Mechanically manufactured selective solar absorber surfaces

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Abstract

This study describes the development of manufacturing processes for a mechanically manufactured selective $C/Al_2O_3/Al$ surface and its basic characterization. The composition and structure of the surfaces were characterized by scanning electron microscopy and electron microprobe analysis. Spectroradiometer and FTIR-spectrometer were used for optical characterization. The manufacturing process has been developed from manual abrasive grinding followed with an acid bath to mechanically operated grinding alone. The surface consists mainly of Al_2O_3, with some C adsorbed on the surface during the grinding process. The microstructure of the surface consists of small grooves, organized in a heterogeneous two-dimensional matrix. The width of the grooves varies typically between 1 and $2\,\mu m$. The absorptance of a surface from the latest stage of development is 0.90 and the emittance 0.25.
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1. Introduction

Spectrally selective surfaces for solar absorbers have been studied since the 1950s, when the idea of using wavelength discrimination and wavefront discrimination was introduced [1]. A great deal of the early work was connected with the development of electroplated black chrome [2–7] absorber coatings. Other major selective surfaces

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developed include black nickel [8], cermet [9] and sputtered surfaces [10–12]. Another interesting production method utilizes selective paints [13–15]. Today's state-of-the-art selective surfaces have good optical properties: $90\% < \alpha < 98\%$ and $3\% < \varepsilon < 10\%$. A comprehensive review of different types of selective absorber surfaces has been reported by Lampert [16].

Some of the manufacturing methods of the above-mentioned surfaces require chemicals or contain processes that may be harmful to the environment. Other methods, e.g. sputtering based ones, may require high investments of the manufacturing infrastructure.

The aim was to develop an environmentally friendly and low-cost method for mass-production of selective surfaces. Mechanical manufacturing was found quite attractive for this purpose. Another target was high durability and aging resistance in order to reach long service life. This study describes the development of manufacturing processes for and basic characterization of the mechanically manufactured selective $C/Al_2O_3/Al$ surface. Comprehensive durability tests are also under way, and will be published separately.

2. Development of manufacturing processes

Aluminium was chosen for the substrate because of earlier experience, non-toxicity, relatively low cost and good properties for a solar absorber substrate. Selective surfaces based on aluminium/alumina have been reported in the literature as a combination of M/Al_2O_3, $M = $(Ta, Mo, W, Pt, or Ni) [17,18], or as electrodeposited thin Al_2O_3 layers on aluminium [19,20].

Targets for the optical properties during the product development process were set as $\alpha \geqslant 0.90$, with ε as low as can possibly be achieved with the manufacturing technology. While judging the optical quality of different absorber sheets manufactured with different process parameters, we considered a 1% increase in the α to be equivalent to a 4% decrease in the ε.

2.1. Preliminary experiments

The mechanical manufacturing of the $C/Al_2O_3/Al$ selective surface has gone through many phases, starting from the early experiments based on well-known methods of aluminium dyeing [21]. The first tests were conducted by treating the surface with different acidic solutions. The latest of these solutions, referred to as the acid bath from this point forward, contained potassium permanganate (10 g/l), cupric nitrate (25 g/l) and nitric acid (4 ml/l). However, this treatment alone was not sufficient to produce selective optical properties. In order to increase oxidation of the Al-substrate surface before acidic treatment, sand blasting was tested. This experiment was not successful. Nevertheless, it gave rise to the idea of using mechanical grinding for achieving the oxidation effect needed.

2.2. Methods based on grinding of the surface

The first objective for grinding-based manufacturing was to identify suitable abrasive materials for pre-treating the surfaces before the acid bath. After numerous tests with different abrasives and grinding methods, the best ones were identified. In this abrasive grinding process, the selective coating is based mainly on a combination of alumina and carbon.

All further manufacturing process changes and parameter adjustments are based on the abrasive grinding method. The grinding parameters, such as speed, time, pressure, temperature and 2-D grinding pattern were tested systematically to find the most suitable ones for industrial manufacturing. This multi-optimization task was much more difficult and time-consuming than expected. Whenever one of the parameters was changed, sometimes even slightly, the whole process gave completely different results for optical properties and surface homogeneity.

At first, grinding was done manually and the aluminium sheets were subjected to the acid bath after grinding. In order to speed up the delivery cycle of the process and to reduce waste from the process, a large amount of tests were made without the acid bath. Eventually, this proved to yield equally good results (Table 1). The latest phase in the manufacturing has been the change from manually operated grinding to mechanically operated grinding, which seems to be a promising method for manufacturing the surface.

