The wettability of sintered nanocrystalline oxide powders (CeO$_2$, TiO$_2$, Y$_3$Al$_5$O$_{12}$, and ZrO$_2$-yttria stabilized) and Al$_2$O$_3$ basis powder (60–70% purity) (product originated in the secondary aluminium production, composed mainly of nano and micrometric aluminium oxide) by liquid Armco Fe and by 22CrNiMoV5-3 steel grade was studied using sessile drop wettability technique. The powders were pressed and sintered under different pressures, heating rates and holding times. The later grinding and polishing surface treatments were characterized by infinite focus microscope. The wetting experiments were carried out under pure Ar atmosphere. A small piece of Armco Fe and steel grade was melted on sintered nano oxides, heating up to 1600°C with a holding time of 10 minutes for each experiment. The contact angles were measured and chemical analyses were conducted on tested samples to characterize the wetting reactions. It was found that sintered nano TiO$_2$ not only suffered considerable wetting by Armco Fe and 22CrNiMoV5-3 steel in both cases, but also reacted with the substrate to form ilmenite and pseudo-brookite. The CeO$_2$ substrate and Armco Fe system also showed good wetting behavior. In general terms, it was concluded that wettability was affected by substrate chemical composition, and surface characteristics by sintering conditions. The preliminary results of this investigation may help to determine the suitability of the nanoparticle to be added in a liquid iron based matrix in order to influence the microstructure evolution improving mechanical properties by a fine distribution in the metallic alloy.

KEY WORDS: high temperature wettability; metal/ceramic system; sessile drop technique.

1. Introduction

The study of the wetting behavior at elevated temperatures constitutes one of the most important scientific aspects of high temperature liquid phase materials processing stimulated by the needs of modern metallurgy and foundry industry.\(^1\)

Many non-metallic inclusions continously change their composition in the steel bath and even in the solid state, and the final products take part in the future life of the steel. Not all non-metallic inclusions are always detrimental to the steel properties, they may even improve certain properties. Among others, grain growth and grain boundary movement in the steel are phenomena which may influenced by the presence of non metallic phases.\(^2\) These not harmful inclusions (also called dispersoids)\(^3\) can interact with dislocations, pinning grain boundary motion and limiting austenitic grain growth via Zenner pinning. The effectiveness of dispersoids as pinning sites is inversely proportional to their diameter, thereby, finely dispersed particles should have a size below 100 nm to function optimally.\(^4\)

The addition of non metallic nanopowders to liquid iron matrix by conventional casting methods seems to be a potential and an innovative way of achieving the dispersion of second phase nanometric range particles. In this sense, until now, powder metallurgy was the only technique proposed as the ultimate production route to obtain a dispersion of non metallic nanoparticles in a steel matrix aiming the enhancement of creep strength at elevated temperatures.\(^5,6\) However, this method does not allow the production of large quantities exhibiting excellent quality, in terms of microstructural and mechanical properties homogeneity.\(^7\) Furthermore, recent research works have reported laboratory scale investigations aiming at the dispersion of nanopowders based on liquid metallurgy with promising results.\(^8,9\)

Hence, the addition of appropriate non metallic nanoparticles into a liquid steel matrix involves the understanding of high-temperature wetting behavior in liquid metal/solid ceramic system that is critical for improving industrial liquid phase-assisted processes and the quality of the final product. Methods to characterize the wettability are diverse, however, most interfacial properties of liquid steel on solid oxides have been investigated by the sessile drop technique.\(^10\) The liquid deposited on the solid surface under
series 2, is a low alloyed high strength steel for quenching typically found in steel grades. The steel grade tested in simultaneous chemical reactions with other alloying elements is between the tangent drawn at the triple point in order to avoid the complexity of simultaneous chemical reactions with other alloying elements.

