Effects of CaO on the compaction and sintering by plasma of Powder-metallurgical iron

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Abstract. This work the effect of the addition of Calcium Oxide (CaO) in the compaction and sintering of powder metallurgical iron Ancor Steel 1000® is studied. Iron samples were made with proportions of 0.5%, 1%, 1.5% and 2% by weight of CaO. The samples were sintered in a luminous discharge furnace, in an atmosphere of H2+Ar at a temperature of 1150°C. XRD analysis was used to determine the formation of compounds, this analysis evidenced the formation of: hematite and magnetite, which were found both on the surface and in the volume. A characterization of the ability to protect against corrosive effects was carried out using the EIS electrochemical impedance spectroscopy method on the samples, in a solution of 1000ppm of chloride, with this procedure it was found that at a concentration of 0.5% and 1% CaO, the electrochemical impedance value is increased with values of 11.7MΩ, 2.2MΩ respectively.

1. Introduction
The Calcium oxide (CaO), is widely used since ancient times and has many applications in various sectors of industry. The CaO is used as catalyst for biodiesel production [1], is also used for the treatment of soils, and contaminated soils [2,3], and in the construction industry for the preparation of concrete [4,5]. The CaO is used in metallurgy as an oxide extracting agent in metals, it is also used to remove slag in the manufacture of steel and other metals [6,7]. The lubricating effect of CaO is mentioned in the wire-drawing process [8], however in the manufacture of parts via powder metallurgy it is not registered its use as lubricant. In this work, the effects of CaO in the powder metallurgy process were studied, the behaviour as lubricant during the production of samples in the green state was evaluated and its effect of oxide extraction in the sintering was observed. The oxides formed by the interaction of Fe and the oxygen present in the mixture are compounds such as hematite α-Fe₂O₃, magnetite Fe₃O₄, maghemite and goethite. The magnetite can form a protective layer that separates the metal from the aggressive environments [9,10], which improves the properties against corrosion.

2. Methodology
Four groups of test samples were made with the mixture of powder metallurgical CaO and Fe AncorSteel 1000®, The chemical composition of CaO is shown in Table 1. The samples were compacted at 700MPa, in a cylindrical steel matrix and sintered in glow discharge plasma. The sintering conditions were: temperature of 1150°C for 30 minutes, atmosphere composed of H2+Ar, pressure of 6 Tor and heating rate of 100°C/min. The density of the green state samples and the sintered samples was calculated from their dimensions.
The compounds formed in the sintered samples were determined by X-ray diffraction test (XRD) on a PAN'alalic X'pert PRO, with cobalt anode. The equipment configuration was: range from 25° to 104° for 2θ, a step of 0.0130° with permanence of 21.42 seconds, and a wavelength of 1.78901Å.

| Specifications | Real value |
|----------------|------------|
| Richness       | 95.8%      |
| Chloride       | <0.05%     |
| Fe             | <0.1%      |
| Ni             | <0.01%     |
| Pb             | <0.01%     |

The microhardness measurement was obtained using a Qualitest Vickers Microdurometer, the microdurometer was calibrated with 100gr of load for a time of 15 seconds. An analysis of electrochemical impedance spectroscopy EIS, was used to evaluate the behaviour of the test specimens in a corrosive environment, in a GAMRY PCI4G750. The EIS analysis which has been used to evaluate magnetite layers [11,12], The value of the electrochemical impedance is useful to show the interaction between the electrode and the electrolyte [13]. The solution used was sodium chloride of 1000ppm, the parameters used in the impedance analysis were: frequency scan of 10mHz to 100KHz, a cell composed of a working electrode with an exposed surface of 0.8cm², a Ag/AgCl reference electrode, and a platinum wire as a counter electrode.

