

Exergy analysis of ceramic composite manufacturing processes. The case of liquid silicon infiltration

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Abstract:

A relevant barrier for the massive use of composite materials is the high energy consumption needed for their manufacturing, what affects negatively to their cost. For this reason, exergy analysis of these processes is proposed in order to quantify this consumption by using the Second Law of Thermodynamics. Since this analysis would lead to the identification of the main issues affecting this energy consumption, it can contribute to the detection and quantification of potentials of energy savings.

As an example of this application, an energy and exergy study of a Liquid Silicon Infiltration process (LSI) is carried out. In the LSI process, silicon is melted and infiltrated in a ceramic porous preform (usually C or SiC) in order to obtain a final fully dense ceramic composite through a reaction bonding between the silicon and the carbon preform. These preforms are placed on a silicon powder bed, into a vacuum-reaction chamber. After that, temperature increases until the silicon melting point is exceeded and thereafter, melted silicon penetrates into the carbon porous body and reacts with it forming silicon carbide.

In this study, a whole process found in the literature [1] is analyzed, knowing the volume fraction of every component along the reaction stage and the changes in the preform porosity. In order to determine the time-evolution of furnace energy consumption, a simple model of the furnace is also developed. This kind of furnace is considered as a typical lab-scale equipment to carry out a LSI process. Besides the global exergy analysis, the time-evolution of exergy balance terms are computed.

Keywords:

Exergy Analysis, Ceramic Composites, Silicon Carbide, Liquid Silicon Infiltration (LSI).

1. Introduction

Currently, ceramic composites have found an important field of application in numerous industrial applications due to their special physical and chemical characteristics, particularly at high temperature and in hostile environments. Some sectors where ceramic composites play a key role are in aerospace applications [2], nuclear and energy industries [3] [4] or in thermal systems [5].

Silicon carbide composites are one of these ceramic materials with a large number of applications. This fact is mainly because of its low electrical conductivity, its excellent thermal conductivity and a very good thermal shock resistance in hot environments, giving it a great potential [6].

Liquid Silicon Infiltration (LSI) is a frequent method to convert porous carbon preforms to dense SiC in a low-cost way and even using complex shapes. LSI is a densification technique where a porous preform reacts with liquid silicon through a reaction bonding process and following the reaction [6]:



Silicon needs to be in liquid state, so temperature must be high enough to achieve its fusion (about 1400 °C).

The use of exergy analysis in processes like this is a novel methodology and it is not easy to find other references in literature. However, numerous studies about exergy analysis in different industrial manufacturing process have been developed [7, 8, 9]. Hader et al. [10] introduced and explained the methodology to apply a standard exergy analysis in a real process of ceramic manufacturing located in Jordan; Kita el al. [11] applied the exergy analysis and the life cycle assessment in an aluminum casting process where ceramic materials were using in the furnace.

Given these antecedents, the aim of this work is to evaluate and quantify the exergy change in the ceramic preform along the densification process, and for this reason, a real process found in the literature has been analyzed [1]. Here, Margiotta shows the volume fraction of every compound as well as the total porosity into the preform along a LSI process (measures after 10, 15, 30, 60, 120 and 300 min). His results were similar than in other experiments developed by other authors, for instance, Zollfrank and Sieber [12]. Knowing how the piece increases its weight and the amount of SiC formed in every point, it is possible to calculate the energy required to move from one state to another, the exergy in different times or its variation along the process. Besides, a simple model of the furnace has been developed in order to quantify the electricity required for the process, and, finally, to determine irreversibility produced.

2. Description of the LSI process

As it was mentioned before, Liquid Silicon Infiltration is a method whose goal is to obtain densified SiC preforms through a reaction bonding process. Carbon based porous preforms are place in a furnace along with silicon flakes (it is the most common geometry). Upon reaching its melting temperature, silicon liquefies and infiltrates into the preform though its pores, producing Si/SiC material. The process is carried out under vacuum or using an inert gas, but it has been determined that the best results are obtained working with the first conditions [13]. SiC preforms can be also fabricated by either pyrolysis of a polymerized resin (PIP process) or by chemical vapour deposition (CVD). However, ceramic materials formed by LSI are the only fully dense (have zero or low residual porosity) [14].

A variety of carbonaceous precursors can be used to obtain a carbon preform such as pitch, phenolics, furfuryl alcohol, carbohydrates, etc [15]. These compounds are mixed, shaped and carbonized in an inert atmosphere under high temperature to convert the precursor to carbon. After that, preforms are placed in contact with the infiltrating material (silicon or alloys of silicon), followed by heating above the silicon melting point. Liquid silicon wets the surface of the carbon preform and forms the ceramic matrix due to capillary forces, taking place the chemical reaction. A simplified process scheme is illustrated in Figure 1 [16].

