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Characterization of a Novel Coating Process to Darken Sand Particles

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Abstract. The use of solid particles in Concentrated Solar Power (CSP) plants can enhance energy conversion efficiency by elevating the working temperature. For this reason, many researchers are exploring various materials such as silica sand and SiC, among others, and methods to enhance the optical properties while cost is reduced. In this context, this study proposes a novel fabrication method based on the Mn^{2+} diffusion to darken silica sand particles and, therefore, enhancing their absorptivity. Colorimetry analysis reveals that the obtained particles color closely resembles that of the reference material SiC, while morphology analysis, Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) confirm an effective fabrication method.

Keywords: Darken Particles, Sand, Characterization of Particles

1. Introduction

The global energy consumption increases every year, showing increasing growth rates in recent years. According to the International Energy Agency (IEA), the electricity demand grew by 2.2% in 2023 [1]. In this context, the development of renewable and low-carbon energy sources is a mandatory task to achieve the reduction of CO_2 concentration levels in the atmosphere [2].

As solar energy is renewable and inexpensive, it has been considered as a promising alternative to current energy technologies. Furthermore, the next Concentrated Solar Power (CSP) plants - could achieve working temperatures over the current limit of 565 ºC, when molten salts are used, resulting in an improvement of the energy conversion efficiency via the use of solid particles [3], [4], [5]. In addition, the use of solid particles as Thermal Energy Storage (TES) system could mitigate the inherent intermittences of sun energy generation [6].

Different solid particles have been previously characterized for CSP applications, such as silica sand (SiO_2), silicon carbide (SiC), Carbo Accucast ID50, alumina (Al_2O_3), zirconia (ZrO_2) and basalt [7], [8]. The required particle properties are high thermal stability, low cost, high thermal energy storage capacity, good flowability, high mechanical stability and high absorptivity [8]. Material such as Carbo Accucast ID50 and SiC are the most suitable materials from the thermal and optical point of view, but they are more expensive than sand, so sand remains as a very competitive option [4], [8].

To improve the performance of raw sand, coating is a typical process to darken it, enhancing its solar absorptivity. The addition of graphite, black carbon and spinel oxide ($Cu_{0.5}Cr_{1.1}Mn_{1.4}O_4$ and $CuCr_2O_4$) results in an enhancement of the original absorptivity from 0.44 up to 0.9, allowing also improved long-term durability[9], [10], [11]. However, nanoparticles are expensive materials with not fully clear environmental and health impact effects, so alternative processes need to be studied.

In this work, a novel coating process to improve the absorptivity of sand is presented. This method promotes the solid diffusion process of Mn^{2+} ions into the SiO_2 crystal lattice, resulting in a permanent darkening of the sand particles.

2. Methodology

For sample preparation, manganese carbonate ($MnCO_3$) and sand are mixed in a 1:30 weight ratio using an agate mortar. After homogenization, the samples were heated at 600, 700, 800 and 900 ºC in a muffle furnace for 6 hours using a ramp rate of 5 ºC/min. Resulting materials are shown in Figure 1. These temperatures are high enough to promote a solid-state diffusion process, but not enough to agglomerate the sand particles by sintering [12].

Figure 1. *Raw sand and resulting samples from different thermal treatment temperature.*

The samples were characterized using several analytical techniques: X-ray diffraction (XRD) was performed with a PANalytical X'Pert PRO MRD diffractometer, scanning electron microscopy (SEM) was conducted using a JEOL JSM-6490LV, colorimetric analysis was carried out with a StellarNet BLUE-Wave spectrophotometer, and morphological evaluation was performed using a Malvern Panalytical Morphologi 4 microscope.

3. Results and discussion

Figure 2 shows the Le Bail analysis of sample obtained at 600 ºC. Obtained material maintains the structural characteristics of raw SiO_2 (trigonal symmetry group, P 31 2 1), as the rest of samples in the 600 to 800 ºC temperature range. The most significant differences as the temperature increases are found for the subtle diffraction peaks shift, as depicted in the inset of Figure 3 for the diffraction peak at $2\theta \approx 26.6º$. According to this, the diffusion of Mn^{2+} ions into the silica structure is responsible for the parameters lattice modification up to 800 ºC, although at 900 ºC the diffusion of Mn2+ ions goes further towards a phase transformation [13] in agreement with the peak shape evolution.

