1. Introduction

In recent decades tremendous advances have been made in the development of new materials capable of working under increasingly extreme conditions. This advance is linked to the development of Materials Surface Engineering. The utilisation of techniques based on high density energy beams (laser, plasma, electron beam or arc lamps) in surface modification and metallic material treatment allow for the creation of non-equilibrium microstructures which can be used to manufacture materials with higher resistance to corrosion, high temperature oxidation and wear, among other properties.

These techniques, despite their multiple possibilities, have one inconvenient property in common: their low overall energy efficiency. While it is true that the energy density obtained through a laser is three to four magnitudes greater than that which is obtained by solar energy concentration facilities, Flamant (Flamant et al. 1999) have carried out a comparison of the overall energy and the capital costs of laser, plasma and solar systems and came to the conclusion that solar concentrating systems appear to offer some unique opportunities for high temperature transformation and synthesis of materials from both the technical and economic points of view.

It is important to bear in mind that the use of this energy could lower the cost of high temperature experiments. Combined with the wide array of superficial modifications that can be carried out at solar facilities, there are numerous other advantages to using this energy source. The growing (and increasingly necessary) trend towards the use of renewable clean energy sources, which do not contribute to the progressive deterioration of the environment, is one compelling argument. Solar furnaces are also excellent research tools for increasing scientific knowledge about the mechanisms involved in the processes generated at high temperatures under non-equilibrium conditions. If, in addition, the solar concentration is carried out using a Fresnel lens, several other positive factors come into play: facility costs are lowered, adjustments and modifications are easy to carry out, overall costs are kept low, and the structure is easy to build, which makes the use of this kind of lens highly attractive for research, given its possible industrial applications.

These are the reasons that justify the scientific community’s growing interest in researching the possible uses of highly concentrated solar energy in the field of materials. But this interest is not new. At the end of the 18th century, Lavoisier (Garg, 1987) constructed a...
concentrator based on a lens system designed to achieve the melting point temperature for platinum (1773°C). But it was not until the twentieth century that the full range of possibilities of this energy source and its applications to the processing and modification of materials started to be explored in depth. The first great inventor was Felix Trombe who transformed German parabolic searchlights used for anti-aerial defence during WW II into a solar concentrator. Using this device he was able to obtain the high temperatures needed to carry out various chemical and metallurgic experiments involving the fusion and purification of ceramics (Chaudron 1973). In 1949 he was able to melt brass resting in the focal area of a double reflection solar furnace which he constructed using a heliostat or flat mirror and a parabolic concentrator (50kW Solar Furnace of Mont-Louis, France). But his greatest achievement was the construction of the largest solar furnace that currently exists in the world, which can generate 100kW of power. The “Felix Trombe Solar Furnace Centre” is part of the Institute of Processes, Materials and Solar Energy (PROMES-CNRS) and is a leader in research on materials and processes.

Another of the main figures in the use of solar energy in the materials field and specifically in the treatment and surface modification of metallic materials is Prof. A.J. Vázquez of CENIM-CSIC. His research in this field started at the beginning of the 1990’s, using the facilities at the Almería Solar Plant (Vazquez & Damborenea, 1990). His role in encouraging different research groups carrying out work in material science to experiment with this new solar technology has also been very important.

Our group’s main focus at the ETSII-UCLM involved using concentrated solar energy (CSE) from a Fresnel lens to propose new sintering processes and surface modifications of metallic components. The aim was to increase the resistance of metallic materials (mainly ferrous and titanium alloys) to wear, corrosion and oxidation at high temperatures.

The initial studies with CSE at the ETSII-UCLM involved characterising a Fresnel lens with a diameter of 900 mm, for its use as a solar concentrator (Ferriere et al. 2004). The characterisation indicated that the lens concentrated direct solar radiation by 2644 times, which meant that on a clear day with an irradiance of 1kW/m² the density of the focal area would be 264.4 W/cm² (Figure 1). This value is much lower than this obtained with other techniques based on high density beams, but is sufficiently high to carry out a large number of processes on the materials, and even a fusion of their surfaces.

![Fig. 1. Concentration factor of the Fresnel lens](www.intechopen.com)
The investigations carried out to date include processes involving the sintering of metallic alloys, surface treatment of steel and cast irons, cladding of stainless steel and intermetallic compound, high temperature nitriding of titanium alloys and NiAl intermetallic coating processing through a SHS reaction (Self-propagating high temperature synthesis). This research has been carried out in European and national programmes for Access to Large-Scale Facilities which allowed us to collaborate with the groups of A. J. Vázquez (CENIM-CSIC, Spain), A. Ferriere (PROMES-CNRS, France) and I. Cañadas (PSA-CIEMAT, Spain) and to use higher powered solar facilities such as the solar furnaces of PSA and the PROMES laboratory.

The aim of our research was not just to make inroads on the use of new non-contaminating technologies, which resolve environmental issues arising from high temperature metallurgy, but also to increase scientific knowledge about the mechanisms involved in these processes carried out at high temperatures under non-equilibrium conditions. In the studies we have conducted to date we have seen a clear activating effect in CSE which results in treatment times that are shorter, and which add to the efficiency of the process as well as increase in the quality of the modified surface. This is due to, among other factors, the properties of solar radiation. The visible solar spectrum extends from the wavelengths between 400 and 700 nm where most metals present greater absorbance, making the processes more energy efficient. In figure 2 (Pitts et al., 1990) the solar spectrum is compared to the absorbance values of the different wavelengths of iron and copper. The figure also includes the wavelength at which certain lasers (those which are habitually used in treating materials) operate. Here we see the high absorbance of iron for the more energetic wavelengths of the solar spectrum, and that its absorbance is low at the wavelengths, which the most common lasers use.