In this study, Margiotta results [1] are going to be analysed since an exergy point of view. As described in that reference, the initial porous preform was prepared from a precursor blend of crystalline cellulose (FMC Biopolymer, Avicel PH-105) and phenolic resin (Borden, Durite AD-5614). Both components were mixed for 12 hours using different mass fractions of phenolic resin in order to detect the best combination. The precursor blends were pressed in a cylindrical mould obtaining pieces with 12 g of weight. The next step consisted in carrying out an oxidative thermal treatment aimed to thermoset the phenolic resin and to oxidize the cellulose phase thus maximizing its weight loss and potential for microporosity. The last step to obtain the porous carbon preform was to carbonize the piece in a high-temperature retort furnace with an inert argon atmosphere [13]. The chosen mass fraction was crystalline cellulose: phenolic resin 60:40, with a maximum carbonization temperature of 1000 °C [1].

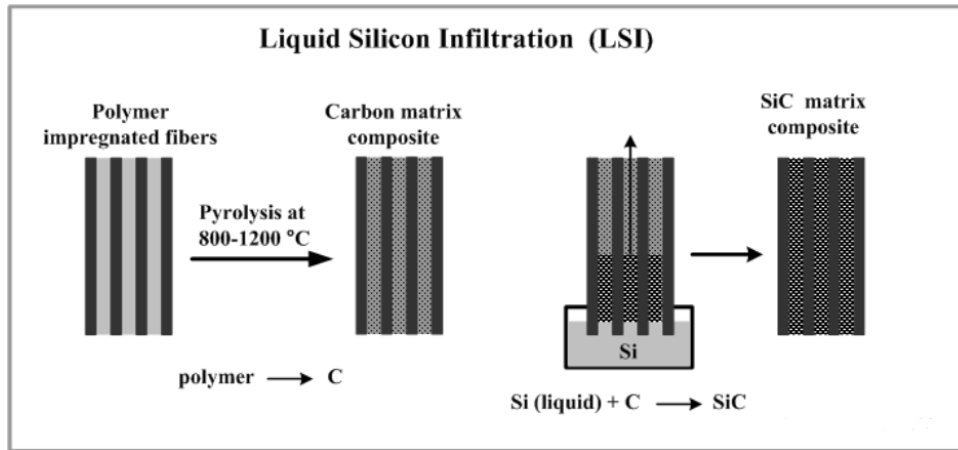


Figure 1. Formation of SiC by molten silicon infiltration in a porous carbon preform.

The carbon preforms were packed in a bed of silicon powder (crystalline, -325 mesh, 99.5 %, Alfa Aesar: Ward Hill, MA, USA) within a covered graphite crucible and LSI reaction were carried out for periods of 0, 10, 15, 30, 60, 120 and 300 min (it is considered that reaction starts when the melting point of Si is exceeded and liquid Si spontaneously infiltrates and reacts with carbon). Temperature and pressure within the reaction chamber were 1800 °C and 65 Pa of argon. Digital optical micrographs (Zeiss ICM405, Thornwood, NY, USA) were collected and analysed to determine the volume fractions occupied by silicon carbide, carbon, silicon and porosity during the reaction evolution. These results allowed one to follow up the progress of the densification reaction as time passes.

The evolution of every compound within the preform is shown in Figure 2. It must be taken into account that the total weight of the preform increases during the silicon infiltration and that at the end, when the reaction has finished, a small amount of silicon remains unreacted within the preform.