2.1.2. Armco Iron and 22CrNiMoV5-3 Steel Grade

Bayerite crystallographic phases; $d_{0<10}$ follows:

$$ \gamma_{LG} = \gamma_{LS} \cdot \cos \theta $$

where $\theta$ is the contact angle and $\gamma_{LG}, \gamma_{LS}, \gamma_{GS}$ are the liquid/gas, liquid/solid and solid/gas interfacial tensions respectively. The contact angle characterizes the ability of a liquid to wet an homogeneous and smooth surface of a solid surface and is between the tangent drawn at the triple point between the solid-liquid and gas phases and the substrate surface. Furthermore, it is the most widely used parameter for the estimation of the degree of wetting.

Thus, the present work attempts to analyze the contact angles and the reactions that may take place in two iron based metallic alloys and ceramic materials tested by the sessile drop wettability technique.

2. Experimental

The wettability of various sintered nanopowders and a highly aluminous concentrate (60–70% in purity) powder by Fe Armco and with 22CrNiMoV5-3 steel grade at elevated temperatures were investigated using the sessile drop technique as described in the next section.

2.1. Materials

2.1.1. Nanocrystalline Oxide Powders Used as Substrates

In order to assess the wettability by the iron based metallic alloys, commercial CeO$_2$ (Tecnan; $d_{0<8-10}$ nm), TiO$_2$ (Aeroxide®, P25; $d_{0<21}$ nm), Y$_3$Al$_5$O$_{12}$ (d$_0<150$ nm) and ZrO$_2$ (yttria stabilized; $d_0<100$ nm) (both from Sigma Aldrich) nanopowders were purchased. The highly aluminous concentrate, 60–70% in purity, is mainly composed by Al$_2$O$_3$ micro and nanometric particles (Corundum and Bayerite crystallographic phases; $d_{c<10}$ μm) and in smaller amounts Ca, Si, Mg oxide types can be found. It is worth noting that the use of this secondary raw material with an aluminium oxide basis (Paval®)* aims at giving added value to this product.

2.1.2. Armco Iron and 22CrNiMoV5-3 Steel Grade

A very low alloyed Armco Fe was used in series 1 wetting experiments in order to avoid the complexity of simultaneous chemical reactions with other alloying elements typically found in steel grades. The steel grade tested in series 2, is a low alloyed high strength steel for quenching and tempering. This steel grade will be used to evaluate the influence on wettability caused by the alloying elements.

The chemical compositions of the iron based alloys used as droplets in the wettability experiments are listed in Table 1.

### Table 1. Chemical compositions of the drops used in the sessile drop wettability experiments (wt.%).

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armco</td>
<td>0.005</td>
<td>0.060</td>
<td>0.040</td>
<td>0.006</td>
<td>0.0048</td>
<td>0.026</td>
<td>0.020</td>
<td>0.012</td>
<td>0.003</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>22CrNiMoV5-3</td>
<td>0.220</td>
<td>1.040</td>
<td>0.310</td>
<td>0.008</td>
<td>0.003</td>
<td>1.210</td>
<td>0.650</td>
<td>0.190</td>
<td>0.360</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Experimental Set Up and Conditions

2.2.1. Substrate Preparation

With regard to the fact that in the sessile drop method a liquid small droplet is contacted with the substrate, it is important to prepare a flat and smooth surface. Accordingly, powders where cold pressed followed by sintering, leading to fully dense and poreless surfaces. It was assessed experimentally that during densification and thermal treatment steps it is extremely difficult to avoid cracking, thus, great effort was done to adapt the pressing and heating condition parameters in order to obtain the optimal surface. The pressing and sintering parameters for the powders tested in the wetting experiments are summarized in Table 2. Green body structures where obtained by dry pressing (uniaxially and isostatically), and it is worth mentioning that all powders showed high shrinkages. Afterwards, these green bodies where dried at 105°C, followed by a sintering heat treatment that was carried out in an air furnace measuring the temperature with a S thermocouple. Finally a stable pellet shape was obtained. In order to improve surface roughness, later polishing surface treatments where required. The final polishing step was adapted to each pellet type due to problems regarding powder releasing.

