ELABORATION AND TESTING OF MATERIALS USING CONCENTRATED SOLAR ENERGY

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Summary

Solar furnaces are very useful tools to process and study materials at high temperature because they achieve very high temperatures in a very short time (3000 °C in few seconds), they allow operation under controlled and very clean atmospheres using quartz reactors (transparent to solar radiation), and irradiation of large sample sizes according to the size of the solar furnace (typically the order of 0.5 cm for a 1 kW solar furnace and of 20 cm for the 1 MW solar furnaces of Odeillo). Moreover combining these characteristics the control of material heat cycling (heating and cooling periods) according to requirements may be performed. This paper gives an overview of materials elaboration and materials testing (qualification) using concentrated solar energy. Materials elaboration addresses surface treatment (hardening, cladding, alloying); melting and purification of bulk materials (oxide ceramics, glass, metal recycling and separation, silicon purification); production of chemical commodities and ceramics (lime, aluminum, nitrides, carbides); and synthesis of nanomaterials and nanophases (fullerenes, carbon nanotubes, oxide nanoparticles, Si thin film). Materials testing addresses space and energy applications. Refractory materials are concerned.

Experiments are performed in original chambers that combined solar heating and another constraint on the surface such as vacuum, excited species, UV radiation or ion bombardment. Mechanisms of materials degradation, surface properties and surface chemistry are studied specially, oxidation, sputtering, high temperature emissivity and atoms recombination.

1. Brief history of the use of solar energy to transform matter

Just a few words first to retrace the history of the use of solar concentrated energy as reported by Trombe.Buffon has reported the oldest and famous history of Archimedes. In 215 before JC, Archimedes using solar energy with bronze mirrors had probably reduced to ashes the roman naval fleet composed of wooden ships that were besieging Syracuse. Buffon tried himself to reproduce this experiment and succeeded to burn a wood pile and to melt metals using one hundred forty mirrors oriented on the same surface.But this try was not the first one to use solar energy to obtain high temperatures.

At the 17th century, some mirrors and lens (called "*ardent*" mirrors) allow to reach temperatures of around 1000°C, like the one of Cassini with a diameter of 1 m, called the King mirror, as it was a gift to king Louis XIV. Using this mirror, they have melted iron and silver very quickly. At the same time, wood mirrors covered with copper were used to change stones to glass. It was also the birth of image furnaces: two concave mirrors with different focal distances are placed face to face. At one focus a heat source is placed and at the focus of the second, high temperature can be obtain on a target.

At the end of the 17th century and during the 18th one, lens were used in place of concave mirrors for fusion experiment at high temperature, as these lenses have the advantage to concentrate the solar radiation from top to down.