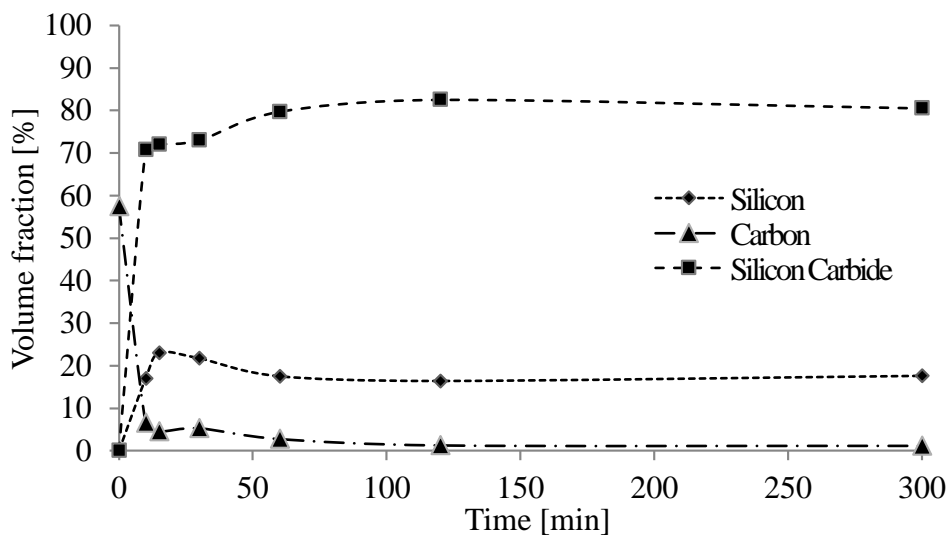


Figure 2. Volume fraction of carbon, silicon and silicon carbide in time-controlled reactions (adapted from [1])

3. Methodology

Since the aim of the paper is to perform exergy analysis, this methodology is summarized in next section. Besides, since energy consumed by the furnace was not reported, a model of a generic furnace has been developed in order to quantify heat losses (and, finally, electricity consumption). This model is also presented.

3.1. Exergy analysis

At the beginning, the preform is constituted only by carbon. When silicon fusion temperature is reached, it penetrates into the piece and SiC is formed. As a consequence of this, it is assumed that only three components are going to be involved in the reaction analysis: carbon, silicon and silicon carbide.

Knowing the composition in different points of time, exergy evolution is calculated as the sum of its physical and chemical exergy [5]. The first term refers to the maximum work obtainable as the system passes from its initial temperature and pressure (T and p) to the temperature and pressure of the reference environment (T₀ and p₀):

$$e_{ph} = (h - h_0) - T_0(s - s_0) \quad (1)$$

On the other hand, the chemical exergy is the maximum work obtainable as the system at T₀ and p₀ comes into total equilibrium with the reference environment:

$$e_{ch} = \Delta G_f^0 + \sum_y n_y e_y^{ch} \quad (2)$$

where ΔG_f^0 is the formation Gibbs free energy at T₀ and p₀, e_y^{ch} is the standard chemical exergy of the element y and n_y is the amount of the element y.

In the present study, it will be assumed that compounds form an ideal mixture, so the chemical exergy can be calculated as follows:

$$e_{mix}^{ch} = \sum_i x_i e_i^{ch} + RT_0 \sum_i x_i \ln x_i \quad (3)$$

where x_i is the mole fraction of component i in the mixture. The standard chemical exergy can be obtained from the Exergoecology Portal [17].

These are the formulae which will be use to prepare a complete exergy analysis in following sections.

3.2. Thermal simulation

Since electricity consumed by the furnace was not available, a generic furnace model has been defined. This model allows the calculation of furnace losses, what, along with the energy variation of the process (figure 6a), determines the power requirements of the furnace and, finally, irreversibility of the process.

Figure 3 represents the simple cylindrical furnace defined, which is a simplification of the actual component used in the experiment. It has a cylindrical cavity and is made of graphite felt (k = 0.08 W/m·K).

As it is known, temperature distribution in the furnace walls is given by conduction equation in cylindrical coordinates for a steady state situation, without generation and with constant thermal conductivity is:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} = 0 \quad (4)$$

Boundary conditions of the problem are constant temperature (1800 °C) in the cavity walls (red lines) and convection in the outer surface. A finite difference method has been applied by using EES Software and considering $\Delta z = \Delta r = 1$ mm.

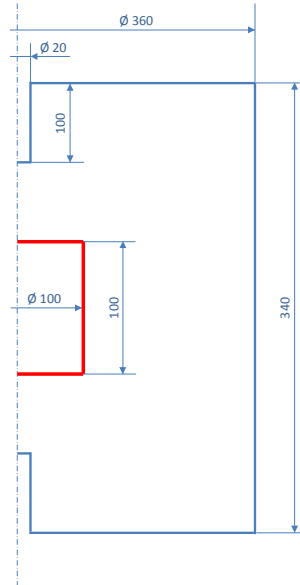


Figure 3. Furnace geometry.

For the sake of simplicity, constant convection coefficient has been considered, which includes also apparent radiation coefficient.

$$h = h_{\text{conv}} + h_{\text{rad}} \quad (5)$$

h_{rad} is calculated as:

$$h_{\text{rad}} = \sigma \varepsilon (T_s^2 + T_{\text{env}}^2) (T_s + T_{\text{env}}) \quad (6)$$

Considering that the outer surface of the furnace is made of aluminium anodized with an emissivity of 0.77, that the average surface temperature is 65 °C, and that the environment is at 25 °C, the value of h_{rad} is 5.65 W/(m²K).

