CHARACTERIZATION OF SELECTIVE ABSORBERS PREPARED THROUGH A MECHANICAL TREATMENT

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ABSTRACT

This paper describes the manufacturing process for a low-cost mechanically manufactured selective $C/Al_2O_3/Al$ surface and its microstructural and optical characterization. The elemental composition and geometrical structure of the surface was characterized by XPS, SEM, EDS and optical microscopy. The manufacturing process has been developed from manual abrasive grinding followed with an acid bath to a mechanically operated grinding alone. The mechanical grinding method implements a soft grinding pad containing silicon carbide grinding particles. During the grinding process the pad is saturated with carbon dust, which reacts with the Al-substrate and atmospheric oxygen forming a matrix structure on the final surface. This structure consists mainly of Al_2O_3 , with some C in graphite form adsorbed on the surface. The microstructure of the surface consists of small, typically 1-2 μ m wide grooves organized in a heterogeneous 2-dimensional matrix. Additionally, agglomerated graphite clusters are formed on the surface. The thickness of the clusters varies, with the maximum measured thickness being in the range of 300 nm. A solar absorptance of 0.90 and a thermal emittance of 0.22 have been achieved so far. Increasing graphite coverage and decreasing graphite cluster thickness could increase the absorptance to \geq 0.94 and lower the emittance. This could be achieved by altering the composition and the structure of the grinding pad and by finding suitable manufacturing parameters for the advanced pad. Adding an antireflective coating could also be an option.

INTRODUCTION

Optical performance, durability, friendliness to the environment and cost are key factors for selective solar absorber surfaces. Absorbers manufactured with prevailing sputtering technologies [1-3] can be quite expensive. Selective paints [4-5] may provide a promising low-cost manufacturing method. Another interesting environmentally friendly low-cost method can be mechanical manufacturing. The manufacturing process has been developed from manually operated abrasive grinding followed with an acid bath to a mechanically operated grinding alone [6]. The surface has passed accelerated aging tests recommended by IEA-SHCP [7] for high temperature, testing of combined high moisture/condensation and elevated temperature are to be finished [8]. In addition, the surface has been found to be insensitive to extensive UV irradiation, and to withstand 383 days of temperature and irradiance cycling with total irradiance level of 1000-7000 W m⁻² and temperature range of -40°C...120°C [8-9].

PRINCIPLE OF SURFACE MANUFACTURING

Selective $C/Al_2O_3/Al$ surfaces can be manufactured with several different processes [6,10]. Earlier methods incorporated labour-intensive manually operated grinding followed with an acid bath containing KMnO₄, CuNO₃ and HNO₃. The whole manufacturing process took at this stage some 25-40 minutes. In order to get rid of chemical waste produced and to shorten the delivery cycle, the acid bath was abandoned. In the beginning, manual grinding was preferred over mechanical grinding because even small changes in the manufacturing parameters (speed, time, pressure, grinding pattern) gave completely different results for optical parameters and surface homogeneity. After gaining some experience, a skilled craftsman learnt to manufacture the $C/Al_2O_3/Al$ -surface with the best surface homogeneity. Optical properties of the surfaces were characterized for identifying the grinding practices which provided with the highest solar absorptance α and lowest thermal emittance ϵ . The best practice manual manufacturing parameters were determined. Due to better learning to understand the microscopical phenomena occurring during the grinding process, it became possible to interpret the manual manufacturing parameters into mechanically operated grinding parameters. Eventually this yielded even better optical properties (Table 1) [6,10].

The mechanical grinding is typically done on 99.5% pure Al-substrate sheets with dimensions: 2 x 0.12 x 0.005 m. The latest version of the method implements an electrical control and guiding mechanism: A non-correlating white noise signal generates the X/Y -direction control voltage for the electromagnetic control units of the grinding unit, which drive a grinding pad attached to a wheel head (Figure 1, left). As a result, the grinding pad moves locally across the Al-substrate forming a 2-dimensional grinding pattern on the surface. In order to obtain a homogeneous pattern over the whole surface, the Al-sheet is moved slowly back and forth under the grinding unit (Figure 1, right). A typical mechanical process lasts for about 15 minutes. Parallel grinding units can be used for manufacturing several sheets at the same time, and their number can be scaled up inexpensively.

Very hard grinding particles, e.g. silicon carbide are attached in the grinding pad thus forming a 3-D matrix. The size of the particles varies and is typically between 300 nm - 2 μ m. During the grinding process the grinding pad is saturated with carbon dust, which is bound to the pad by static electricity. Carbon dust reacts with the scratches of the surface containing Al_2O_3 and unoxidized Al and atmospheric oxygen forming a matrix structure on the final surface. This structure consists of mainly of Al_2O_3 and C, with insignificant traces of other elements [6, 10].