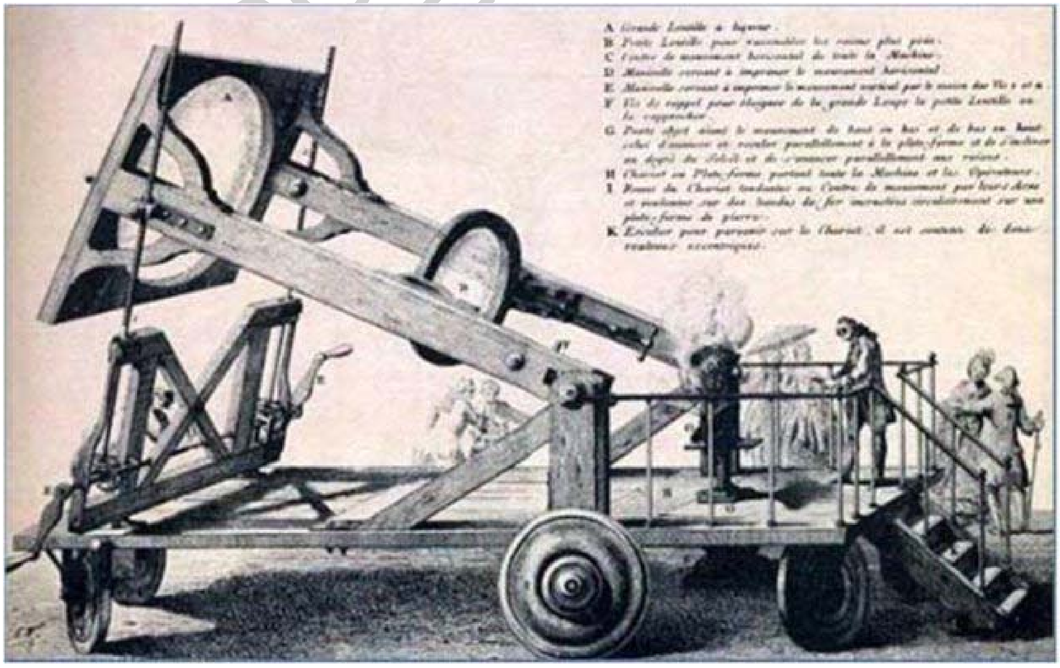


Figure 1: Solar furnace of Lavoisier

After these several tries, done in a non-systematic way, most efficient experiments were carried out. Lavoisier in 1773 managed (i) to melt rapidly iron (1500°C) and to approach the melting temperature of platinum (1773°C) with a lens full of alcohol and (ii) to prove that diamond is an allotropic form of carbon as he burnt diamond at the focus of his solar furnace in air (Fig. 1). He has also shown that it was possible to treat metals under special atmosphere like nitrogen. The experiments performed by Lavoisier were the last done in order to produce high temperatures and to study the interaction of solar energy with matter. Then, the following researches with solar energy were used to cook food (Herschell, 1834) and to build a boiler (Mouchot, 1861).

Then, Trombe, using a 2 m diameter german mirror recovered after the second world war, two centuries after Lavoisier, had shown the efficiency of concentrated solar energy to melt high refractory ceramics like alumina (2050°C), chromium oxide (2260°C), zirconia (2680°C), hafnia (2780°C) and thoria (> 3000°C). The first experiments conducted by Trombe in the 50’s, were:

- synthesis in gaseous phase ;
- continuous treatment of refractory compounds in order to have samples of great size ;
- study of the fusion of mixing of oxides, of reaction of dissociation and chemical reactions using different compounds.

After all these experiments on a 2 kW solar furnace, he explained that it is necessary to work on solar furnaces of huge size to obtain high temperatures on great surfaces but also to prepare new refractory materials for industrial purposes. Moreover, he thank that he will be important to separate two functions: the following of the apparent moving sun and the concentrator. This was the birth of the 50 kW solar furnace of Mont-Louis (F) and then the 1 MW solar furnace of Odeillo (F) in 1970 that is still the biggest in the world (Fig. 2).

Figure 2: 1 MW solar furnace in Font-Romeu Odeillo (France)

2. Main characteristics of solar furnaces

Solar furnaces are very useful to process and study materials at high temperature as they achieve very high temperatures in a very short time (3000 °C in few seconds), to work under controlled and very clean atmospheres using quartz reactors (transparent to solar radiation), to irradiate large sample sizes according to the size of the solar furnace (typically the order of 0.5 cm for a 1 kW solar furnace and of 20 cm for the 1 MW solar furnaces of Odeillo) and to control material heat cycling (heating and cooling periods) according to requirements. Moreover, solar radiation may be associated with other light or chemical sources in order to simulate various ‘extreme’ conditions on tested samples. Additional light source may be UV radiation and additional chemical species may be supply by microwave discharge or ion gun (see part 4).

Typical characteristics of Odeillo solar furnaces are listed in Table 1.

Power (kW)	Maximum flux Density (MW/m^2)	Heating rate (K/s)	Cooling rate (K/s)	Pressure Atmosphere	Additional source
1 6 1000	16 5 10	1000	100-10 000	10^{-5}–10^5 Pa Air, Ar, H_2, N_2, O_2, CO_2...	UV lamp m.w. plasma Ion gun

Table 1: Some characteristics of solar furnaces in CNRS-Odeillo.

Medium size solar furnaces are also available at PSA (Spain), PSI (Switzerland) and DLR (Germany), their power are 60 kW, 40 kW and 25 kW respectively and maximum flux density is about 5 MW/m^2.