![Solar spectrum](https://www.intechopen.com)

Fig. 2. Solar spectrum (Pitts et al. 1990).

Although the use of solar energy for industrial applications suffers a disadvantage due to its intermittent nature, it should be noted that according to Gineste (Gineste et al. 1999) in Odeillo where the Felix Trombe Solar Furnace Centre is located, the peak value of the direct normal irradiation is 1100 W.m$^{-2}$ and it exceeds 700 W.m$^{-2}$ during 1600 hours per year and 1000 W.m$^{-2}$ during only 200 hours per year. In Ciudad Real, Spain, at latitude 38°, the availability of the solar energy reported by the Spanish “Instituto Nacional de
Solar Energy

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Meteorologia” (Font Tullot, 1984), is 11% higher than in Odeillo. Direct solar radiation measured with a pyrheliometer between 19 June and 31 August, 2009, at the ETSII-UCLM (Ciudad Real, Spain) registered values higher than 950 W.m\(^{-2}\) for 20% of the days and higher than 800 W.m\(^{-2}\) for 97% of the days. The peak value has been attained in this period was 976 W.cm\(^{-2}\).

2. Experimental Installations

There are various types of installations for concentrating solar energy. One way of classifying these installations uses the concentration process as a reference for differentiating between the different types. In this manner we can distinguish between installations which use reflection and those which use refraction.

*Reflection installations*

Reflection installations use mirrors to concentrate solar energy producing one diversion (direct concentrators) or several diversions (indirect concentrators) of the radiation. The light is reflected along the entire spectrum of wavelengths, since the mirror does not absorb anything. Direct concentrators are cylindrical parabolic mirrors and dish parabolic reflectors. First one uses the heat energy generated mainly to heat the fluids which circulate through the conduit located in the reflector focal line (Figure 3). Dish parabolic reflector may be full-surface parabolic concentrators when the entire surface forms an approximately parabolic shape or multifaceted concentrators composed of various facets arranged in a parabolic structure that reflects the solar radiation concentrating it in its focal point. The concentration factor depends on the size, aperture and quality of the surface. The solar radiation hitting the focal point has a Gaussian distribution and its energy efficiency is very high due to the high concentration.

![Fig. 3. Cylindrical parabolic concentrators at the PSA (Almería Solar Plant).](image)

The indirect concentrators are mainly the solar furnaces. They are systems that take advantage of the thermal energy generated by the sun for use in applications requiring medium to high temperatures. They are indirect concentrators that produce several diversions of the radiation through optical systems specially designed to deflect the incident light. To deflect the radiation, they use mirrored heliostats, completely flat surfaces that deflect the direct solar radiation. They are composed of flat reflective facets and have a sun-
tracking system on two axes. Given that a single heliostat is usually totally flat, it does not concentrate. Therefore, a field of heliostats pointed towards a parabolic concentrator is used for this purpose (Fig. 4). The power concentrated may be regulated through an attenuator which adjusts the amount of incident solar light entering.

![Fig. 4. Parabolic reflector at the PSA (Almería Solar Plant, Spain)](image)

When the heliostat field is pointed towards a tower (Figure 5) is a direct concentrator because this system produces only one diversion of the solar radiation.

![Fig. 5. Heliostat field with a central tower Solar Two, in Barstow, California](image)

**Refraction installations**

In these installations solar light travels through a concentrator device that redirects the light towards its axis. These types of installations absorb part of the wavelength of the solar light. The most common way of concentrating solar radiation is through the use of converging lenses, which concentrate radiation in its focal point. Conventional lenses would need to be too large and too expensive to make them worthwhile for concentrating solar radiation at the required levels. An alternative to these types of lenses are Fresnel lenses, which serve the same function, but are much lighter and cheaper.

In Fresnel lenses, the curve of the surface is composed of a series of prisms or facets, in such a way that each of them refracts the radiation in the same manner as the surface of which they are a part. This is why a Fresnel lens functions like a conventional lens. The different
polymers used in the manufacture of the lens determine the part of the spectrum in which it will be effective, and therefore, its applications. The lenses used for concentrating solar radiation are made of acrylic, rigid vinyl, and polycarbonate. Figure 6 shows how the facets of a Fresnel lens can be created from a conventional lens.

![Fig. 6. Diagram of Fresnel lens](image)

There are several research laboratories that use solar installations to experiment and study materials at high temperatures (higher than 1000ºC). Table 1 lists the solar installations in operation across the globe, among which is the installation at ETSII in Ciudad Real.

<table>
<thead>
<tr>
<th>Country</th>
<th>Location</th>
<th>Technology</th>
<th>Maximum power density (kW/m²)</th>
<th>Power (kW)</th>
</tr>
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<tbody>
<tr>
<td>China</td>
<td>Guangzhou</td>
<td>Parabolic concentrator*</td>
<td>3000***</td>
<td>1.7</td>
</tr>
<tr>
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<td>Solar Furnace*</td>
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<td></td>
<td></td>
<td>Solar Furnace</td>
<td>4700</td>
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</tr>
<tr>
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<td>Solar Furnace</td>
<td>5200</td>
<td>22</td>
</tr>
<tr>
<td>Spain</td>
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<td>Solar Tower*</td>
<td>1000-2000</td>
<td>3360-7000</td>
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<td>60</td>
</tr>
<tr>
<td></td>
<td>Ciudad Real, UCLM</td>
<td>Fresnel lens*</td>
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<td>15</td>
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<td>70</td>
</tr>
<tr>
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<td>2500</td>
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<td>Solar Furnace*</td>
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<td>25</td>
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<tr>
<td></td>
<td>Denver, NREL</td>
<td>Solar Furnace*</td>
<td>2500-20000**</td>
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<tr>
<td></td>
<td>Minneapolis, Univ. Minn.</td>
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<td>7000</td>
<td>6</td>
</tr>
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<td>Uzbekistan</td>
<td>Tashkent</td>
<td>Solar Furnace</td>
<td>17000</td>
<td>1000</td>
</tr>
</tbody>
</table>