In the latest version of the manufacturing machinery, the surfaces are manufactured by mechanically operated grinding, which lasts about 15 min for the whole sheet of 2 m in length and 0.12 m in width. Three sheets are ground simultaneously by using three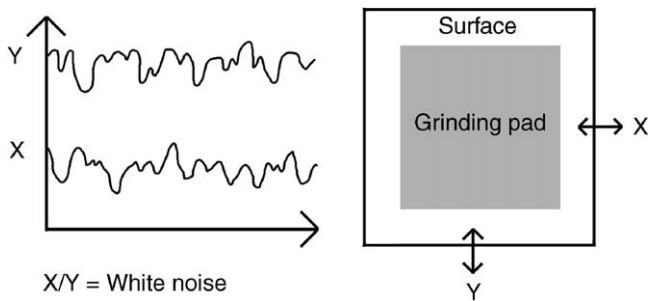 grinding machines. The mechanical grinding method implements a non-correlating white noise signal, which generates the control voltage for the X/Y—electromagnetic control units of the grinding unit. The grinding unit drives the grinding pad attached to the wheel head (Fig. 1).

3. Microscopic characterization of the surface

The surfaces were characterized by scanning electron microscopy (SEM, model JEOL JSM-820) and electron microprobe analysis (EDS, model PGT IMIX). The microstructure of the surface as seen by SEM (Figs. 2 and 3) consists of small grooves, organized in a heterogeneous two-dimensional (and partly three-dimensional) groove matrix. The width of the grooves varies typically between 1 and 2 μm. Due to continuous grinding process, some of the grooves are deeper and/or have sharper edges than the others. The probable cause for this is that during grinding the grooves formed earlier are ground over multiple times with grains of different size and shape, causing only the latest formed grooves to appear very clear and sharp-edged.

Al substrate sheets of 99.5% purity (EN AW 1050A, hardness number 14) have been used in all manufacturing phases. The electron microprobe analysis (Fig. 4) reveals that the surface of a typical absorber surface sample, subjected to 15 min of

Table 1
Manufacturing parameters and optical properties of samples A–G

Sample	Manual grinding time (min)	Acid bath time (min)	α	ε	α/ε
A	15	—	0.82	0.29	2.8
B	15	10	0.81	0.25	3.2
C	20	20	0.86	0.29	3.0
D	15	—	0.84	0.25	3.4
E	20	—	0.87	0.24	3.6
F	15 (mechanical grinding)	—	0.88	0.27	3.3
G	19 (mechanical grinding)	—	0.90	0.25	3.5

Fig. 1. The non-correlating white noise which generates the control voltage for the X/Y—electromagnetic control units of the grinding unit. The grinding unit moves the grinding pad attached to the wheel head.

grinding, consists mainly of Al and O with some traces of C. Analysis of the unground backside of the same sample shows that the grinding process adds O and C to the surface. Further XPS, SEM and EDS analyses have verified these results [22]. Some of the C measured from the backside may be due to carbon dust contamination during the grinding process, although the surface was cleaned with methanol prior to the analysis. In the other EDS analysis (of surface of sample A, described in ch. 4) very small traces of Si, Mn, Fe and Cu were detected. According to the Al-sheet manufacturer, the sheet can contain these as well as Mg, Zn and Ti in a percentage of 0.00–0.40, the maximum content being different for each element. Prior to the EDS analysis, the surface was coated with a very thin layer of gold, which was detected as well.