Previous characteristics of solar furnaces are used to elaborate materials and to test physical and chemical behavior of metals and ceramics. The next paragraphs address both applications.

3. Elaboration of materials using concentrated solar energy

Proper characteristics of solar furnaces are combined to perform heat treatments of matter or materials that result in phase change, chemical reaction, component segregation or mixing and various transformations in the solid, liquid or gas states thus providing the conditions to create new materials.

For example, combining rapid heating and cooling of a surface results in hardening, combining melting and vaporisation in controlled atmosphere results in material purification, and combining vaporisation and controlled cooling of the vapors results in nanoparticles formation.

The various routes for materials elaboration using concentrated solar energy are detailed hereafter. They include: surface treatments, melting and purification of bulk materials, production of chemical commodities and ceramics, and elaboration of carbon molecules, nanomaterials and thin films.

3.1 Surface treatments

Surface treatments include surface hardening and surface cladding. Thermal superficial treatment of metallic materials that was investigated is called transformation hardening. It consists of heating the surface to produce the expected phase transformation without heating the bulk material. When the heat source is cut off, a hard phase is formed in the heated zone by self-quenching. The transformation hardening of steels is combined with a compression resulting from the expansion of the lattice when the phase transformation occurs. The most commonly used phase transformation is the austenization of iron-carbon alloys. The starting material, ferrite (centered cubic Fe-α) plus perlite (Fe-α and cementite Fe_3C) is transformed into austenite (Fe-α cubic centered faces) at temperature above 850°C. When rapidly cooled (quenched), the compound is replaced by a much harder phase, called martensite, which is quadratic centered. The non-alloyed XC55 steel was selected to perform solar hardening with peak flux density of 14 MW/m^2. Results are illustrated in Figure 3.