* Used in the surface modification of materials (papers published), ** Used as secondary concentrator, *** Calculated values

Table 1. Solar Installations in the World (Rodríguez, 2000).
2.1 Fresnel lens
The installation is on the roof of the Escuela Técnica Superior de Ingenieros Industriales building in the UCLM in Ciudad Real (Figure 7). The lens is affixed in a metal structure, and has a single-axis sun tracking system, connected to a software system in which the different data generated by the experiment can be collected, such as the values of different thermocouples. It also has a pyrheliometer which measures the direct incident solar radiation over the course of the day. The geometry of the lens is circular, with a 900 mm diameter and centre that is 3,17 mm thick. It is made out of acrylic material, which gives it a long useful life with low maintenance. The specification of the lens was determined in previous studies (Ferriere et al., 2004) which allowed the measurement of the concentration factor along the focal axis. The focal point of the lens is 757 mm from its centre. This is the point where the greatest density of energy is reached. The lens concentrates direct solar energy by up to 2644 times (maximum value at the focal point), which means that for exposure of 1000 W/m² the maximum power density at the focal point is 264 W/cm².

Fig. 7. Fresnel lens at the ETSII (Ciudad Real, Spain).

The density of the solar radiation has a Gaussian distribution in function of the distance from the focal point within the focal plane. This variation is what allows us to choose the temperature to be used for the experiment. We can control the energy density of the solar radiation, adjusting the distance of the sample in the Z axis. (Figure 1).
The Fresnel lens has a reaction chamber where experiments can be carried out in a controlled atmosphere. The reaction chamber features a quartz window and a refrigeration system. In order to measure the temperature a thermocouple is welded to the bottom of the samples.

2.2 Solar Furnace
The second installation used on a regular basis for generating concentrated solar energy is the Solar Furnace of Almería Solar Plant (PSA), which belongs to the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT, in English, Centre of Energy, Environmental and Technological Research). The solar furnace consists of a heliostat which tracks the sun and reflects the solar rays onto a parabolic mirror. The furnace of PSA has a heliostat of 160m² composed of 28 flat facets which reflect solar rays
perpendicular and parallel to the optic axis of the concentrator and continuously tracks the sun through a tracking system with two axes (Fig. 8). The mirrors have reflectivity of 90%.

Fig. 8. Heliostat of the PSA solar furnace (Almeria Solar Plant, Spain).

The concentrator disk is the main component of the solar furnace (Fig. 9). It concentrates the incident light of the heliostat, multiplying the radiant energy in the focal zone. Its optic properties especially affect the distribution of the distribution of the flow on the focal zone. It is composed of 89 spherical facets covering a total surface area of 98.5 m$^2$ and with a reflectivity of 92%. Its focal distance is 7.45 m. The parabolic surface is achieved with spherically curved facets, distributed along five radii with different curvatures, depending on their distance from the focal point.

Fig. 9. Concentrator disc of PSA

The attenuator (Fig. 10) consists of a set of horizontal louvers that rotate on their axes regulating the entry of incident solar light hitting the concentrator. The total energy on the focal zone is proportional to the radiation that passes through the attenuator. The concentration and distribution of the power density hitting the focal point is key factor in a solar furnace. The characteristics of the focus with the aperture 100% opened and solar radiation of 1000 W/m$^2$ are: peak flux: 3000 kW/m$^2$, total power: 58 kW, and a focal diameter of 25 mm. In this case, the reaction chamber also allows work to take place in a controlled atmosphere. The chamber also has a quartz window which allows concentrated
solar energy to enter and also allows researchers to monitor the experiment using different kinds of cameras (digital and IR).

Fig. 10. Attenuator of the solar furnace of PSA (Almería Solar Plant)

2.3 Solar Furnace at PROMES-CNRS

Another solar facility used in our research is the 2kW parabolic solar furnace at the PROMES-CNRS laboratory (France). The furnace is composed of one heliostat and a parabolic reflector with a 2 m diameter. The parabolic concentrator has a vertical axis which allows the samples used in the experiments to rest in a horizontal position without the need to add more optical diversion systems to the device. Furthermore, given that the parabolic reflector is the only mirror which is not faceted, it has a higher quality optical properties and allows a greater concentration factor that that which is obtained with the faceted reflectors. The focal zone behind the second reflection has a diameter of 15 mm and Gaussian distribution with the maximum energy at the centre, of 16,000 times the impinging solar radiation.

3. Surface hardening of steels by martensitic transformation.

Surface quenching is a widely used treatment by the industry to harden and improve wear resistance of the steel pieces. These types of treatments may be carried out using conventional heating methods (flame and electromagnetic induction) and high-density energy beams (laser, electron beams, plasmas, etc.). In all cases the source should be sufficiently powerful to guarantee that only the surface layer of the piece heats up to a higher temperature than the austenizing temperature. After cooling off, only the zones which were previously austenized will have undergone the martensitic transformation that results in the hardening. In the internal zones, where no microstructural transformations would have taken place, the mechanical properties would remain unchanged. Therefore, the end result is pieces that combine a high degree of hardness and toughness and greater resistance to wear.