4. Optical characterization of the surface

The solar absorptance was determined by measuring the spectral hemispherical reflectance from 0.39 to 1.1 μm with a LI-COR LI-1800 type spectroradiometer and an integrating sphere, and α_λ was calculated for each wavelength. The infrared emittance was determined by measuring the spectral (semi)hemispherical reflectance
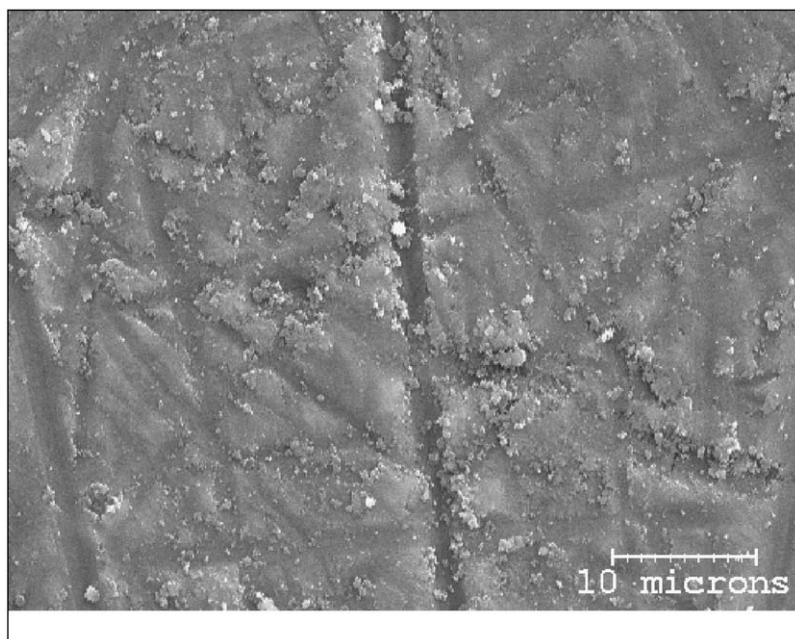
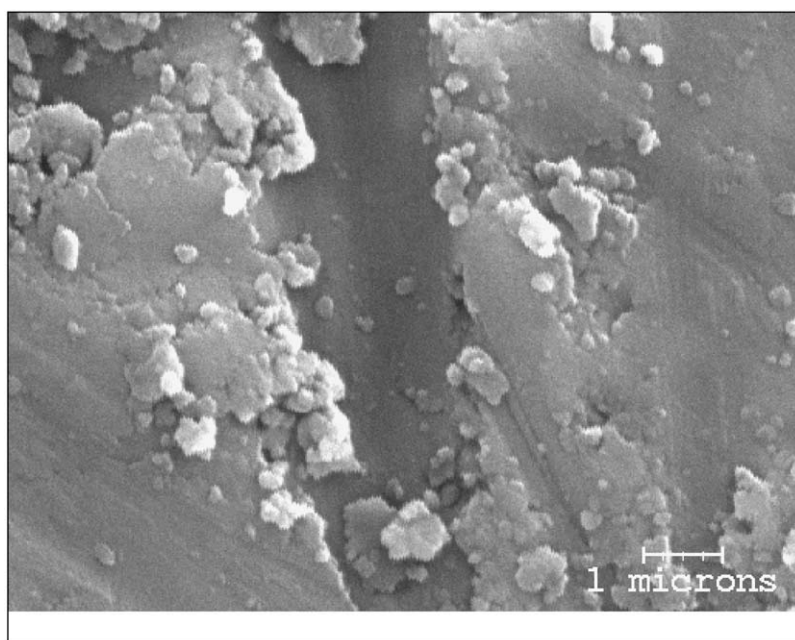Fig. 2. SEM photograph of the surface A, 2000 × magnification.

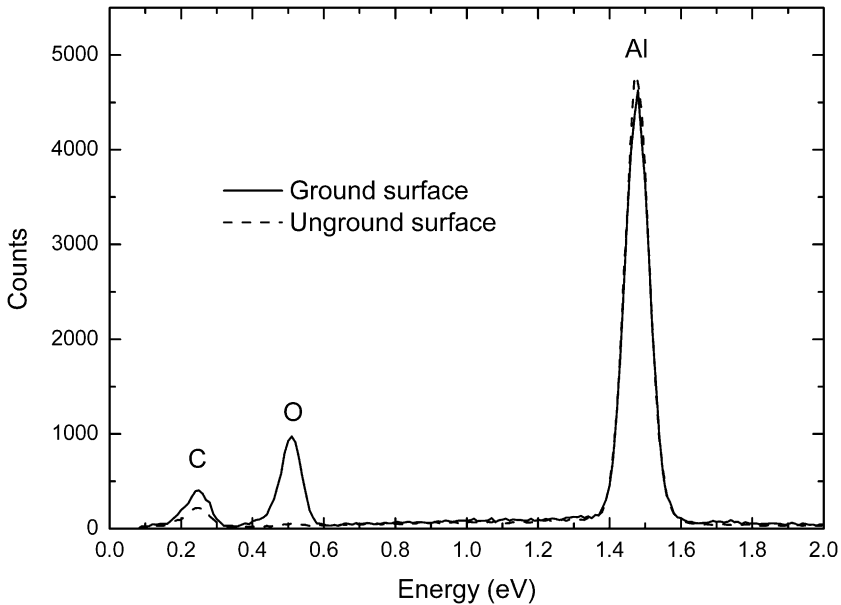Fig. 3. SEM photograph of the surface A, 11,000 × magnification.