2.2.2. Surface Analysis

Many metal/ceramic couples are far from equilibrium, and the resulting interfacial reactions can strongly modify the chemistry, structure and topography of the contact area. These changes affect both the spreading kinetics and the ultimate degree of wetting. Thus, substrate and droplet contact surfaces are really important because the physical characteristics as roughness, microcavities, cracking, coatings or adsorbed layers can alter the spreading or the wetting behaviors. Accordingly, a detailed surface analysis of samples subjected to different surface finishing procedures (grinding and polishing) was carried out using a IFM microscope (Infinite Focus Microscope, Alicona). This optical microscope was used to obtain primary, roughness and waviness analysis of the surface sample, obtaining profiles, advanced parameters and bearing ratio for each type of analysis. This optical microscope is combined with small depth of focus of an optical system with vertical scanning analysis of the surface sample, obtaining profiles, advanced parameters and bearing ratio for each type of analysis.

*The Paval® powder, a trademarked form of aluminum oxide basis is provided by Befesa (Spanish aluminium producer). This product is originated in the treatment of the salt slags obtained from first cycle of the aluminium production.
The 3D morphological analysis was performed, composed by a detailed primary, roughness and waviness analysis along the approximate contact area between the droplet and the substrate. This area was selected for each substrate after each wetting experiment because the spreading was different for each case.

Figure 1 shows the squared area selected for surface analysis in the \( \text{Y}_3\text{Al}_5\text{O}_12 \) substrate/22CrNiMoV5-3 steel grade system laying on it (c) Roughness profile for the selected area.

Besides, volume analysis (3D image in Fig. 2) provided information about surface flatness. This analysis is very helpful for placing the substrate in an accurate way in the sample holder inside the furnace used for the wettability experiments. In this sense, the contact surface view between substrate and droplet was optimal for later calculations.

### 2.2.3. Sessile Drop Wettability (Technique Conditions)

The experimental equipment used to measure the contact angle by the sessile drop method consists essentially of a graphite tube which is located horizontally inside a high temperature furnace. A schematic diagram of the experimental set up is shown in Fig. 3. All the heated furnace parts, including the element and heat shields, are constructed of graphite, allowing both extremely fast and slow heating or cooling rates. The temperature of the furnace is measured with a type C thermocouple. A firewire digital video camera (Sony XCD-SX910CR) with a telecentric lens (Navitar 1-50993D) is used to record images from the furn-

### Table 2.
The experimental parameters used for the production of sessile drop wetting substrates from powders and the average surface values \( \langle R_a \rangle \) for the contact area between drop and substrate (measured by IFM analysis).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pressing Parameters</th>
<th>Sintering Parameters</th>
<th>( R_a ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nano-CeO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1597</td>
</tr>
<tr>
<td>2. Nano-TiO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1205</td>
</tr>
<tr>
<td>3. Nano-TiO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1597</td>
</tr>
<tr>
<td>4. Nano-Y₃Al₅O₁₂</td>
<td>Uniaxial</td>
<td>6</td>
<td>1205</td>
</tr>
<tr>
<td>5. Nano-Y₃Al₅O₁₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1205</td>
</tr>
<tr>
<td>6. Nano-ZrO₂</td>
<td>Uniaxial</td>
<td>113</td>
<td>1000</td>
</tr>
<tr>
<td>7. Nano-ZrO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1205</td>
</tr>
<tr>
<td>8. Nano-ZrO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1205</td>
</tr>
<tr>
<td>9. Nano-ZrO₂</td>
<td>Uniaxial</td>
<td>2.85</td>
<td>1205</td>
</tr>
<tr>
<td>10. Nano-ZrO₂</td>
<td>Uniaxial</td>
<td>113</td>
<td>1000</td>
</tr>
<tr>
<td>11. Aluminium oxide basis powder</td>
<td>Isostatical</td>
<td>200</td>
<td>1000</td>
</tr>
<tr>
<td>12. Aluminium oxide basis powder</td>
<td>Isostatical</td>
<td>200</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Fig. 1.** (a) Substrate-drop contact area selection for a tested wetting sample for later surface analysis by the IFM microscope in a (b) \( \text{Y}_3\text{Al}_5\text{O}_12 \) (substrate) and 22CrNiMoV5-3 (droplet) steel grade system laying on it (c) Roughness profile for the selected area.
nace at 960×1280 pixels. The telecentric lens is especially suitable for this type of measurement, with a 12 times zoom that allows for a image size from 50 to 4 mm across the frame, which at maximum magnification is equivalent to 3 μm per pixel. A Cambridge Sensotec Rapidox 2100 (with range from 10⁻¹⁷ ppm to 100% O₂) was used to continually measure the partial pressure of oxygen in the gas outlet during the experiments.