Regarding h_{conv} , (and if the holes of 2 cm diameter are neglected), three situations appear: upper horizontal surface, lower horizontal surface and vertical surface. Applying EES subroutines, values obtained are, respectively, 5.66, 2.58 and 4.32 W/(m²·K). A value weighted by the areas involved results in 4.25 W/(m²K). Accordingly, the value of h is 9.9 W/(m²K).

4. Results

4.1. Energy analysis

Energy of the preform along the process is plotted in Figure 4.a. At the beginning of the reaction, energy in the preform is about 1.2 kJ, and this value becomes greater during the SiC formation. Energy increases during the 15 first minutes, when the reaction happens, and after that, it decreases until it is stabilized around a constant value slightly higher than the initial energy. As a consequence of this weight gain, energy per gram (Figure 4.b) decreases along the process, and energy per mol curve (Figure 4.c) has the same shape as the first graph because the total number of moles hardly varies. It should be noted that, for coherence with figure 1, the value of zero for x axis of the following graphs corresponds to the beginning of infiltration process; since the analysis also includes the silicon melting process (whose duration has been estimated in 10 minutes), negative values appear.

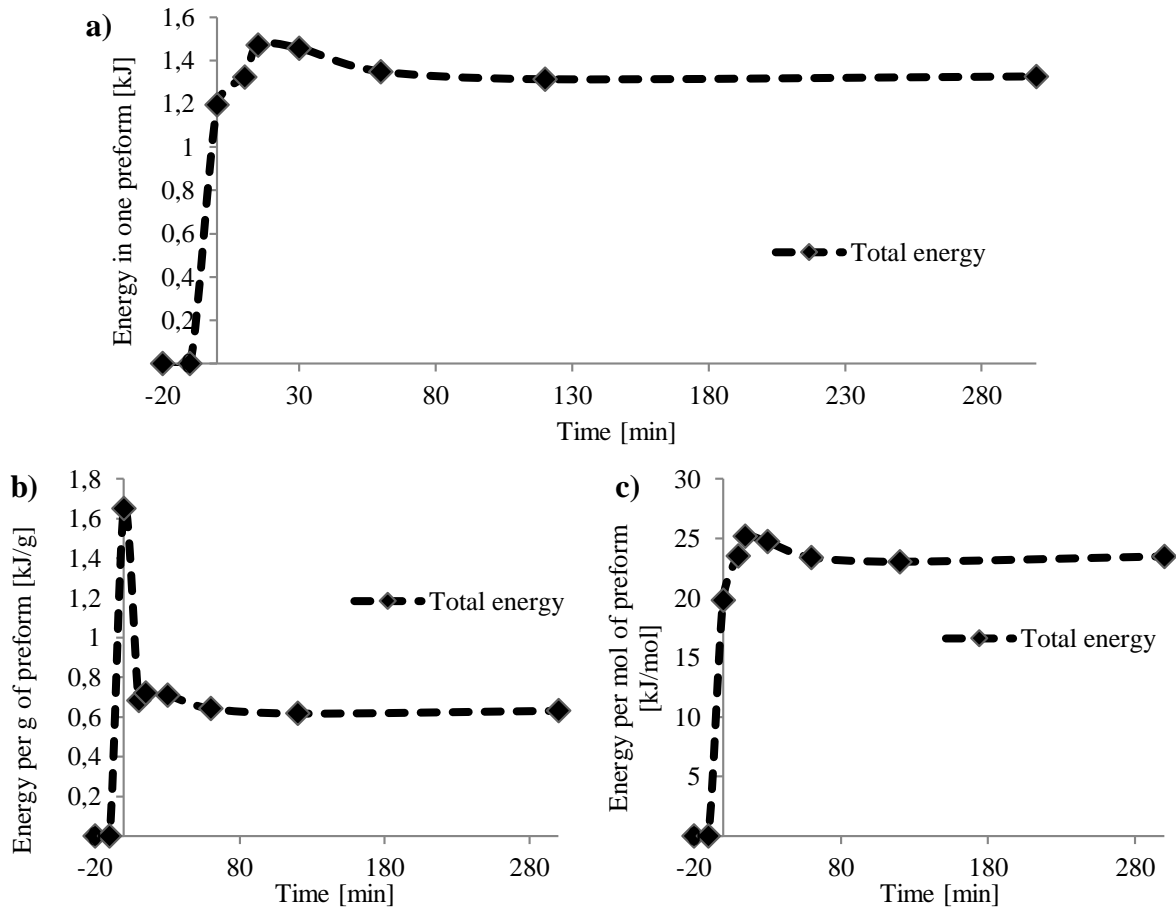


Figure 4. Energy variation a) in one preform, b) per gram of preform and c) per mol of preform.

