppants fabricated by Carboceramics were indentified as the most promising candidates.

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 857768 and from the Technology Marketing of the German Aerospace Center (grant no. LRV 2020/004.

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