The furnace is designed to study the contact angle and the interaction between a small liquid sample and a substrate with the maximum size of 10 mm in diameter and 2 to 5 mm height. The liquid drop must be small enough to sit on top of the substrate without touching the edges. In this study the Armco Fe and the 22CrNiMoV5-3 steel pieces with a typical sample mass of 30–60 mg were placed on each sintered nano oxide.

The furnace chamber was evacuated initially and then it was filled with scientific grade argon gas (99.9999%). All the experiments were carried out in pure argon. The furnace was heated to 1 000°C at 300°C/min and then to 1 350°C at 50°C/min. Afterwards, the sample was heated with the rate of 10°C/min to 1 450°C and finally to 1 600°C at 5°C/min with a holding time of 10 minutes, followed by a rapid cooling to room temperature. The power was turned off, and approximately after one hour, the sample was removed from the furnace.

During the experiments the photos were captured every second, and the contact angle values were measured at different temperatures after the formation of a complete drop. After the experiments were completed the samples were mounted in epoxy and the cross sections were prepared for Electron Probe X-ray microanalysis (EPMA) supported by wavelength dispersive spectroscopy (WDS). The substrate and the drop chemical compositions were measured in different points.

3. Results and Conditions

The results derived from the wettability experiments on sintered powders are presented and discussed in this section.

3.1. Ceramic Powder Sintering and Surface Analysis

One of the most crucial features observed in the ceramic nanopowders during compaction step, was the elimination of large pores of the green bodies. In this sense, during the cold die compaction, the powders were densified by powder rearrangement, including sliding and rolling so as to decrease the porosity. To reduce the friction between the fine powder and the metal surfaces, stearic acid was spread on the inside surface of the mold. This waxy solid is expected not to have any effect on the reactions between the droplets and the ceramic pellets at high temperatures since it has a melting point of 69–72°C and it has a boiling point of 376°C. The ceramic raw powders were compacted uniaxially by a traditional cold die compaction method by a manual hydraulic press using a steel mold having an internal diameter of 25 mm. It was observed that some of the powders cracked during this higher pressing step due to the high shrinkages, so it was concluded that the compaction not only depends on the composition and the size of the powder material but also in the powder rearrangement, so the densification step was adapted for each powder sample in order to obtain an appropriate and fully densified pellet. A green structure formed after uniaxial pressing and a sintered TiO₂ are shown in Fig. 4.

A subsequent sintering cycle was developed for each nanopowder to attain improved densification. The optimal pressing and sintering parameters developed for each powder are summarized in Table 2. It is worth mentioning that it was extremely difficult to obtain a nano CeO₂ powder pellet without cracks and small pores, thus, it was tested just once using Armco Iron as the droplet phase.

3.2. Surface Analysis

After appropriate pellets were produced, they were cut with the maximum size of 10 mm in diameter and 2 to 5 mm in height, followed by surface progressive grinding in order
to improve as-sintered surfaces roughness. In the case of the aluminium concentrate substrate, no polishing was carried out because there was powder releasing. According to this polishing lack, roughness parameters showed higher values compared with the other tested samples.

As a result of the different properties of the sintered and polished materials, as hardness, grain size, machinability, etc. and the different sintering procedures, different $R_a$ (average surface roughness) values were achieved as shown in Table 2. The most promising roughness values were obtained for the sintered $Y_3Al_5O_{12}$ and $ZrO_2$ nanopowders after polishing with a 4000 emery paper. These surfaces are closer to an ideal (smooth) surface, which could give more repetitive contact angles values than a rougher surface. However, the experimental results are not as repetitive as expected. In the following picture, sintered nano $ZrO_2$ roughness profile is depicted, with the corresponding arithmetic mean deviation of the profile and the 3D surface images measured with the infinite focus microscope (Fig. 5).