In order to know how much energy is required to develop the process, it is not enough to analyze the energy in the preform. The silicon flakes need also be heated up and melted before to react with the preform. The silicon mass used was the enough to convert a mass of 1.5 times of the carbon sample to SiC [13]. The real results are illustrated in Figure 5. In the first graph, it can be checked that the energy required by the silicon is even greater than by the preform. This fact is due to the silicon needs to stay in liquid state and quite energy is needed. When the reaction starts, the total energy decreases because densification is an exothermic reaction. Nevertheless, although at the end the amount of silicon is much lower, it still has a greater energy. Silicon enthalpy at that temperature is much higher than the silicon carbide enthalpy.

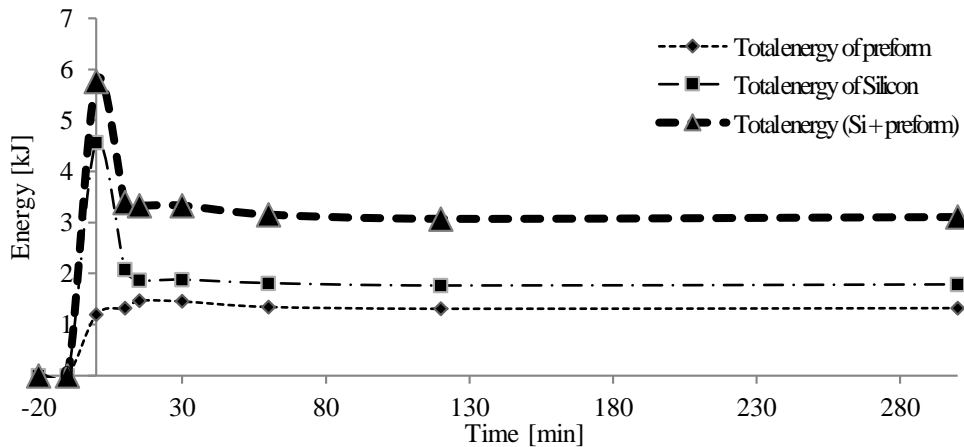


Figure 5. Energy of the preform and the molten silicon.

As a result of the simulation, it is obtained that heat loss of the furnace is 153.7 W. This value is constant along the process, because the internal temperature does not change (isothermal system); in other words, due to the boundary condition of 1800 °C, it can be considered that the furnace

isolation is in steady state, although the cavity does not. Besides, simulation shows that temperature values in the outer part of the furnace are always below 70 °C, which corresponds to the specifications of the real furnace.

By using heat losses and energy variations of the reaction, the electricity demand of the furnace has been calculated and plotted in Figure 6. When the preform has not yet been introduced in the furnace, it is only necessary to compensate the heat loss (153.7 W). When preform is placed into the furnace, it needs to be heated up. Power demand increases up to about 163 W, and the densification reaction can start (in this point, $t = 0$ min). Almost all the reaction takes place during the first 10 minutes, and due to its exothermicity, is not demanded as much power as at the beginning. When the most of silicon is inside the preform and reaction proceeds more slowly, the required power increases again until it stabilizes around a value of 153.7 W (the heat loss value).

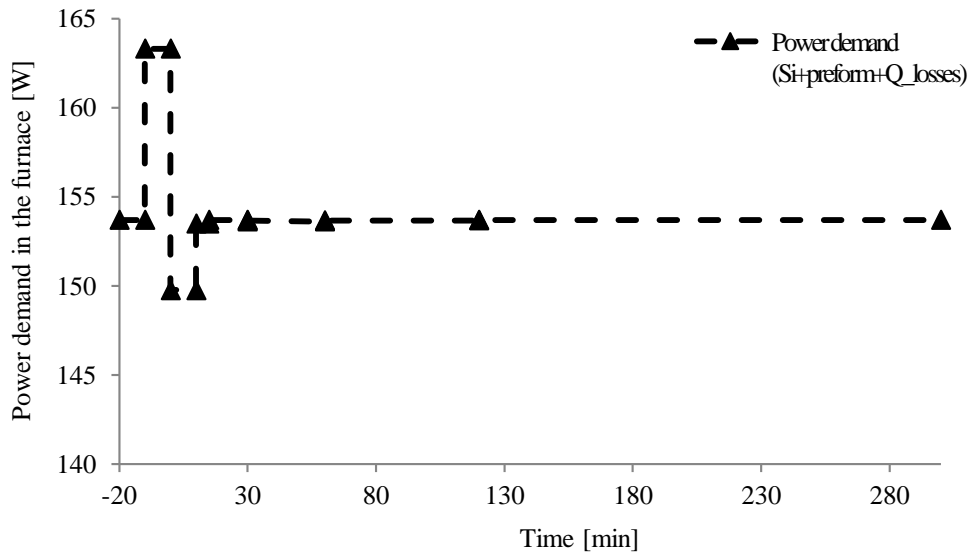


Figure 6. Power requirement along the LSI process including the furnace simulation

4.2. Exergy analysis

Knowing the composition of the preform along a LSI process was possible to calculate the exergy evolution as the silicon infiltration and the silicon carbide formation take place.