Of all the different types of modifications and treatment of materials carried out in the solar furnaces, surface hardening of ferrous alloys has been the most widely studied. Since the first study was published by Yu and others in 1982, several research groups have been exploring the possibilities of this process (Maiboroda et al., 1986; Stanley et al., 1990;
Ferriere, 1999). This first study showed how the high concentrations obtained in the solar focal area of a parabolic concentrator with a 1.5 m diameter produced self-quenching in a surface zone 0.5 mm deep and 5 mm in diameter in a steel piece after a second of exposure to solar radiation (Yu et al. 1982). In addition, the initial investigations show how localised treatments can be carried out on industrial pieces with complicated geometries by moving the sample with respect to the focal area of the furnace (Yu et al., 1983) (Zong et al., 1986).

In Europe, the first experiments were carried out in the 1990’s by a group led by Prof. Vázquez of CENIM-CSIC (Spain). The research carried out was highly important because it demonstrated the viability of using the different types of solar facilities available at the Almería Solar Plant to surface harden steel pieces. The experiments were carried out using the SSPS-CRS facility, which comprises a heliostat field and a central tower (Rodríguez et al., 1995), and the Parabolic Solar Furnace which comprises a group of heliostats and a faceted parabolic concentrator (Rodríguez et al., 1997). The results indicated that under the best conditions of direct solar radiation it was possible to obtain homogeneous quenched layers between 1 and 3 mm thick with heating times of between 30 and 60 seconds. The study was completed using a Fresnel lens with a 900 mm diameter which was available at the Instituto de Energias Renovables of CIEMAT in Madrid (Rodríguez et al., 1994). The study added to knowledge regarding the advantages and limitations of each one of the facilities. With the facility comprising the central tower and the heliostat field, a surface of 10 cm² can be quenched, much more than what is possible using other techniques and types of solar facilities. But with the PSA Solar Furnace and the Fresnel lens it is possible to obtain greater energy densities in the focal area (250-300W.cm⁻²) depending on the incident solar radiation, which allows for self-quenching in steel alloys.

Using the ETSII-UCLM Fresnel lens described above, our group carried out research on surface hardening steels and cast iron, with the ultimate aim being the discovery of industrial applications for this process. The first experiments consisted of surface hardening through martensitic transformation of three types of steel and a nodular cast iron piece. In all cases the influence on the treatment of the different variables was assessed: heating rate, maximum temperature reached, cooling medium, size of the treated pieces (diameters: 10 and 16 mm, height: 10 and 15 mm). The study entailed determining the microstructural transformations, the profile of the hardness and the depth of the quenching (total and conventional).

Figure 11 shows the results obtained using a sample with a 10 mm diameter and 10 mm high of tool steel AISI 02, where the homogeneous quenching can be seen along the entire diameter of the test sample, as well as the surface hardness values obtained. Figure 12 shows the results obtained after carrying out a surface quenching treatment of a nodular cast iron piece.

In addition, studies were carried out to assess the possibility of carrying out localised treatments on the surfaces of pieces that required greater hardness and resistance to wear. The microhardness curves in Figure 13 show the effect of heating time on the diameter of the quenching zone of a 1 mm plate of martensitic stainless steel AISI 420.

Due to the fact that the heating conditions depend on the direct solar radiation it is necessary to have a predictive tool that can set the treatment conditions in function of the direct solar radiation present. To this end, a finite element model (FEM) (Serna & Rodríguez, 2004) has been developed which gives the distribution of the temperatures of the pieces during treatment. The model takes into account both the Gaussian distribution of the energy density in the focal area and the variation in the temperature of the phase transformation of the steel in function of heating speed.
Fig. 11. Surface quenching of 10 mm high test sample after 45 seconds of heating.

Fig. 12. Microhardness profile of a nodular cast iron piece heated for 40 seconds in the focal area of a Fresnel lens.

Fig. 13. Influence of heating time on the diameter of the quenching zone of a 1 mm thick plate of martensitic stainless steel.

The size of the focal area of the lens limits the possible application to small pieces (surface areas of between 50 mm² and 100 mm², depending on the maximum required temperature), or to localised treatments on larger sized pieces. Obviously treatments and modifications of
metallic materials with small surface areas are carried out on an industrial scale for a large number of applications, but there are few bibliographic references concerning specific applications for localised treatments using solar facilities.

4. Hardening through surface melting of cast iron

The surface melting treatment of grey cast iron leads to the formation of superficial layers with excellent resistance to wear. The rapid cooling from the melted state gives rise to the formation of extremely hard white cast iron with great resistance to wear. Given this profile, this type of melting process is an excellent candidate for machine pieces that are subject to movement and vibrations and which are in contact with other components. At present, industrial processes are using various heating techniques such as TIG, electromagnetic induction, and electron or laser beams, among others, in order to carry out this type of surface melting treatment.

Recent experiments at the ETSII show how it is possible to use concentrated solar energy to carry out at the melting treatments on industrial cast iron pieces. The study to date has centred on hardening through surface melting and quenching of camshafts used in the automobile industry and manufactured with grey cast iron. In order to carry out the treatment a specimen support device was created which allowed the cam to spin in the focal plane of the Fresnel lens. The results obtained are compared with those of a camshaft manufactured using conventional industrial processes (TIG). Figure 14 shows the hardness profiles of the hardened area of the two pieces, one that was hardened with concentrated solar energy, and the other through TIG (both made of the same cast iron). The graph shows us that the camshaft treated with CSE attained a far greater hardness and had a smaller heat affected zone. In addition, the surface finishing attained from the solar treatment is better than that obtained after treatment with TIG, which would translate into lower costs (Figure 15). Current research is focused on automating the system in such a way that the entire camshaft may be treated continuously.