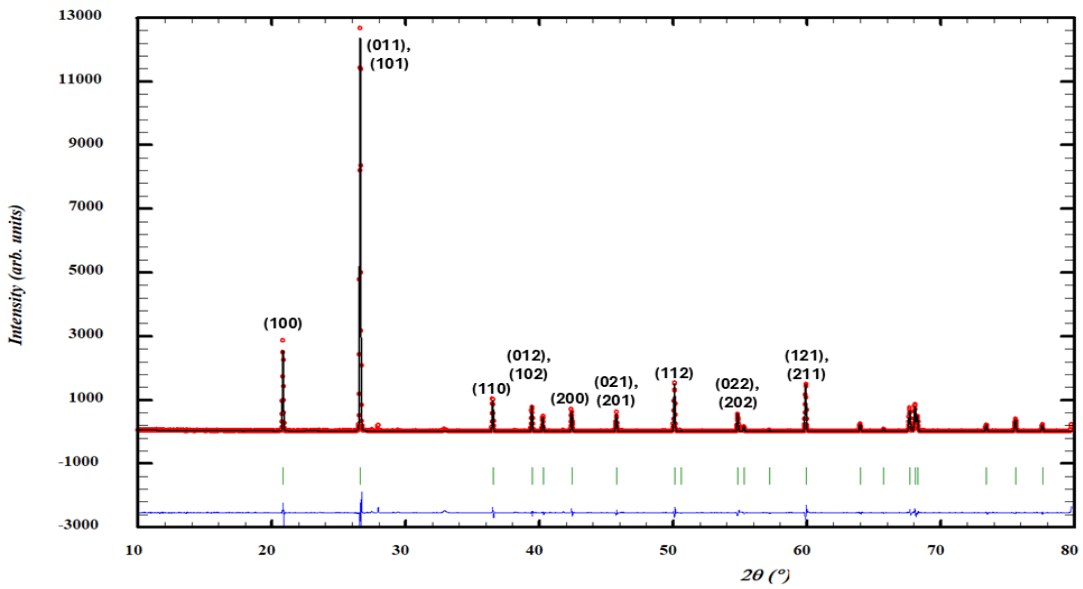

Figure 2. *Le Bail analysis of Main difraction peaks of SiO2 identification on samples 1:30 600 ºC*