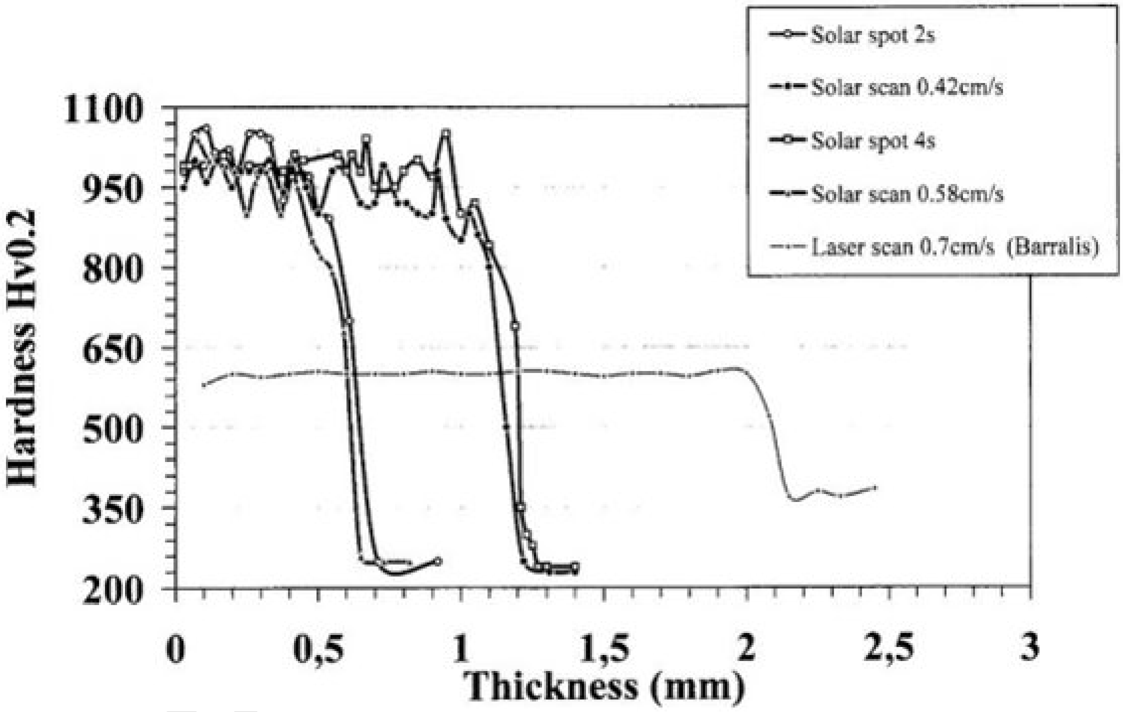


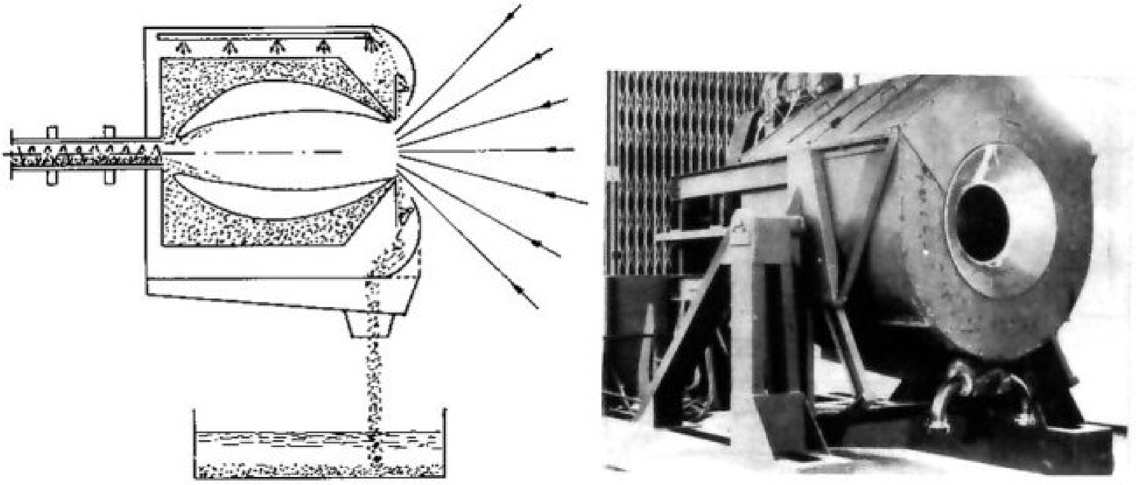
Figure 3: Hardness profiles of solar and laser treated steel

The hardness is drastically increased by the solar treatment from about 200 Hv in the non-affected zone up to super-hardness of 1000 Hv in the surperficial layer (0.5 – 1 mm thickness). In Figure 3 laser treatment is related to a 5 kW CO_2 laser beam.

Solar cladding was studied at NREL (Denver), at PSA and at CNRS. Recent results deal with melting of stainless steel powder (AISI 316) on carbon steel followed by a rapid solidification. A continuous scanning process was performed by moving the sample with a controlled velocity (0.8, 1.6 and 1.8 mm/s) at the focus of a vertical axis solar furnace. A vacuum chamber was used and operations have been carried out under an average flux of 13.4 MW/m^2 . Strip55 mm in length, 6 mm in width and 2 mm in thickness of dense solid layer were obtained. The resulting austenitic stainless steel offered good resistance to corrosion. Moreover NiAl intermetallic coatings were elaborated by a similar route: a solar assisted SHS (self-propagating high temperature synthesis) process.

3.2 Melting and purification of bulk materials

Melting of refractory oxides was intensively used by Trombe and Foex in the fifties-sixties to produce bulk materials from powders. SiO_2, Al_2O_3 and ZrO_2, for example were melted in rotary furnaces using the self-crucible concept in order to avoid pollution of the material by metallic walls. The main principle consists of using a water-cooled rotary cavity (cylindrical shape) filled with oxide powders and placed at the focus of a solar furnace. A liquid cavity starts to form at the beginning of the process because the density of the liquid is higher than the density of the powder. Then the liquid cavity enlarges inside the kiln stabilized by the centrifugal forces. At equilibrium, the kiln is filled with a molten bath (amphora shape) surrounded by solid particles at the vicinity of the wall. All the particles are not melted because of the thermal gradient existing beween the liquid surface and the wall. The process may be batch or continuous as illustrated in Figure 4a. A 500 liters rotary kiln was developed and tested (Figure 4b). 340 kg SiO_2 crucibles have been produced. Moreover oxide purification was demonstrated for quartz and alumina. The latter material was purified (segregation during solidification) from 99.8% to 100 ppm total impurities and the former from 99.5% to 200 ppm total impurities.