3. Results

3.1. Compaction of the Fe-CaO mixture
The mixtures of the metallurgical powders were compacted at a pressure of 700Mpa, as seen in Figure 1. The shaped samples of 0.5%, 1%, 1.5%, and 2%, by weight of CaO was extracted from the compaction matrix without the use of any commercial lubricant for powder metallurgy. The compacting process shows that CaO has lubricating properties.

![Figure 1. Compaction of the powder mixture Fe-CaO.](image)

3.2. Density of samples with Fe-CaO mixture
The density values of the in green state samples and the sintered samples are shown in Table 2. The density is maintained around 6.9g/cm³, for all groups of samples. The percentages of 0.5% and 1% by weight of CaO show an increase in density as a result of good sintering.
Table 2. Density of samples in green state and sintered

| % of CaO | Density (g/cm³) | Green state | Sintered 1150°C |
|----------|----------------|-------------|-----------------|
| 0.00%    | 6.88           | 6.92        |
| 0.50%    | 6.95           | 6.96        |
| 1.00%    | 6.92           | 6.94        |
| 1.50%    | 6.91           | 6.89        |
| 2.00%    | 6.93           | 6.91        |

A weak layer was formed on the surface of CaO samples during sintering, this layer increases the diameter and height dimensions affecting the density value.

3.3. Microhardness of sintered samples with Fe-CaO mixture

The microhardness values of the samples sintered at 1150°C are recorded in Table 3. The microhardness increases as a function of the CaO content, with a maximum value of 132.35 HV0.1 for a concentration of 0.5% by weight CaO and a minimum value of 127.74 HV0.1 at a concentration of 2% by weight CaO.

The highest microhardness values correspond to the samples with the highest density values.

Table 3. Microhardness of sintered samples to 1150°C.

| % of CaO | Microhardness HV0.1 |
|----------|---------------------|
| 0.00%    | 92.05               |
| 0.50%    | 132.35              |
| 1.00%    | 130.36              |
| 1.50%    | 129.05              |
| 2.00%    | 127.74              |

3.4. XRD analysis of the sintered samples

The analysis of XRD made to the specimens with 0.5%, 1%, 1.5%, and 2% by weight of CaO, showed in all the concentrations the characteristic peaks of the Iron-alpha, and the presence of the oxides of Iron. The iron oxides formed during sintering were magnetite and hematite. The results of the X-ray diffraction tests of the sintered samples are shown in Figure 2.

Figure 2. XRD analysis of samples whit 0.5, 1.0, 1.5 and 2% by wt of CaO
3.5. Electrochemical impedance spectroscopy analysis of the sintered samples

The electrochemical impedance analysis was performed on the sintered samples and their Bode diagrams are shown in Figure 3.

![Figure 3. Bode diagrams of EIS spectra corresponding to mixture CaO-Fe sintered at 1150°C](image)

The electrochemical impedance values for the different percentages of CaO in the test samples are shown in Table 4, the impedance value of the test sample without CaO is 3.56kΩ, and with an addition of 0.5% by weight of CaO the impedance value increases to a maximum of 11.7MΩ. Another significant value of 2.27MΩ is found with a content of 1% CaO. Test samples containing 1.5% and 2% by weight CaO do not have a significant impedance value.

| % of CaO | Impedance (Z) (Ohm) |
|----------|---------------------|
| 0.00%    | 3.56x10³             |
| 0.50%    | 11.70x10⁶            |
| 1.00%    | 2.27x10⁶             |
| 1.50%    | 8.87x10⁵             |
| 2.00%    | 12.54x10³            |

The high impedance values show that the samples have a more compact surface and there is less porosity, causing a lower transfer of charge and this is related to the density values obtained previously.

4. Conclusions

Samples were made via powder metallurgy of the CaO and Fe mixture, it was observed that CaO increases the microhardness and acts as a lubricant in the compacting step. The CaO reacts with the Fe during the sintering, formed Iron Oxides (hematite and magnetite) which were detected in the analysis of XRD. The impedance value of the EIS analysis is related to the density and porosity characteristics of the test specimens.
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