As can be seen in Figure 7, at the beginning the exergy in one piece (when only is composed by carbon) is about 55 kJ. When reaction takes place, exergy increases a bit, but shortly after, it stabilizes around a certain value (close to 70 kJ). This is the expected result, because as can also be seen in Figure 2, the silicon carbide production mainly happens in the first 30 minutes. The remaining time, the goal is to achieve a fully dense product, and it is very costly to eliminate porosity completely.

If the total exergy of a piece is decomposed into the physical and the chemical exergy, as it has been done both in Figure 7 and in Figure 8, it can be quickly seen that the chemical contribution is significantly higher. This fact is due to the high standard chemical exergy of silicon carbide (1204.9 kJ/mol [18]) and silicon (854.25 kJ/mol [17]). Carbon standard chemical exergy is 410.25 kJ/mol [17]. If exergy in every time is divided by the total weight in that moment or the total number of moles, the results are the curves illustrated in Figure 8.a and Figure 8.b respectively. In the first one, exergy decreases as time passes because the total weight increases when silicon penetrates into the preform. As the volume is the same, at the beginning the preform is very porous and its weight is lower. The second graph shows the opposite trend. As a mol of SiC is produced per mol of C, and the standard chemical exergy is greater for silicon carbide, the exergy increases while the reaction is developed. The growth of exergy is more obvious in this case, but it happens almost entirely during the first 15 minutes.

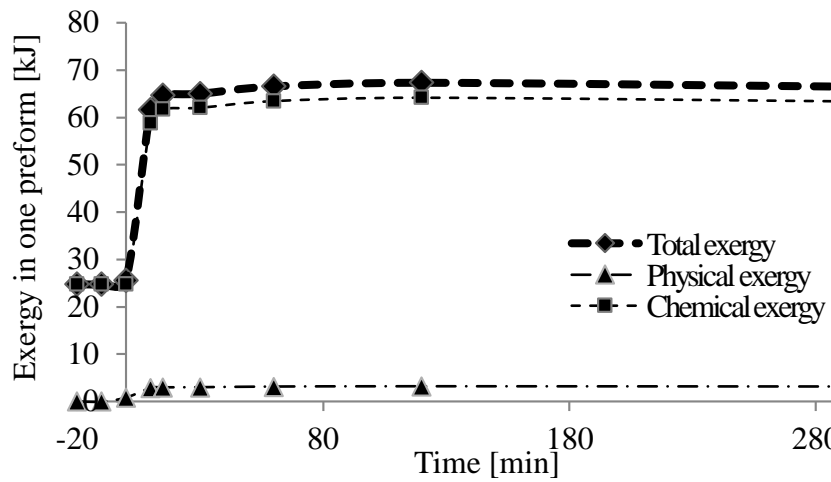


Figure 7. Physical, chemical and total exergy variation in one preform during densification process