![Fig. 14. Hardness profile of samples treated by TIG vs. CSE](www.intechopen.com)
5. Cladding of stainless steel and intermetallic compounds onto steel substrates.

There are many types of surface modification techniques that aim to improve the corrosion and oxidation resistance. One widely studied surface modification technique is cladding. A material with the desired properties is melted on the base metal by means of an energy beam. The mixture between the coating material and the base metal must be as small as possible in order to guarantee the original properties of the coating. In this way it is possible to use a cheap structural material and to coat it with another that confers its surface the desired properties.

The literature contains several references that describe the use of different solar installations to obtain cladding coatings. In the USA Pitts et al., (Pitts et al., 1990) obtained cladding coatings on stainless steel. Subsequently, in Spain, Fernandez et al. performed Ni cladding on steel at the Almeria Solar Plant (Fernandez et al., 1998).

We have studied the possibility of obtaining cladding coatings using the parabolic solar furnace of the PROMES-CNRS laboratory previously described (Ferriere et al., 2006). The high energy densities obtained with the solar beam allowed stainless steel and NiAl to be cladding coated through rapid melting-solidification of powders pre-deposited on carbon steel samples. Coatings have been processed in tracks by scanning the concentrated solar beam across the specimen surface with the aim of modifying larger areas than are possible with a stationary treatment. The scanning process is performed by moving the specimen at a controlled speed that depends on the direct solar irradiation. The coatings processed are homogeneous, adherent and have low porosity. In addition, the formation of dendritic microstructures results in increased electrochemical corrosion resistance.

The fundamental disadvantage that has been encountered in this research is the difficulty of achieving a coating with a composition close to that of the initial powder while at the same time guaranteeing good adhesion to the substrate. A possible solution to this problem consists of using a powder injector (nozzle), in order to carry out the process in one single step as is habitual in the case of laser cladding.


It is possible to harden the surface of different kind of steels using a novel technology that combines the use of non-contaminant salts with the activator effect of the concentrated solar energy. Groundbreaking research (Shen et al. 2006a), (Shen et al. 2006b) has studied the
possibility of the substituting highly contaminating cyanide salts used in liquid nitriding for common salt $\text{KNO}_3$, which avoids this high toxicity. In line with this innovative research vector, our research has tried to explain the different mechanisms through which nitrogen from the salt is introduced into the steel matrix, thereby achieving the desired surface hardening. In addition, we are researching the use of concentrated solar power as an energy source (Herranz & Rodríguez 2008). The experiments were carried out using the Fresnel lens at the ETSII and the solar furnace at the Almeria Solar Plant. The results were compared to those that were obtained using an electric muffle furnace. Steels with a wide range of characteristics were selected for the research. One was a relatively cheap, low alloy steel with low carbon content, the AISI 1042. The other steel used was the high-speed tool steel M2 which is commonly used in industry. These two types of steel were used to highlight the different characteristics made evident during the nitriding process. The treatment resulted in the surface hardening of the two steels through the interstitial diffusion of nitrogen in the steel network and in some samples nitrides were formed. The exhaustive study of these results interprets the nitriding mechanism that occurred in each steel. In addition, the traditional treatment times were reduced to a large degree. This evidences the viability of this nitriding process using concentrated solar energy (CSE).

The maximum surface hardening of AISI 1042, which is not a conventional steel to use for nitriding, increased 61% with respect to its nominal value. Nitried M2 steel attained a surface hardness of 900HK (Herranz & Rodríguez, 2007) (Fig. 16).

![Hardness profile obtained in a nitried M2 piece using a treatment of nitrate salts during 15 minutes using concentrated solar energy.](image)

Fig. 16. Hardness profile obtained in a nitried M2 piece using a treatment of nitrate salts during 15 minutes using concentrated solar energy.

The diffusion layer obtained in both steels submitted to the nitriding process in $\text{KNO}_3$ salts are greater than those obtained in earlier experiments with other nitriding methods. Therefore, the maximum diffusion layer obtained in AISI 1042 steel has an approximate thickness of 1300 µm and 550 µm in the M2 steel.

The other fundamental conclusion of our research is that concentrated solar energy activates the process, notably reducing the treatment times. Treatment time was greatly reduced in the treatment of the AISI 1042 using the Fresnel lens. Only 35 minutes was needed, versus the 90 minutes needed in a muffle furnace for the same treatment. This reduction is especially notable if we compare it with other conventional nitriding methods, such as with plasma, which requires 3 hours. In the case of the nitriding of the M2 sample, the reduction in treatment time using concentrated solar energy is more significant. With a Fresnel lens, only 60 minutes was needed (a muffle furnace requires 3 hours). The reduction was even
more remarkable in the case of PSA (Almería Solar Plant), which only needed 15 minutes of treatment.
The nitriding of low alloy steel characterised by its free interstices, such as AISI 1042 steel, occurred primarily through the interstitial diffusion of nitrogen coming from the salts towards the interior part of the steel piece. In the nitriding mechanism for the M2 high-speed steel, high alloy tool steel, part of the nitrogen originating from the salts was introduced through interstitial diffusion towards the interior of the steel, while another part formed iron nitrides and/or iron alloy nitrides. These compounds contribute to the surface hardness.