Fig. 4. EDS -analysis of a typical surface, ground manually for 15 min. Untreated aluminium backside of the same sheet shown as a reference.

from 2.5 to 20 μm with a MIDAC Prospect IR type FTIR-spectrometer with a semi-integrating device, and ε_λ was calculated for each wavelength. The hemispherical absorptance and the hemispherical emittance were calculated from these values. In this study the hemispherical absorptance is referred to as α, and the hemispherical emittance as ε.

Reference measurements were conducted at the Ångström laboratory of the Uppsala University, Sweden. The equipment used for the reference measurements includes a Beckman spectrophotometer UV 5240 with a $BaSO_4$ integrating sphere for UV–Vis–NIR and a Bomem Michelson 110 FTIR spectrometer with a golden integrating sphere for IR. With these reference measurements, we could measure the whole UV–Vis–IR spectrum needed and verify the results of the measurements carried out at the Helsinki University of Technology (HUT).

The solar absorptance measurements done at the HUT comply within 3% (absolute) with those done in the Ångström laboratory. The emittance measurements vary more, mainly due to the lack of a proper integrating sphere at the HUT. Differences in ε (in all cases absolute %) in the mechanically manufactured samples vary from -4% to $+2\%$ and $+11\%$ for the reference sample between the ε measurements done at HUT and the ε measurements done at the Ångström laboratory. The same samples were measured in both places, but the exact measured area varied slightly. The absorptance and emittance measurements were repeated several times for some samples in the Ångström laboratory. The differences in these results were insignificant.

Figs. 5–7 show the spectral hemispherical reflectance, ρ_λ, of the samples from 0.3 to 20 μm. All these figures are based on the measurements conducted at Uppsala. A commercial selective surface based on sputtering and copper substrate was used as a reference surface (Fig. 6).

With the grinding process, the first samples of somewhat satisfying optical quality are shown in Fig. 5. Of these, the sample A was manually ground for 15 min. Samples B and C were manually ground for 15 and 20 min, and after grinding they were subjected to acid bath for 10 and 20 min, respectively. α increased from 0.82 to 0.86, when the grinding time was increased from 15 to 20 min together with the introduction of the surface to the acid bath for 20 min (Table 1). Adding a 10-min acid bath after 15 min of grinding did not have any significant effect on α. The emittance of the samples A, B and C was 0.29, 0.25 and 0.29, respectively. Differences between these values are within the measurement accuracy. The acid bath was abandoned from the manufacturing process quite soon after manufacturing these samples.

Due to learning to understand and thus better control the manufacturing processes, α (and in some cases, also the α/ε ratio) of the subsequently manufactured samples (from D to F, Fig. 6) increased, when compared to the best of the earlier samples (such as C). This improvement was achieved both when comparing the new samples to the older ones subjected to the grinding method alone, and by comparing them to the ground and acidulated older samples. In most cases, ε stayed relatively low despite the increase of α. Table 1 shows the corresponding α and ε values. The
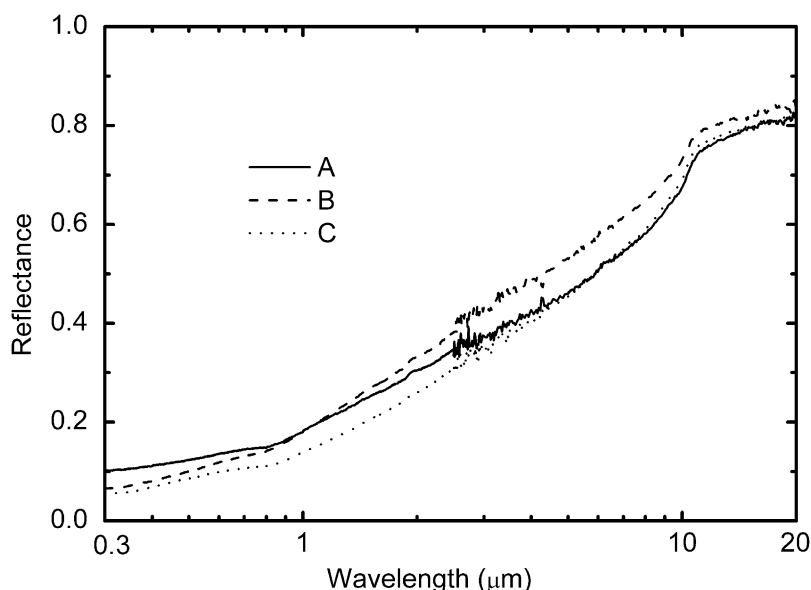