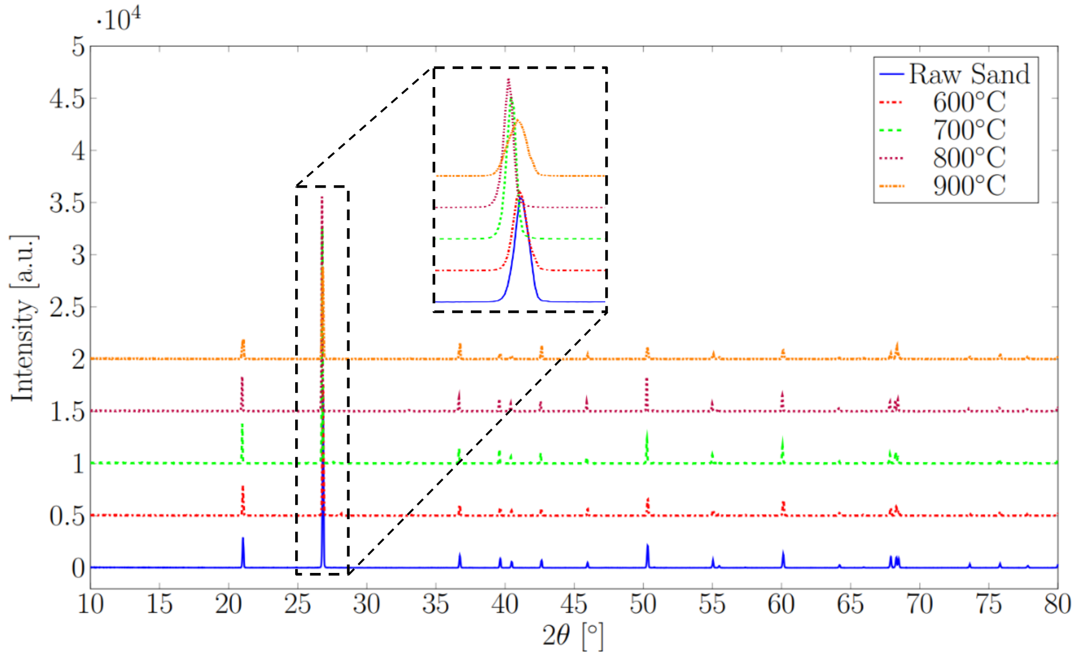

Figure 3. *XRD diffraction patterns for the different coating thermal treatments*

Secondly, the color change is measured using a colorimeter and expressed using the CIELAB color space, in which the absolute color difference respect to the ideal black as a reference is quantified. The results are plotted in Figure 4, in which lower bar values mean darker color. Additionally, the reference materials used are SiC, because of its high solar absorptivity (around 0.9) and the raw sand used during the coating process.

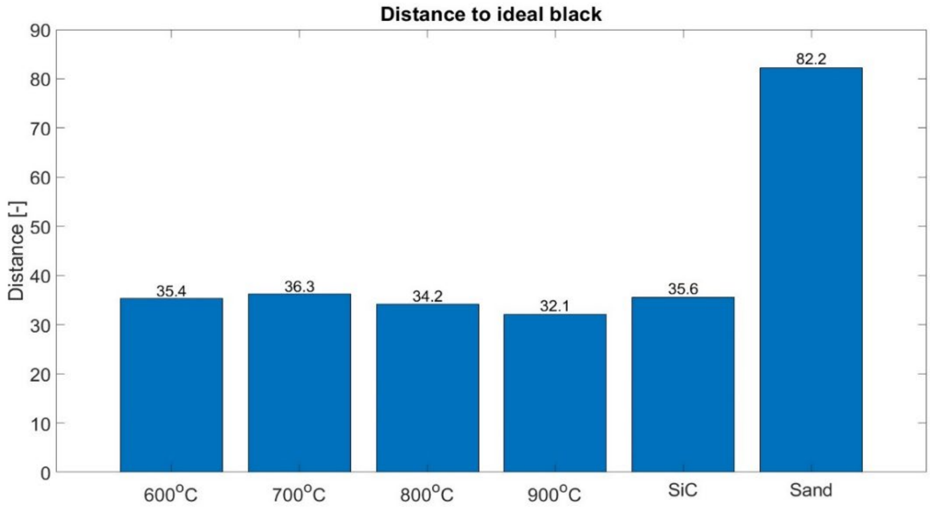

Figure 4. *Distance to ideal black of the coated samples and reference materials*

As a result, the absolute color difference to ideal black of SiC and sand are 35.6 and 82.2 units, respectively, whilst for coated samples values ranges between 32.1 and 36.3 units for those heated at 900 and 700 ºC, respectively, so all of them are quite close or even are darker than the reference material, i.e. SiC. Therefore, a similar absorptivity to SiC is expected.