7. Gas nitriding of titanium alloys.

In recent years, Ti alloys have been widely studied due to their properties: low density, high melting point, good mechanical properties, high corrosion and oxidation resistance and biocompatibility. These properties explain their appeal to the aerospace industry and as biomaterials. However, their use in these fields remains limited because of their poor tribological properties. These problems can be overcome by changing the nature of the surface using thermochemical treatments. In the case of the Ti alloys, the most widely used surface treatment is nitriding. There are different ways to nitride the surface. One of the most frequently used methods is gas nitriding.

Gas nitriding is a diffusion process that involves heating the surface at high temperatures for a long time. In most cases, the equipment is expensive both start up and to maintenance. For this reason, there is significant interest in developing more economic and energy efficient systems.

Nitrogen is soluble in titanium and forms an interstitial solid solution, resulting in a hardening by solid solution caused by deformation in the crystalline network. It is important to assure that no oxygen is present in the process in order to prevent the formation of TiO$_2$ oxides on the piece. The types of dissolution of nitrogen in the titanium may be seen in the equilibrium diagram of the Ti-N system (Fig. 17) (Wriedt & Murray, 1987).

![Fig. 17. Phase diagram Ti-N. (Wriedt & Murray, 1987).](www.intechopen.com)
Murray, 1987). We observe a solid phase $\alpha$ solution with a high degree of solubility of nitrogen (from 0 to 8% in weight) which remains stabilised at high temperatures. At levels of over 8% of nitrogen (in weight) the alpha phase saturates and intermetallic compounds are obtained, such as Ti$_2$N and TiN. These nitrides have very high hardness values and give the maximum hardness to the surface layer.

Existing studies indicate that there are some problems related to the use of this treatment in the traditional manner, which uses electric furnaces, such as the need for long treatment times of over 16 hours and at high temperatures of over 1000º C. In contrast, the use of concentrated solar energy obtains high temperatures at high heating and cooling rates (that allow the creation of non-equilibrium microstructures) with short treatment times. We have found that due to the photoactivation capability of the concentrated solar energy, the duration of the process can be greatly reduced. To our best knowledge, the study by Vazquez in 1999 is the only significant research that has been conducted in this area (Sánchez Olías et al, 1999).

Our research focuses on the gas nitriding of the Ti6Al4V alloy. The base material has a biphasic microstructure ($\alpha+\beta$) and a hardness of 400 HK. Tests involved applying heat of between 1000º C and 1200ºC for between 5 to 30 min. In order to measure the temperature, a thermocouple was welded to the bottom of the samples and the samples were situated in the reaction chamber where the nitrogen atmosphere was controlled (Fig. 18). The chamber has a quartz window which permits the entrance of the concentrated solar energy and also it allows to observe and record the experiment by different kind of cameras (digital and IR).

Fig. 18. (A) The samples in the reaction chamber. (B) Sample with the thermocouple. (C) Digital record of the experiment in the solar furnace. (D) Direct observation of the experiment in the Fresnel lens.

The results obtained indicate that with the solar facilities significant hardening can be obtained from processes carried out at 1050ºC for only 5 minutes. In the microstructure we observed a layer of a different kind of nitrides identified by X-Ray diffraction that increase...
the hardness of the samples. In addition, nitride layer growth occurred where the treatment time was increased. Besides the hardening due to the formation of nitrides, we also observed a deeper hardening due to the interstitial solid solution of the nitrogen in titanium matrix. As shown in Figure 19 we have been able to distinguish between the different hardened layers. The first is a compound layer, then a diffusion layer that can achieve 400 μm for the longest treatment times and then, the base material.

Fig. 19. Microstructure of sample nitrided during 10 min at 1050°C using concentrated solar energy.

The compound layer was identified through X-ray diffraction as Ti₂N, which was the maximum hardness detected (1200HK). The presence of TiN was also detected, but its density was so scant that it was impossible to measure its hardness. In addition, it was evident that the process did not result in a completely continuous layer at this temperature. Compound layers grew considerably as the treatment temperature rose or time was increased. These layers covered the pieces more homogeneously and the diffusion layer was thicker. As shown in figure 20, at 1200°C, after 15 minutes of treatment, two totally continuous layers were formed. According to the X-ray diffraction, the exterior layer was TiN, and the second layer was Ti₂N. Under these parameters, the TiN layer had a maximum hardness of 2600 HK.

Fig. 20. Microhardness evolution in the samples nitrided during 15 min at 1200°C using CSE
After these experiments, wear resistance was evaluated using a pin on a disc test machine. The tests were made in dry conditions against a ball of aluminium oxide. In the case of the samples nitrided in the Fresnel lens, the samples showed a lower coefficient than the as-received material, with a friction coefficient of 0.5, showing values of 0.2 for treatment of only 15 minutes at 1200°C. In regard to the wear rate, compared with the base material it decreased by two orders of magnitude after only 15 minutes of treatment. The track width was decreased from 1.890 μm in the Ti6Al4V alloy to 180 μm in the nitrided sample. These experiments show the significant potential of this new modification process consisting of gas nitriding with concentrated solar energy. The great reduction of nitriding time can be explained by the photo-activation effect of the concentrated solar energy.