Fig. 5. Spectral reflectance of samples A, B and C. Samples were ground manually for 15, 15 and 20 min, respectively. After grinding, samples B and C were subjected to acid bath for 10 and 20 min, respectively.
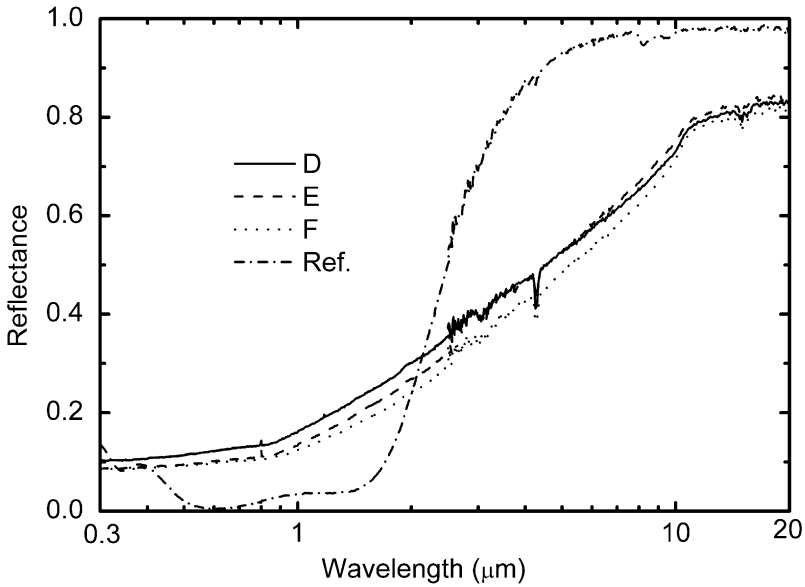
Fig. 6. Spectral reflectance of samples D–F and a reference surface. Samples D and E were ground manually for 15 and 20 min, respectively. Sample F was ground mechanically for 15 min.
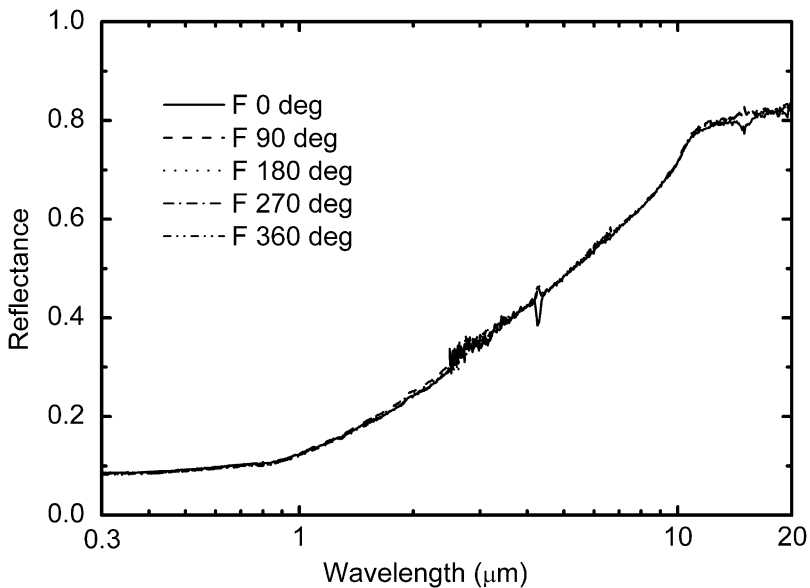

Fig. 7. Spectral reflectance of sample F, ground mechanically for 15 min. The sample was rotated 90° clockwise between each measurement to verify the possible interrelationship between sample orientation and measurement results.

optical properties of the latest, mechanically ground surface G are: $\alpha = 0.90$ and $\varepsilon = 0.25$.

According to Roos [23], even with an integrating sphere, the results might vary significantly depending on the structure of the sample and its rotational orientation at the sample port while measuring. In order to verify possible interrelationship between the sample orientation and the measurement results, the sample F was rotated 90° clockwise between five measurements (Fig. 7). The differences of the results are insignificant. On the other hand, due to the nature of the manufacturing process and instrument accuracy and precision, some variations in the α and ε values are typically measured within the same sheet of absorber.