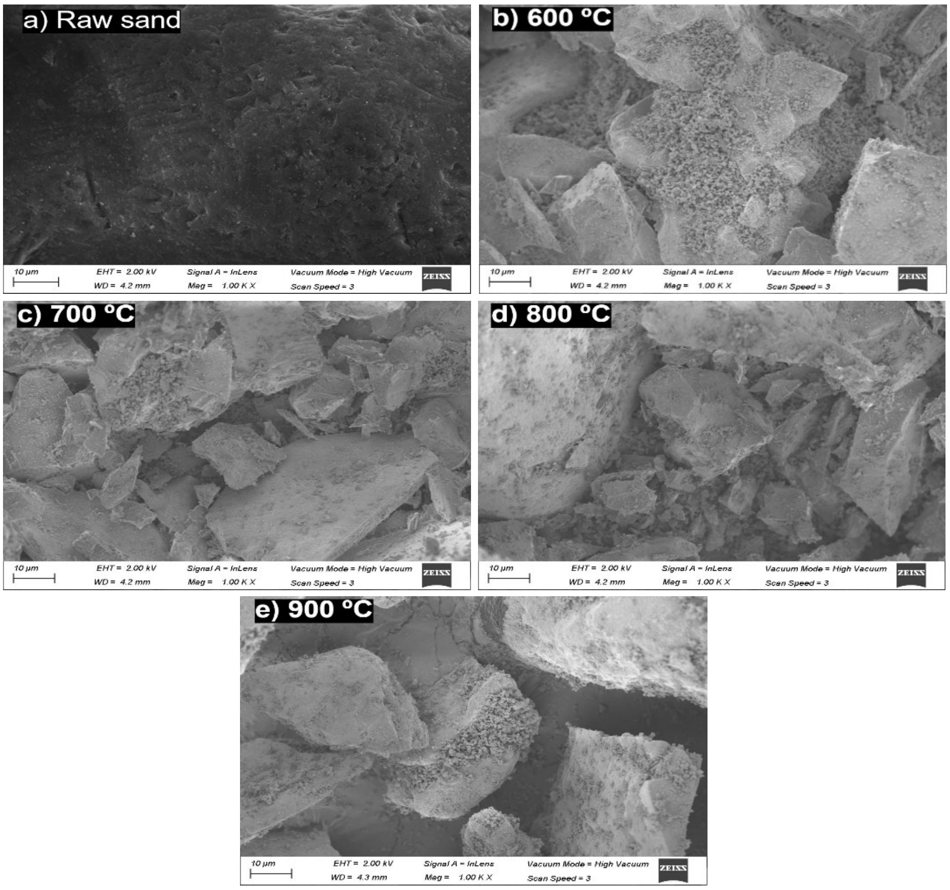

***Figure 3**. SEM images of raw sand and coated samples.*

SEM images show that high coating temperature results in higher adhesion of MnO_X (from thermal decomposition of $MnCO_3$) producing a more homogenous particle surface (Figure 5). Also, the particle surface roughness must be considered regarding the manganese deposition, as it boosts larger accumulation in particle grooves. Thus, while raw sand has a clean surface, without the deposits of MnO_X, coated samples show their grain surface grooves partially covered. Furthermore, as the temperature increases, the location of MnO_X particles is more homogenous along the grain surface. This homogeneous MnO_x distribution likely enhances the consistency of diffusion processes along the grain surface.

Finally, the main morphological parameters (Table1) were measured to quantify the changes suffered by raw silica particles upon the coating. The mean diameter of particles dramatically drops after coating process due to the grinding and the abrasion during mixing process. Also, the coated particles exhibit geometries closer to a sphere, with a high circularity and aspect ratio in comparison to the raw material. These changes could be explained by the abrasion undergone.

Table 1. *Morphology parameters for raw sand and coated samples*

Sample	dp [µm]	Circularity [-]	Convexity [-]	Asp. Ratio [-]
Raw Sands	183.0	0.23	0.95	0.16
$MnCO_3$+Sand 600ºC	34.8	0.94	0.97	0.81
$MnCO_3$+Sand 700ºC	27.3	0.95	0.97	0.80
$MnCO_3$+Sand 800ºC	31.1	0.94	0.97	0.77
$MnCO_3$+Sand 900ºC	62.7	0.92	0.97	0.79

4. Conclusions

These results demonstrate the darken of silica sand by manganese ions diffusion using an easy and cost-effective procedure, rendering a color similar to that of several other high absorptivity materials such as SiC. Due to the nature of this process, high durability should be also expected because this is not just a surface treatment but a chemical coating by ionic diffusion. The effect of the thermal treatment temperature on the absorptivity properties of the materials is not currently obvious, and therefore, further studies are necessary.

Future works must address the performance of samples under CSP applications and determine the durability and degradation of the coating under several operative cycles. Also, it would be interesting to quantify the actual absorptivity enhancement of the coating samples.

Author contributions

- LM Cerutti-Cristaldo: Investigation, Writing - original draft and Visualization.
- M Díaz-Heras: Supervision and Writing – review & editing.
- JC Pérez-Flores: Supervision, Methodology, Investigation and Writing – review & editing.
- J Canales-Vázquez: Supervision and Methodology, Writing – review & editing.
- JA Almendros-Ibáñez: Supervision and Writing – review & editing.

Competing interests

The authors declare that they have no competing interests.

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