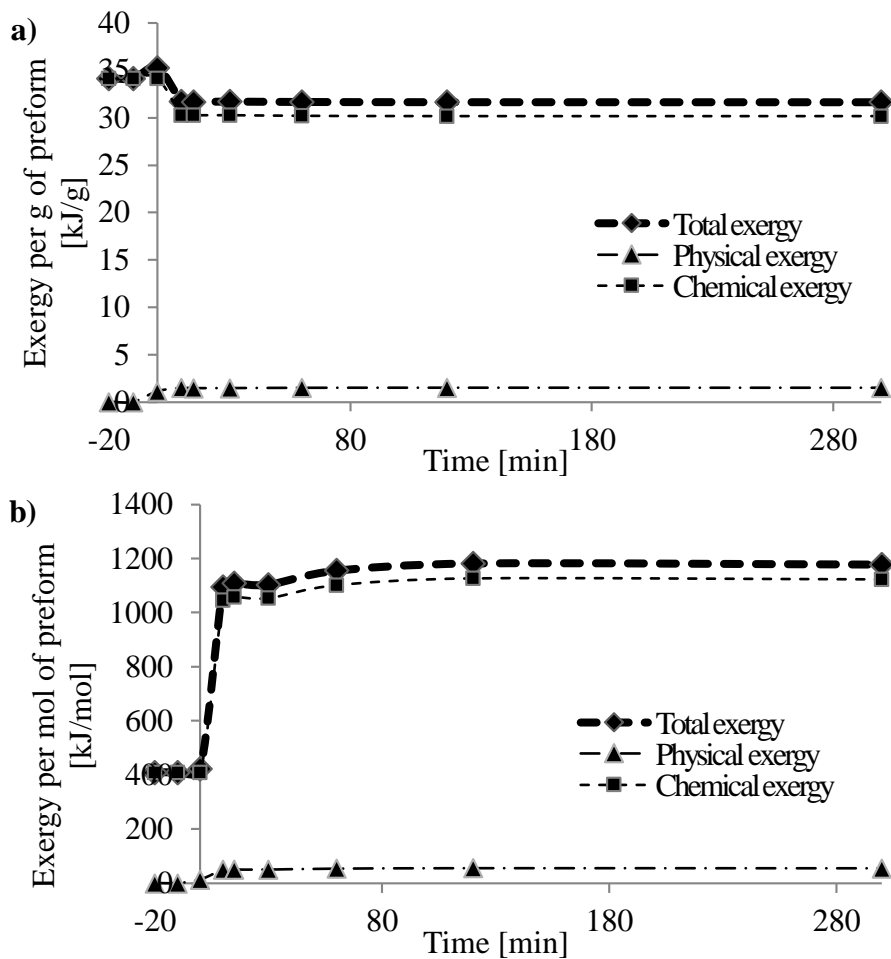


Figure 8. Physical, chemical and total exergy variation a) per gram of preform b) per mol of preform

If exergy evolution of one preform and non-infiltrated silicon are compared (Figure 9), it can be seen that the sum of both curves remains nearly constant. At the beginning, silicon exergy is greater, but soon things change and exergy of the piece becomes larger.

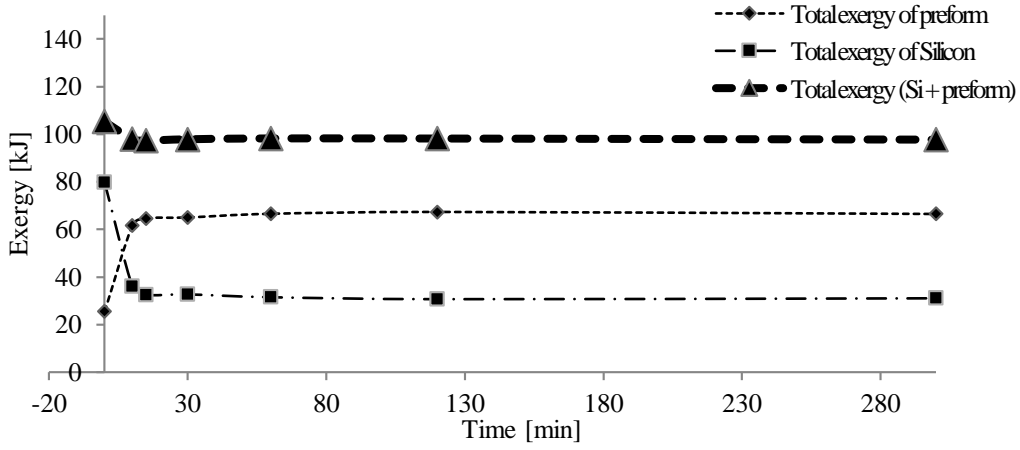


Figure 9. Exergy of the preform and the molten silicon.

As a final analysis, an exergy balance of the process is carried out taking into account all exergy inputs and outputs in the system in order to be able to identify how much energy is destroyed in each time interval. The only exergy input in the furnace system during the reaction time is through its electricity consumption. In this case, exergy has the same value than energy due to the fact that this kind of energy has the highest quality. This magnitude was plotted in Figure 5.

With respect to the exergy outputs, a flow of heat is continuously lost through the furnace walls. As it is considered that both internal and external temperature are constant, exergy lost by the furnace cavity is also constant and is calculated through the following expression:

$$B_T = Q_{\text{walls}} \left(1 - \frac{T_{\text{ref}}}{T_{\text{wall}}}\right) \quad (7)$$

It should be noted that the previous value includes both irreversibility in the furnace walls and exergy losses from the furnace.