The fluid spreading will be affected by surface roughness because a rough surface provides additional interfacial area for the spreading of the liquid. Thus, the contact angles measured are apparent contact angles, with parameters measured in a real and rough surfaces.

3.3. Sessile Drop Wettability Experiments

The contact of various sintered nanoparticle oxides with Armco Fe and 22CrNiMoV5-3 steel grade was investigated using the sessile drop wettability technique as described. The first experimental series was carried out with Armco Fe as the drop phase and sintered $TiO_2$, $CeO_2$, $Y_3Al_5O_{12}$, $ZrO_2$ (yttrium stabilized) commercial nanopowders and the $Al_2O_3$ basis powder (60–70% purity). A second wettability experimental series was carried out with 22CrNiMoV5-3 steel grade and with the same compositional ceramic substrates as in the previous experimental series, except for the sintered nano $CeO_2$.

Although the experiments were performed as two series with one steel grade in each, it is chosen to present the results in pairs for each or in groups of the oxide materials.

3.3.1. Wettability on Sintered Nano $TiO_2$

The nano $TiO_2$ powders were uniaxially compacted and thermally treated, as described in Table 2, for the production of one substrate for each steel grade. Several nano $TiO_2$ substrates were produced, but only the most appropriate surfaces were tested and described for the wettability assessment. The maximum heating treatment temperature is different in each case, and the higher the temperature is, the higher the average surface roughness value is measured.

3.3.1.1. Wettability of Armco Fe Drop

The sintered nano $TiO_2$ and the Armco Fe drop system showed reactive wetting. The squared iron specimen began to collapse because the melting was initiated from the contact area between iron and the ceramic substrate, observing metallic spreading through the ceramic surface. The contact area between the drop piece and the substrate where heat is transferred to the slag is important, because the sample melts faster when higher contact area exist. The tested specimen was characterized by EPMA analysis supported by WDS, and it revealed that iron had penetrated into the substrate, accompanied by a reaction layer with thickness of about 100 $\mu$m between the metallic drop and the substrate as shown in Fig. 6. The atomic ratio analysis, summarized in Table 3 complemented by element mapping revealed that Armco iron had reacted with the $TiO_2$ substrate to form ilmenite and pseudobrookite in the reaction layer. The drop and further analysis along the substrate showed the same element distribution as the original samples, thus reaction had taken place only throughout some microns thickness. In addition, some isolated bright points are also observed along the layer which corresponds to metallic iron.

An additional XRD analysis of the contact area between drop and substrate confirmed the presence of the mentioned...
crystalline ilmenite and pseudobrookite crystalline phases.

3.3.1.2. Wettability of 22CrNiMoV5-3 Steel Drop

This steel grade also shows reactive wetting on sintered nano TiO$_2$. However, it is worth mentioning that the TiO$_2$ sample prepared does not have an optimal $R_a$ value. Generally, an average roughness less than ~100 nm yields fair repeatability of measured contact angles, whereas large roughness values yield significant dispersion of the measured angles.$^{17,18}$ In this case the liquid is not supposed to penetrate well the rough surface asperities, so the valleys can strongly influence the $\theta$ value. Anyway, this experiment will help evaluating reactivity of the system. The steel sample begins to melt from the bottom, increasing the contact area with the substrate becoming a non spherical drop, as shown in Fig. 7. Finally the liquid metallic drop penetrates into the substrate revealed by the cross section EPMA analysis. As a consequence of the high wetting and penetration within the substrate, a layer is found, where the element mapping reveals remarkable areas with different Fe, Ti and O distributions.

EPMA analysis supported by WDS and a XRD analysis of the cross sections revealed that iron had penetrated the substrate, accompanied by an irregular layer where ilmenite and pseudobrookite appeared as reaction products.

3.3.2. Wettability on Sintered Nano CeO$_2$

As described before, it was extremely difficult to produce an optimal CeO$_2$ substrate from the commercial nanopowders for the subsequent wettability experiments. Not only were the nanopowders uniaxially pressed, but also isostatically. However, isostatical pressing led non compact and cracked nano CeO$_2$ substrates, but it was possible to produce one CeO$_2$ substrate uniaxially, as shown in Fig. 8. The sintering parameters are shown in Table 2.