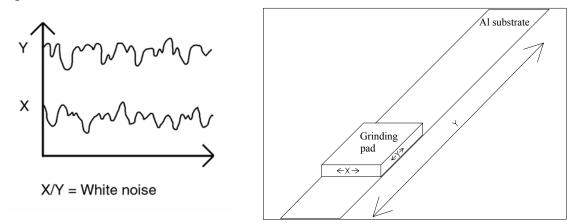


Figure 1: The non-correlating white noise used for moving the grinding pad in X/Y -directions across the substrate (left and right). The substrate moves back and forth slowly in Y-dimension (right, not on scale).

OPTICAL CHARACTERIZATION

The solar absorptance α was determined from 0.39 to 1.1 μ m with a LI-COR LI-1800 type spectroradiometer and an integrating sphere. The infrared emittance ϵ was determined from 2.5 to 20 μ m with a MIDAC Prospect IR type FTIR-spectrometer. Reference measurements were conducted for some of the samples at the Ångström laboratory of the Uppsala University [6, 8-9]. Results for samples A-C are shown in Table 1. As can be seen,

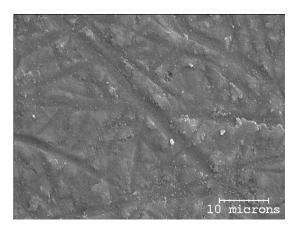
improvements in the manufacturing processes have increased α from a level of 0.8 to a level of 0.9, and decreased ϵ from a level of 0.3 to a level to 0.2. At the same time, the process has been simplified and the delivery cycle has been shortened. A reference surface D was disassembled from a solar collector, which has been at a test site for four years (most of the time without fluid circulation inside). Unfortunately α and ϵ of the reference surface D before natural aging of four years are unknown. Most likely they were in the same range with samples A and B due to same manufacturing period. Both α and ϵ of sample D are higher than α and ϵ of samples A-B, but the increased α more than compensates the higher ϵ . Similar behaviour has been observed for other samples in accelerated aging tests [8-9]. It must be noted that sample D does not represent the latest stage of production, and therefore ϵ of the latest samples (being originally lower) does not probably rise to the same level after aging.

TABLE 1
MANUFACTURING PARAMETERS AND OPTICAL PROPERTIES OF SURFACE SAMPLES A-C

Sample	Grinding time (min)	Acid bath time (min)	α	3	α/ε
A	15 (manual)	-	0.82	0.29	2.8
В	20 (manual)	20	0.86	0.29	3.0
С	15 (mechanical)	-	0.90	0.22	4.1
D	Reference surface: a collector was disassembled after four years of natural exposure and α and ϵ were measured		0.89	0.31	2.8

MICROSTRUCTURAL ANALYSIS OF THE SURFACE

The microstructure of the surface consists of inhomogenous grooves with a typical width of 1-2 µm. An example of how the microgrooves are organized is shown in Figure 2 (left). Optical microscopy revealed that the surface is inhomogenously covered by a dark substance (Fig. 2), which has been identified as graphite by XPS [10].



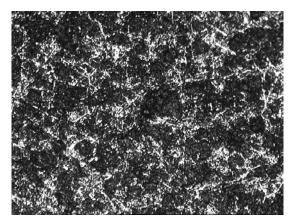
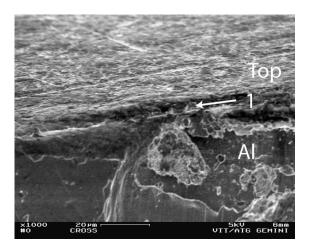


Figure 2: Scanning electron micrograph (left) and optical microscope photograph (right) of two typical surface samples, 2000x and 100x magnification, respectively.

On an area of 50 x 40 μ m (as in Figure 2, left) one to three 2 μ m wide grooves, which are quite clear and sharp on the edges (compared to the narrower grooves) are typically visible. This can be explained by the size of the silicon carbide particles (\sim 300 nm - 2 μ m) of the grinding pad and the nature of the grinding process. Particle size below 1-1.5 μ m most probably constitute a majority of the particle frequency distribution thus resulting in the majority of the groove widths being in the range of 1 μ m. As the surface is being grinded over multiple times during the whole manufacturing period (e.g. 15 min), only the latest formed grooves remain sharp-edged. Figure 3 shows partial and complete crosscut scanning electron micrographs of surface samples. A clear 2 μ m

wide oblique microgroove is visible on top of the surface in Fig. 3, left). The sample on the right was manufactured by placing a crosscut section of a surface sample between two pieces of stainless steel and casting it in epoxy, which was sawed in half and the crosscut section was manually diamond-polished. Areas denoted as C can be interpreted as graphite clusters adsorbed and agglomerated on the microgrooves of the Al_2O_3 -surface. The grinding process mechanically incorporates adsorbed graphite onto the grooves of the surface. The graphite matrix structure shown in Figure 2 (right) is composed of agglomerated graphite clusters. More details are reported in [6, 10].