It must be considered the exergy demanded by the preform and the silicon along the process. In order to know the rate of exergy variation, the total exergy curve (Figure 9) was derived to have all magnitudes in watts. Finally, irreversibility in the furnace cavity in every time interval (\dot{I}) is calculated as follows:

$$\dot{I} = \dot{B}_{\text{input}} - \dot{B}_{\text{losses}} - \frac{d\dot{E}}{dt} = \dot{B}_{\text{input}} - \dot{Q}_{\text{walls}} \left(1 - \frac{T_{\text{ref}}}{T_{\text{wall}}}\right) - \frac{\Delta\dot{E}}{\Delta t} \quad (8)$$

Results obtained are plotted in Figure 10. At the beginning, when the furnace is empty, irreversibility is the difference between the exergy input and the exergy lost. When the densification reaction starts, exergy supplied increases and total exergy demand decreases, causing greater exergy destruction and therefore, higher irreversibility. After the first 30 minutes, when reaction proceeds slowly, irreversibility recovers its initial value until the end.

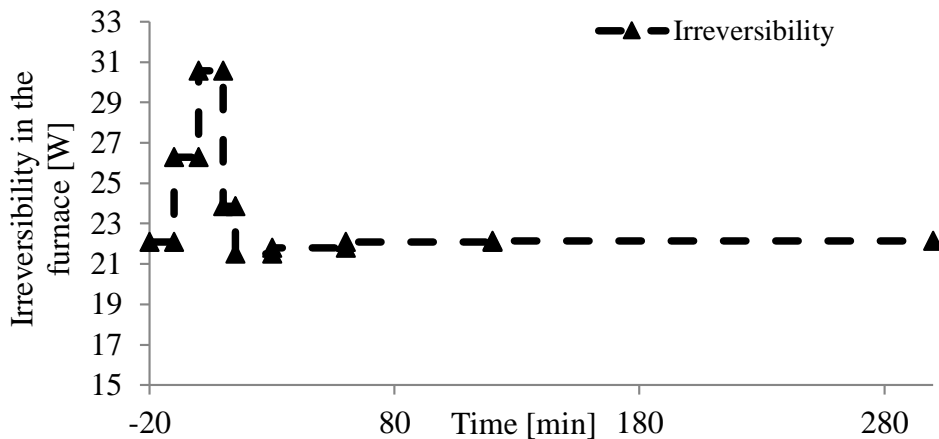


Figure 10. Irreversibility in the furnace along the process

To calculate the total exergy destroyed in the process is necessary to integrate the previous graph, or what is the same, to know the area under the curve. This result, along with the rest of the total exergy inputs and outputs, is included in

Table 1. It can be seen how exergy variation is very small compared to exergy input. Besides, exergy lost due to heat losses represents about 85%, of exergy input.

Exergy input [kJ]	Exergy consumed by Si and preform [kJ]	Exergy lost [kJ]	Irreversibility [kJ]
2,954.15	-4.44	2,526.82	431.77

Table 1. Total exergy inputs and outputs in the furnace system, in kJ.

5. Conclusions

Exergy analysis has been proposed for analyzing an energy intensive process such as liquid silicon infiltration. Data from a reported experiment has been used and, since furnace consumption was not reported, a simplified furnace model has been applied for calculating this consumption.

Results show that at the beginning of the process, exergy consumed by the furnace is used for increasing exergy of the material (silicon melting). Afterwards, furnace consumption decreases due to the presence of exothermal reaction. Finally, exergy of the preform has a very small variation, whereas exergy is destroyed and lost. This part causes the highest exergy destruction due to its long duration and to high heat losses (compared to furnace capacity). In an industrial scale furnace, its relative magnitude would be much smaller. Global analysis shows that almost all input exergy is either lost or destroyed, being exergy consumption for Si and perform very small and even negative. This means that, at least theoretically, there is strong potential for system improvement, especially by reducing heat loss per unit of mass processed.

Besides the particular results of the example analyzed, the paper shows how exergy can be applied to understand in depth the energy and matter transformations taking place in the process. It should be highlighted that the method is able to analyze the time evolution of exergy input, exergy accumulation and exergy destruction in the different stages of the process. This understanding provides valuable information about how to modify the process in order to improve its efficiency. Last but not least, by using exergy, both energy and material inputs can be accounted by using the same units.

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Nomenclature

- \dot{B} exergy flow, W
- E non flow exergy, J
- G Gibbs function, J/mol
- h enthalpy, J/mol convection coefficient, W/(m²K)
- \dot{I} irreversibility, W
- k thermal conductivity, W/(m·K)
- n number of moles
- \dot{Q} heat flow, W

r radius, m
 s entropy, J/(mol·K)
 t time, s
 T temperature, K
 x molar fraction
 z height, m

Greek symbols

σ Stefan-Boltzmann constant, W/(m²K⁴)
 ε emissivity

Subscripts and superscripts

ch chemical
 $conv$ convection
 ph physical
 rad radiation
 s surface
 0 reference

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