The feasibility of using a solar furnace for the sintering-consolidation of green parts previously obtained by compaction has been tested. The use of solar furnaces allows materials to be processed at much higher heating and/or cooling rates, which results in better mechanical properties and a quite significant reduction in the total cycle time. The demand for faster and less expensive techniques for processing pieces has resulted in the development of high energy techniques for manufacturing prototypes and carrying out short series tooling, such as laser sintering (Asgharzadeh & Simchi 2005) and capacitor discharge sintering (CDS) (Fais & Maizza 2008). The use of these faster technologies has usually resulted in finer microstructures, while improving mechanical properties and the sintering window. In the search for new sintering systems that overcome this issue, the use of concentrated solar energy (CSE) appears to be an interesting candidate. The CSE is clean, renewable and pollutant free. In spite of its apparent limitations for industrial applications, due to the unpredictable availability of solar radiation, CSE shows a clear activator effect in different processes (Herranz & Rodríguez 2007); (Herranz & Rodríguez 2008).

Earlier research focused on studying the technique’s viability for manufacturing WC-10%Co ceramic components and complex ceramics (cordierite) (Guerra Rosa et al., 2002); (Almeida Costa Oliveira et al., 2005); (Cruz Fernandes et al., 2000) using concentrated solar energy. These studies have proven that it is possible to use CSE to obtain pieces with very similar characteristics to those obtained using conventional electric furnaces. In the same line, a preliminary study of a copper system has also been published (Cañadas et al., 2005). The results of these studies all share two characteristics: the good mechanical properties obtained, and the major reduction in total treatment time required.

We have assessed the feasibility of concentrated solar energy for sintering-consolidation of green parts previously obtained using compacted metallic powder. The experiments were carried out using the two facilities described in this chapter; a parabolic solar furnace of the Almeria Solar Plant (PSA) and a Fresnel lens at the Castilla-La Mancha University (ETSII-UCLM). The research focused on the microstructural evolution of the samples treated in both facilities. In this work we compared the results of the sintering process in a N2-H2 atmosphere using concentrated solar energy with the conventional furnace results. The main materials we worked with were M2 tool steel, copper-based alloys (such as bronze), and carbon-based steels with alloys such as Astalloy. The energy density obtained in the focal area of the solar furnace or in the focal area of the Fresnel lens is high enough to raise the sample’s temperature to sintering levels. To process the samples at different sintering temperatures, experiments were conducted changing the focal length. The samples were
then heated up to the maximum temperature for 30 minutes. The total duration of the sintering process (including the heating and the cooling) was less than 70 minutes in all cases. In order to compare results, the sintering experiments were carried out in a conventional tubular furnace in the same atmosphere, applying conventional sintering temperatures for 30 min (dwell time). (Figure 21).

We made several interesting findings. For example, we found that the high-speed M2 steel showed major differences in the microstructures obtained, depending on the sintering process used. The microstructure of M2 sintered in a conventional furnace in N$_2$-H$_2$ atmosphere at the optimum sintering temperature, around 1290ºC, presented a ferrite matrix with some retained austenite, Figure 22. We also observed a significant amount of homogeneously distributed bright rounded M6C carbides (identified as rich in W and Mo). The sintering atmosphere has an important influence on the development of the microstructure because the nitrogen content of the steel slightly increases the optimum sintering temperature. The increase in nitrogen content has no effect on the M$_6$C carbides but, as pointed out in a previous study by Jauregi (Jauregi et al 1992), the MC carbides (rich in V) transform into MX carbonitrides that appear with grey contrast inside the grains and at the grain boundaries. In the conventional furnace an increase of the temperature up to 1300ºC produces an over-sintered microstructure in which a continuous M$_6$C carbides film around the grain boundaries is observed. The EDX analysis revealed that at high temperatures the MX carbonitrides were able to transform themselves into black-contrast square VN nitrides detected at the grain boundaries. The maximum hardness achieved was 550 HV.

In the case of the samples treated in the PSA solar furnace and with the Fresnel lens, we observed a completed densification. The most remarkable discovery was that for the processes carried out using concentrated solar energy, the process activated at lower temperatures. Figure 23 shows the densification process and the microhardness evaluation. The feasibility of the sintering process using CSE was demonstrated as the parts displayed well-defined necks and greatly reduced porosity.
Fig. 22. SEM micrograph of M2 sample sintered at (A) 1290ºC and (B)1300ºC in nitrogen-hydrogen atmosphere in the conventional furnace.

Fig. 23. Densification process of the samples treated in the solar furnace of PSA.

As can be seen in the Fig. 24 (A), at only 1115 ºC, some rounded and isolated porosity was observed and a homogeneous distribution of carbides indicates that the sintering process really took place. Microhardness measurements indicate that, at this temperature, the distribution of the carbides was homogeneous and the porosity had disappeared in most of the sample. The microhardness achieved values similar to those of the samples sintered in the conventional furnace (580 HV). The microstructure obtained at this temperature was the
same as that obtained at 1260°C in the electric furnace. When the sintering temperature was increased to 1125 °C, Fig. 24 (B), full density was achieved and there was a sharp increase in grain growth. In addition, massive bright carbide segregation was observed, as well as formations corresponding to the eutectic phase, but only in some areas. Most of the grain boundaries did not show carbides, indicating that they underwent a partial dissolution during the sintering process. Based on EDX analysis, we ascertained that the increase of nitrogen in the matrix due to the sintering gas allowed the formation of VN nitrides both inside the particles and along the grain boundaries. In spite of the grain growth, this sample’s hardness was over 900 HV.

Fig. 24. SEM micrograph of M2 sample sintered at (A) 1115°C and (B)1125°C in nitrogen-hydrogen atmosphere in the solar furnace.