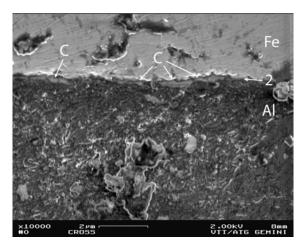


Figure 3: Partial (left) and complete (right) crosscut scanning electron micrograph of a surface sample. Borderlines between top of surface and crosscut section (1), and stainless steel and C/Al₂O₃/Al layer (2). Graphite clusters denoted with C, maximum visible cluster thickness 300 nm.

Another spot of the sample shown in Figure 3 (right) was examined by an EDS analysis to verify the composition of the light areas as graphite (Figure 4). A large amount of C was found, but significant amounts of O and Al were identified as well. Similarly, areas positively known as Al and Fe contained lesser, but still significant amount of C. Most likely the crosscut sample becomes contaminated during the diamond polishing with all the elements present on the surface. Therefore it was not possible to positively identify the composition of the light areas as graphite with the EDS.

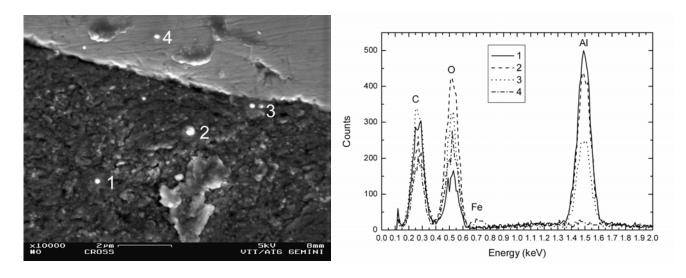


Figure 4: Crosscut scanning electron micrograph of another spot of the sample shown in Figure 3 and an EDS -analysis of bright spots 1-4.

DISCUSSION

Increasing graphite coverage to unity could increase α to \geq 0.94 [11]. The groove structure of the surface should be homogeneous and comprehensive for enabling this. Another way to obtain higher α could be the use of anti-reflection (AR) coating, which could also act as a moisture barrier, thus further enhancing the durability of the surface. On the other hand, adding an AR coating would add cost and complexity to the present low-cost manufacturing method. For example, Farooq and Hutchins [1] have designed a 75 nm thick Al₂O₃ AR layer for a sputtered V: Al₂O₃ selective absorber. It would be difficult to add such a thin and homogeneous AR layer on top of the C/Al₂O₃/Al absorber, which is formed of fundamentally more rough structures. A dip-coating AR treatment resembling the method used for glass by Nostell *et al.* [12] would better suit the current manufacturing principle, if it would be technically applicable.

Decreasing graphite cluster thickness could lower ϵ . This, as well as increasing graphite coverage could be achieved by altering the composition and the structure of the grinding pad and by finding suitable manufacturing parameters for the advanced pad. The grinding pads commercially available today are not specifically designed for manufacturing solar surfaces. An enhanced grinding pad could result in a surface having uniform groove structure with depth and frequency distribution optimized for an optimal homogeneous graphite layer to be formed. At the moment, the graphite cluster thickness (as shown in Figure 3, right) has not been positively determined due to difficulty [10] in manufacturing razor-sharp crosscut samples. A proper method for accurately analysing the groove depth and cluster thickness and their distribution would be required in order to modify the properties of the grinding pad accordingly.

CONCLUSIONS

Spectrally selective $C/Al_2O_3/Al$ solar absorber surfaces have been manufactured with chemical and mechanical treatment. XPS, SEM, EDS and optical microscopy were used to determine the elemental composition and geometrical structure of the surface. The surface consists of an Al-substrate and an inhomogenous matrix of 1-2 μ m wide microgrooves and graphite clusters. A solar absorptance α of 0.90 and a thermal emittance ϵ of 0.22 have been achieved so far. Increasing graphite coverage to ideal and/or adding an antireflective coating could increase α to \geq 0.94 and decreasing graphite cluster thickness could lower ϵ . This could be achieved by more accurate analyses of the groove depth and cluster thickness and their distribution, and by altering the grinding pad and manufacturing parameters accordingly.

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