4a

4b

Figure 4: Rotary kiln for oxide melting at the 1000 kW CNRS solar furnace
Fig. 4a: Scheme of the process ; Fig 4b: The 500 liters rotary kiln

Elaboration of glass results in hazardous elements trapping in the matrix. Consequently solar elaboration of glasses may be used for hazardous mineral waste storage. One study is developed in this field, it is related to nuclear waste storage in rare earth glasses. Lanthanum and yttrium alumino silicates (La_2O_3-Al_2O_3-SiO_2 and Y_2O_3-Al_2O_3-SiO_2 systems respectively) can be easily obtained by melting of mixed powders under air with a solar furnace during about 2 min and cooling with a rate of 200 K/s. The effect of

Na_2O addition in lanthanum alumino silicate is also studied. It is known that 2% Na_2O can improve glass performances for minor actinides (Am, Cm et Np) storage. Solar processing allows the mixing of large amount of Na_2O (up to 13%) in the glass. Consequently, a detailed study of glass structure and stability as a function Na_2O content is possible.

Contrary to trapping of chemical elements in glass, vaporisation of impurities or valuable compounds from molten materials may result in material purification or material recycling respectively. For both applications the same principle is applied. This principle is the following, the equilibrium vapor pressure of chemical species in equilibrium with a liquid depends on temperature, total pressure and oxygen partial pressure. Thus it is possible to achieve a selective vaporisation of one or more chemical compounds by controlling these three parameters. The method has been applied to the separation of Nb and Ta from ores twenty years ago. More recently, the solar team from ETH and PSI used it to recover metal from waste (electric arc furnace dusts, EAFD). They added carbon in order to increase vapor pressure of Zn and Pb in the temperature range 1120-1400 K. The solar reactor is illustrated in Figure 5, it uses the indirect heating concept. Extraction of 99% and 90% of Zn was achieved for batch and continuous processes respectively.

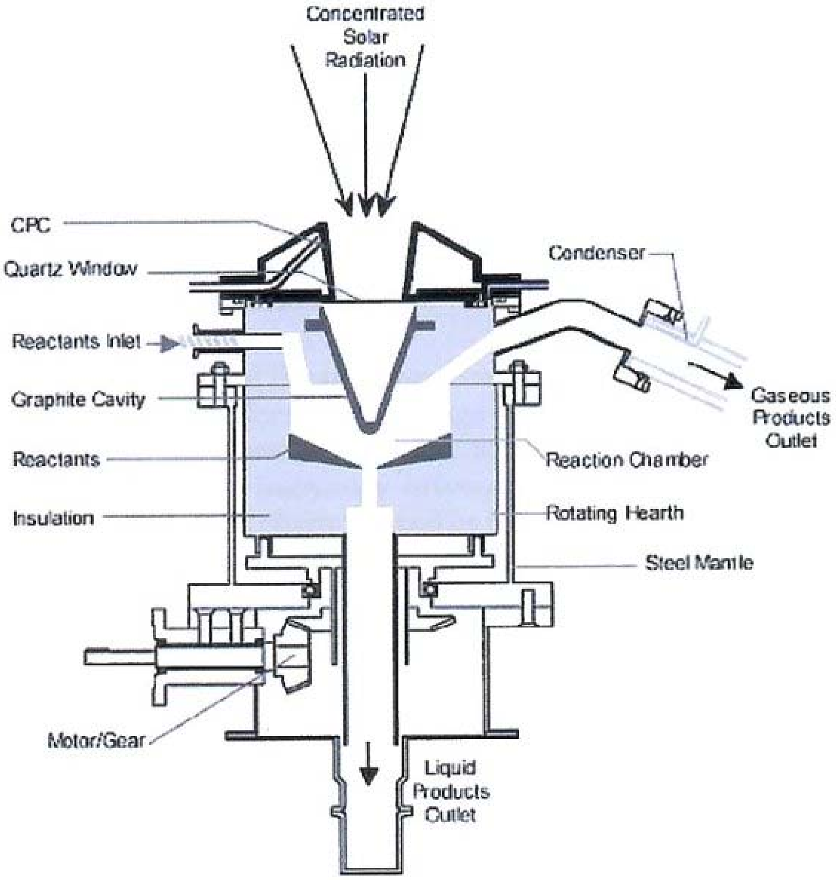


Figure 5: Solar reactor developed at PSI to separate metal from solid wastes.