As part of our efforts to explain these results, we carried out several preliminary studies using transmission electron microscopy (TEM). Initial analysis corroborated that the high velocities obtained had caused the formation of vanadium-rich nanometric particles on the order of 400 nanometres, which in certain cases may be complex and contain small 30 nanometre particles rich in other steel alloy elements (W, Mo and V) in their interior. The presence of these particles would explain the high hardness values obtained. However, it would be necessary to carry out a more in depth analysis to fully understand the mechanism responsible for the formation of these small particles.

The results obtained using the Fresnel lens are similar. In figure 25, the large darker particles (identified as VN) stand out in particular and are precipitated at the grain boundaries or close to them, with an average size of 2 µm. In addition, there are a large number of small nanometric particles dispersed throughout the matrix, which once again explain the high hardness values obtained, despite the rapid growth observed in the grain. Lighter contrast carbides (rich in W and Mo) are concentrated at the grain boundaries while larger particles are distributed homogenously throughout the sample. In addition, eutectic M₆C “fishbone” structures can also be observed at some of the grain boundaries.

We would highlight that certain pieces were totally densified at lower temperatures, 150°C lower than with a conventional furnace. Almost full density was attained after 75 minutes in the PSA and after 50 minutes in the Fresnel lens installation, with higher hardness than the conventional microstructures (760-900 HV). The higher heating and cooling rates could explain these results, since the equilibrium phase diagram changes with the heating rate and in these new heating conditions new sintering mechanisms have occurred. The microstructure and the hardness measurements were similar to those found in the M2 system treated by selective laser sintering (Niu & Chang, 2000).
9. Processing of intermetallic coatings through a self-propagating high temperature synthesis process initiated with solar energy (SHS-CSE).

The intermetallic compound NiAl shows attractive properties such as low density, high melting temperatures, high thermal conductivity and good mechanical behaviour at high temperature. Although its low ductility at room temperature could limit its applications as structural material its good tribological properties and excellent oxidation resistance justify its use as a protective coating for metallic components. Cladding, and self-propagating high temperature synthesis (SHS) processes are among the other techniques used currently for coating this intermetallic compound (Matsuura et al., 2000).

SHS is an energy efficient method to process advanced ceramic materials and intermetallic compounds. Discovered by Merzhanov in 1967 (Merzhanov, 1967) it uses the highly exothermic properties of a chemical reaction that are sustained and propagated through a mix of reactants (usually in powder form) in the form of a combustion wave. The energy savings and the economic benefits obtained from SHS are widely acknowledged (see, for example, Deevi & Sikka, 1997).

Concentrated solar energy was first used for the coating process using an SHS reaction in a study by G.P. Rodríguez et al. (Rodríguez et al., 1999) in which they were able to process coatings of NiAl on circular samples with a diameter of 30 mm, using a Fresnel lens. The solar energy triggered a exothermic reaction between the Ni and the Al at ignition temperature (the melting point of Al). The heat released by this reaction was transferred through conduction to the adjacent zones, initiating the reaction in these zones again, for which reason the reaction is considered self-propagated. The heat released (combined with that of the solar beam) melts the compound obtained, resulting in a dense non-sintered material. This process was optimised by Sierra and others (Sierra & Vázquez, 2005), where the adherence of the coating to the substrate was improved through the electrodeposition of a nickel layer prior to the treatment. The study carried out with the Fresnel lens of the ETSII-UCLM used elemental Ni and Al powders and resulted in adherent NiAl coatings over cast iron. In order to increase the adherence and decrease the porosity that frequently occurs in coating processes that use SHS, a preheating system was designed for the substrate, which also uses solar power.
In addition, the 2 kW solar furnace at the PROMES-CNRS laboratory was used (under the collaboration framework between CENIM-CSIC, PROMES-CNRS and ETSII-UCLM) to obtain NiAl coatings in track forms, processing larger surface areas than those that were processed using the Fresnel lens (Sánchez Bautista et al., 2006). The scanning method is similar to that used when coating surfaces using solar cladding, although the beam-sample interaction times are lower (due to faster movement of the sample). The main difficulty arising when coating surfaces using a solar assisted SHS process lies in controlling the process variables so that the resultant coating is of low porosity, high adherence and with the required chemical composition. A possible solution may involve preheating the substrate. Another challenge is to optimise the processing of coatings over large areas.

10. Conclusions

Concentrated solar energy (CSE) represents an alternative to other types of energy beams for treating and modifying the surfaces of metallic materials. The research conducted by the Metallic Materials group of ETSII-UCLM (Spain) is interesting for two reasons. First, it is breaking new ground in the use of new non-contaminating and environmentally acceptable technologies for processes involving the surface modification of metallic materials at high temperatures. Second, it is increasing scientific knowledge about the mechanisms involved when processing materials at high temperatures under non-equilibrium conditions. In the studies carried out to date, it has been observed that CSE has a clear activator effect, which results both in shorter treatment times and therefore, in increased processing efficiency, and in improved quality of the modified surface.

For high-temperature processes, concentrated solar energy has shown to be highly energy efficient and also competitive in terms of cost. It is especially suitable for countries such as Spain, which has a high number of sunny days per year. Going forward, one of the main challenges for the scientific community will be to develop industrial applications for solar technology, especially in the current context, where energy-efficiency and environmental preservation have become top social priorities.

11. References


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The present “Solar Energy” science book hopefully opens a series of other first-hand texts in new technologies with practical impact and subsequent interest. They might include the ecological combustion of fossil fuels, space technology in the benefit of local and remote communities, new trends in the development of secure Internet Communications on an interplanetary scale, new breakthroughs in the propulsion technology and others. The editors will be pleased to see that the present book is open to debate and they will wait for the readers’ reaction with great interest. Critics and proposals will be equally welcomed.

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