3.3.2.1. Wettability of Armco Fe Drop

The liquid Fe Armco droplet is stable for a short time on...
the substrate, and then it disappears through liquid drop penetration into the CeO$_2$ substrate, as observed in Fig. 9. Figure 10 depicts how the substrate and drop surface looked after wettability experiment. The cross section image of the solidified Armco Fe in the sintered nano CeO$_2$ pellet shows internal cracks, probably related to the thermal shock occurred during the wetting experiment and during the sintering step. If the iron molten phase is disappeared and it penetrates into the substrate it is due to the high wettability. Even if it goes well into the open pores and cracks, it supports the high wetting of CeO$_2$ by molten iron, and it is not against the wetting essence. Moreover, it was observed iron penetration into the substrate, as showed the chemical composition and the element mapping obtained by wavelength dispersive spectroscopy (WDS) by EPMA (Fig. 11).

The element distribution obtained by EPMA shows that Fe is located in the cracks and it stems from the initial metallic drop. However, the chemical composition of the substrate fits well with the original substrate suggesting no reactions have taken place, and the observed penetration can be caused by the high wetting and not by chemical reactions. But it is noteworthy to say that the atomic distribution identifies mainly Ce and O, but with several atomic percent of Fe, it could suggest the formation of some Ce and Fe oxides, however, these results are not entirely clear, and if any reaction has taken place, the reaction products have not been identified. If the wetting is non-reactive or inert wetting type, it could be favoured because the interfacial bond is energetically nearly as strong as the cohesion bond of the liquid itself.\(^{15}\)

3.3.3. Wettability on Sintered Nano ZrO$_2$ and Nano Y$_3$Al$_5$O$_{12}$

The nano ZrO$_2$ and nano Y$_3$Al$_5$O$_{12}$ were pressed and sintered according to the parameters in Table 2. Some extra nano ZrO$_2$ substrates were prepared and characterized, and four wettability experiments were performed with this substrate and Armco Fe as the droplet phase.

3.3.3.1. Wettability of Armco Fe Drop

It was observed in the sintered nano ZrO$_2$ and sintered nano Y$_3$Al$_5$O$_{12}$ in contact with Armco Fe that both ceramic samples showed very poor wettabiity. The contact angles are temperature independent, suggesting the wetting is a non reactive process. This interpretation is verified by results.
The contact angles of some experiments carried out with sintered nano ZrO2 (samples prepared under different sintering conditions) and sintered Y3Al5O12 are plotted in Fig. 12 as a function of temperature. The contact angle decreases slightly with increasing the surface roughness. It is found in the literature that the sharp edges pin the solid-liquid-gas triple line, thus rough surfaces increase contact angle values for non-wetting systems. However, the results from this figure are not supporting the literature. There are several parameters that can alter the spreading of the liquid on the substrate and should also be taken into account. The distribution of roughness is an important consideration because local surface defects as scratches, porosity or voids due to detached and pullet out grains during substrate polishing may lead slightly different contact angles. Flat, dense, smooth and completely homogeneous surfaces yield fair repeatability of measured contact angles. However, the ceramic nanopowders sintered in these experiments have different powder rearrangement and unfortunately, the polishing step leads to different finishes, producing slightly different surface deviations and it may contribute to misinterpretation of experimental results. The inconsistencies in the contact angle values plotted in Fig. 12 may be attributed to surface deviations along the surface.

There are few works about wettability studies in ZrO2/Fe system. In a previous work by Valdez et al. the experimental approach was to measure the undercooling of a pure iron sessile droplet in contact with ZrO2 and some other ceramic substrates. The experiments were performed using pure iron on top of ZrO2 single crystals of (100) orientation, with roughness value Rt=1.11 nm in a Ar atmosphere. The contact angles measured for this system is function of PO2 measurements, at it ranges from 107–117 degrees approximately, the lower value the lower the PO2 it is (PO2=10–19–10–22 atm). Although the wetting experiments may be compared, the use of single crystal or the use of powders in the experiments lead to different contact angle values, the roughness and the porosity are difficult to reconcile. The maximum peak to valley roughness height of roughness profiles (Rt values) for the sintered ZrO2 is around 1 micron, and higher contact angle values (for PO2=10–23 atm) are found as it is expected.