Previous results were obtained at atmospheric pressure. Pressure reduction allows a more efficient separation of impurities. Purification of metallurgical grade silicon to obtain photovoltaic grade silicon was recently demonstrated at laboratory scale. We have carried out a set of solar experimental runs in a solar furnace with batch samples of upgraded metallurgical silicon. The process operated at reduced pressure (0.05 atm) for elimination of phosphorus, and with H_2O (humidified argon) for elimination of boron (mainly as BOH, gas). Concentrations of phosphorus and boron in the samples were reduced by a factor of about 3 after 50 min of solar irradiation in the temperature range 1820-1970 K. Results are illustrated in Figure 6.

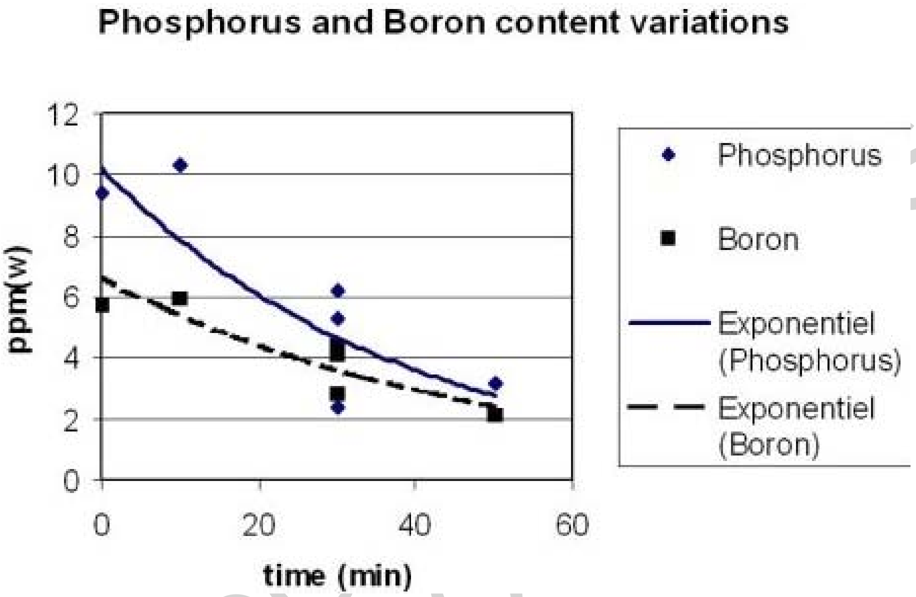


Figure 6: Variation of boron and phosphorus contents as a function of treatment time. Pressure: 0.05 atm, Argon: 1 l/min, water: 2.5 ml

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Biographical Sketches

Gilles Flamant (Dr-Ing, born 1952) is Director of the CNRS laboratory for Processes, Materials and Solar Energy (PROMES) and senior scientist at CNRS. PROMES is located in Odeillo (1000 kW Solar Furnace) and in Perpignan, South of France; about 75 permanent staff and 100 total personnel collaborate in the laboratory. He has been working in the field of concentrated solar energy and high temperature processes for about 30 years. He is co-authors of more than 160 papers in international scientific journals related to radiative heat transfer, chemical engineering, solar chemistry, hydrogen production, CSP, plasma chemistry and fluidized bed technology. He has supervised 30 PhD theses. He currently coordinates an European project related to hydrogen and carbon nanomaterials production from natural gas and solar thermal energy (“SOLHYCARB”). He co-founded the European Alliance on concentrated solar systems “SOLLAB” between CNRS (France), CIEMAT (Spain), DLR (Germany), ETHZ and PSI (Switzerland).

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