5. Discussion

This mechanical manufacturing process has proven to be a promising low-cost method for manufacturing selective solar absorber surfaces. The process itself can easily be duplicated inexpensively. The estimated set-up cost for a manufacturing plant is significantly lower than e.g. a plant using sputtering technology, for equal annual production. The machinery and equipment needed are suitable to be used in the developing countries as well as in the industrialized countries. The optical properties of the surfaces studied in this work cannot compete with the state-of-the-art commercial surfaces, but taken into account differences in the manufacturing infrastructure set-up costs, these surfaces are likely to have their applications in the middle quality—and lower cost—solar heating systems, operating at low to medium temperatures.

For preliminary economical calculations, a single-glazed solar water-heating collector model was used to estimate the absorber surface energy yield. The optical parameters of the absorber samples were put into a sophisticated in-house built collector model, which gives the collector efficiency curve and the average collector overall heat loss coefficient U_L as output. The collector model is based on the solar collector equations by Duffie and Beckman [24]. The boundary conditions, i.e. weather conditions and collector parameters excluding the absorber, were kept constant to analyze the effects of the differences in the optical properties of the metal sheets. The environmental parameters used were solar irradiance $G_T = 850\,\mathrm{W\,m^{-2}}$ (on the collector plane), ambient temperature $t_a = 25°C$ and wind speed $V = 2\,\mathrm{m\,s^{-1}}$. Fixed collector parameters included: aperture area $6\,\mathrm{m^2}$ ($3\,\mathrm{m} \times 2\,\mathrm{m}$), slope $\beta = 45°$, fluid = water with mass flow of $\dot{m} = 0.0084\,\mathrm{kg\,s^{-1}\,m^{-2}}$ ($30.4\,\mathrm{kg\,m^{-2}\,h^{-1}}$) and 8 pipes ($\varnothing$ 0.0124 m) connected in series.

We used a transient simulation model EUROSOL to calculate the hour by hour performance and to yield the yearly solar energy output of the collectors. For comparison, we also show results for a commercial selective collector. The following parameters were employed: Domestic hot water (DHW) energy needs 14,800 MJ/yr, typical Central European climate. The solar collector area used is $6\,\mathrm{m^2}$ and the storage tank volume is 500 l. Hot water consumption is estimated to be 180 l/day. We assumed glass transmittance $\tau = 0.92$ in all cases. The results are shown in Table 2 as

Table 2
Calculated UL-values, normalized annual energy gains and normalized solar fractions for single-glazed collector and solar combisystem

Sample	U_L	Q_u/Q_{uref}	sf/sf_{ref}
A	5.05	0.75	0.81
B	4.87	0.76	0.83
C	5.07	0.78	0.85
D	4.88	0.78	0.84
E	4.85	0.81	0.87
F	4.98	0.81	0.87
G	4.91	0.83	0.89
Reference selective surface	3.96	1	1

Parameters: typical Central European climate, typical solar DHW system, $6 \, m^2$ collectors and a 500-l tank for a single-family house. Hot water consumption 180 l/day. A selective surface ($\alpha = 0.95$, $\varepsilon = 0.05$) is shown as reference.

normalized annual energy gain and normalized solar fraction. The best of the solar DHW systems with mechanically manufactured absorber surfaces yield about 17% lower annual energy gain and 11% lower solar fraction compared to the reference system.

6. Conclusions

This paper describes the basic manufacturing process for a mechanically manufactured $C/Al_2O_3/Al$ selective surface, and the development steps of the manufacturing processes. The surface was characterized by SEM and electron microprobe analysis. The surface consists mainly of Al_2O_3 and a carbon matrix organized as a heterogeneous groove structure. The widths of the grooves typically vary between 1 and 2 μm. The optical properties of the latest surfaces are: $\alpha = 0.90$ and $\varepsilon = 0.25$. These surfaces were manufactured by mechanically operated grinding, which lasts about 15 min for the whole sheet of 2 m in length and 0.12 m in width. Three sheets are ground simultaneously by using three grinding units. This number can be scaled up inexpensively as needed. The grinding process does not produce any environmentally harmful waste.

Comprehensive durability and accelerated aging tests are under way and the results will be published after completing the tests. Solar collectors with mechanically manufactured absorber surfaces have now been satisfactorily in operation for some four years in field tests.

Acknowledgements

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