3.3.4. Wettability on Sintered Aluminium Concentrate (60–70% purity) Powder

It is remarkable that experiment with sintered Al2O3 basis powder as substrate, both Armco Iron and low alloyed steel grade drops showed a very similar spherical shape change throughout the whole heating ramp, achieving a similar contact angle value after the holding time at 1600°C, as shown in Fig. 13. The contact angle value decreases and the liquid spreads on the solid surface until the equilibrium state is reached. According to this results and to the WDS results, all this suggests that both droplets had a non reactive with a very poor wettability.

The apparent contact angles for all non reactive wettings
in series 1 and series 2 at 1600°C are summarized in the following Table 4. Among other things, metallic liquid spreading can be altered by the oxygen presence by substrate and liquid drop surface oxidation. In this sense, great care was taken and the partial pressure of oxygen was measured in the gas outlet.

Several studies have been conducted on the wettability of alumina/Iron system, but these are primarily focused in the wettability study of high purity and monocrystalline alumina surfaces by liquid iron.

There is no reported data for the wettability of Paval® (Al2O3 basis powder and in smaller amounts composed by Ca, Si, Mg oxide types) by liquid Armco Iron, however, comparing the results with pure and monocrystalline alumina and pure iron, contact angles are reported to be from 109–140° at 1823 K.20,21) The results are compared with those reported earlier, and a previous work concludes that contact angles are a function of droplet size and the oxygen partial pressure of the gas atmosphere. Studying pure and monocrystalline alumina and pure iron, a product layer consisting of FeAl2O4 is identified at 1823 K22) and at 1933 K23) over the contact area between the metal drop and the substrate. On the contrary, in the actual work, taking into account that substrate is composed by some other metallic oxides, the formation of Mg2SiO4 is identified. Nakashima et al.24) studied wettabillity of low purity alumina (96% Al2O3) substrate containing other trace impurities as SiO2, CaO, and MgO, with similar impurities as in the actual work, although our substrate is richer in impurities. According to this work performed in argon atmosphere, the oxygen affects the wettabillity of Al2O3 substrate by liquid iron, but the X ray diffractions indicates that the reaction layer formed in the substrate in argon atmosphere is hercynite (FeO.Al2O3). It is observed a decrease in contact angle at higher oxygen concentrations, and it is considered to be caused by the action of oxygen in liquid iron, which works as a surface active element.25,26) In this paper, we have detected much smaller values of oxygen partial pressures measured in the gas outlet are smaller (PO2=10–22–10–23 atm, see Table 4) and the contact angle values are around 119°, higher than the values described in the previous work.

There are no other previous measurements of the contact angle of steel grades on the ceramics studied in the actual work, however, there are some other works with other steel grades and molten iron but they are difficult to reconcile due

<table>
<thead>
<tr>
<th>Sintered substrate R a (nm)</th>
<th>Sessile Drop</th>
<th>Experimental T and atmosphere</th>
<th>Apparent contact angle value θ</th>
<th>O2 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO2 110</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>116°</td>
<td>1.8×10–17</td>
</tr>
<tr>
<td>ZrO2 214</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>115°</td>
<td>1.2×10–17</td>
</tr>
<tr>
<td>ZrO2 179</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>130°</td>
<td>1.7×10–17</td>
</tr>
<tr>
<td>ZrO2 463</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>120°</td>
<td>1.1×10–17</td>
</tr>
<tr>
<td>Al2O3 basis 594</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>119°</td>
<td>1.3×10–17</td>
</tr>
<tr>
<td>Y3Al5O12 250</td>
<td>Armco Fe</td>
<td>1600°C, Argon Gas</td>
<td>147°</td>
<td>1×10–17</td>
</tr>
<tr>
<td>ZrO2 155</td>
<td>22CrNiMoV5-3</td>
<td>1600°C, Argon Gas</td>
<td>125°</td>
<td>1.7×10–17</td>
</tr>
<tr>
<td>Al2O3 basis 552</td>
<td>22CrNiMoV5-3</td>
<td>1600°C, Argon Gas</td>
<td>119°</td>
<td>9×10–18</td>
</tr>
<tr>
<td>Y3Al5O12 183</td>
<td>22CrNiMoV5-3</td>
<td>1600°C, Argon Gas</td>
<td>138°</td>
<td>1.3×10–17</td>
</tr>
</tbody>
</table>

Fig. 13. The change in the contact angle between Armco Fe and 22CrNiMoV5-3 drops and aluminium oxide basis powder substrate after the formation of a complete liquid drop. Note that last data corresponds to 10 minutes holding time at ±1600°C.
to the large variation between the results of different investigators that may be related to atmospheric differences, impurity content, roughness and experimental technique.

These preliminary results evidence that both sessile metallic drops showed very poor wettability tendency but slightly different contact angle values in ZrO$_2$, and in Y$_2$Al$_5$O$_{12}$. However, both droplets showed identical non-wetting behaviors by Al$_2$O$_3$ oxide basis powder substrates. Furthermore, CeO$_2$ and TiO$_2$ substrates showed higher wettabilities, by the Armco Fe droplet. The low alloyed steel grade and sintered nano TiO$_2$ system behaved as with the Armco Fe droplet, showing reactive wetting.

4. Conclusions

Experimental investigation of the wettability of some sintered TiO$_2$, ZrO$_2$ (yttria stabilized), Y$_2$Al$_5$O$_{12}$, CeO$_2$ nanopowders and Al$_2$O$_3$ basis powder by Fe Armco and 22CrNiMoV5-3 steel grade (except for nano CeO$_2$ by this drop) was performed according to the sessile drop wettability technique under argon atmosphere. These experiments provide valuable information about the chemical interactions between droplets and different substrate prepared under different sintering conditions. These surfaces were deeply studied by infinite focus microscope technique. The main results are as follows:

– During the dry pressing step aiming at green body production, agglomerates are formed from the primary particle nanocrystals leading inagglomerate pores and to inter agglomerate pores while the powder rearrangement is taking place. This powder rearrangement is influenced by the original powder mechanical properties and by the initial particle sizes. The elimination of these pores need different sintering conditions in addition to the high shrinkages and cracking problems, that are highly influenced by the powder compact, so the conditions have been adjusted to each case.

– Values of measured apparent contact angles of the real surfaces are influenced by surface roughness which have been studied by infinite focus microscope aiming at evaluating the suitability of the produced surfaces.

– Regarding the wettability experiments, in the case of sintered nano TiO$_2$, high and reactive wetting was observed for both low alloyed iron matrix and steel grade matrix. In both cases, a reaction layer formed by Fe–Ti–O solid solution, and investigation of the addition of some of these nanoparticles into the steel grade matrix. The wetting of sintered nano CeO$_2$ was only studied for the Armco Iron and it is relatively high. Even if some cross section cracks are observed in the sintered nano CeO$_2$, the liquid droplet penetrates the CeO$_2$ substrate because of high wetting. Wavelength dispersive spectroscopy (WDS) by EPMA was used to analyze the composition of the substrate and the solidified drop, iron was found in the cracks but reaction products were not identified.

According to these preliminary results, it is believed that higher wettability values and low reactivity will provide better particle dispersion in a liquid iron or steel grade matrix. However, this is a first attempt to understand and evaluate possible reactions and wettability behavior of the systems, taking into account sessile drop wettability technique experimental conditions. The future work involves the assessment and investigation of the addition of some of these nanoparticles in the liquid armco Fe or the steel grade matrix.

REFERENCES

3) C. Van Der Eijk, O. Grong, F. Haakonsen, L. Kolbeinsen and G. Tranell: ISIJ Int., 49 (2009), 1046.
12) T. Young: Phil. Trans. R. Soc. Lond., 205 (1805), 65.