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Enhancing Properties of Soft Magnetic Materials: A Study into Hot Isostatic Pressing and Sintering Atmosphere Influences

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Abstract: Soft magnetic materials are characterized by achieving a high magnetic induction value in the presence of a small magnetic field. Common applications of these materials, such as transformers or sensors, are in constant evolution and new requirements are becoming more demanding. Nickel and its alloys are employed as smart materials taking advantage of their superior magnetoelastic properties. A metal injection molding (MIM) technique provides high-quality complex-shaped parts with a good density and controlled impurity levels, which are necessary for these applications, by carefully adjusting the sintering stage. Previous investigations have established a sintering cycle for pure nickel consisting of 1325 °C for 12 h within an N2-5%H2 atmosphere. Nevertheless, microstructural, mechanical and magnetoelastic responses can still be greatly enhanced. In this context, the effects of hot isostatic pressing (HIP), and sintering atmosphere have been investigated. The application of an adequate HIP treatment leads to significant improvements in comparison to the reference sintering process. It achieves almost complete densification while increasing field-dependent elastic modulus from 8.1% up to 9.6%. Additionally, the sintering atmosphere has been proven to be a key factor in reducing impurities and hence facilitating magnetic domain motion. Three different atmospheres have been studied: N2-5%H2 (with a higher gas flow), N2-10%H2-0.1%CH4 and low vacuum. Minimum carbon contents have been registered using more reducing atmospheres (N2-5%H2 and N2-10%H2-0.1%CH4) which has led to values of field-dependent elastic modulus higher than 10%. This value is 2.5 times higher than that obtained when nickel parts are processed via conventional techniques. Moreover, although minimizing carbon content has been shown to be easier and more beneficial than achieving complete densification, both strategies could be used in combination to improve and maximize magnetoelastic performance.

Keywords: nickel; metal injection moulding; hot isostatic pressing; sintering atmosphere; soft magnetic alloy; magnetomechanical properties

1. Introduction

Nickel-base materials are widely used for commercial purposes due to remarkable properties, reported extensively in the ASM Specialty Handbook [1], such as corrosion resistance, mechanical strength, thermal expansion, electrical conductivity, and magnetic properties. As a consequence, commercial products can be obtained in a wide range of shapes and sizes.

The increase of the relative density and the reduction of impurities, such as C or S, lends itself to the improvement of magnetic performance as has been shown in multiple studies such as the one carried out by Lall [2] in which the magnetic properties of different Fe-base alloys and a stainless steel type 410L were analyzed. Melting and casting techniques cannot guarantee the high purity and the low level of inclusions required for magnetic applications. On the contrary, Herranz [3] remarks that the processing of a high purity powder via the Metal Injection Moulding (MIM) technique provides contamination control
and results in high-quality parts. Multiple purity grades of spherical or round carbonyl Ni powders with suitable particle size ranges for use in MIM are commercially available. Furthermore, MIM allows high production quantities of complex shapes, exceptional performance, and lower production costs than other manufacturing techniques.

Banerjee and Joens [4] highlight that the main steps in MIM technology are the removal of the binder system followed by the sintering process to ensure the permanent bonding of the particles in a suitable protective atmosphere. Heckel [5] stated that sintering atmospheres must fulfill various functions such as preventing oxygen and other airborne contaminants from entering the furnace, reducing surface oxides on the powder particles, controlling carbon on the surface, removing carbon, controlling oxidation during cooling, and efficiently transferring or removing heat. All these features were also confirmed years later by German [6].

Typical MIM powders have a D90 particle size distribution of around 20 µm. The huge surface area of MIM powders guarantees surface energy that allows the obtention of intense diffusive forces for the sintering process and therefore high densification. This, however, results in an increased risk of oxidation during thermal processing, because nickel is a metal in which the oxides are easily reduced by carbon or hydrogen. For this reason, according to Blais [7], sintering of nickel parts is typically carried out in a sulfur-free reducing atmosphere, such as hydrogen, combinations of nitrogen-hydrogen, dissociated ammonia, or burnt natural gas.

Sintering cycles of time–temperature are carefully aimed to obtain specific density requirements. Nevertheless, MIM does not ensure obtaining fully densified materials in some cases when the particle distribution is too narrow. This fact has been verified by Romero et al. [8] in a previous study in which the sintering process of nickel powders between 3 and 7 microns was done at high temperatures and for long periods of the plateau without achieving relative densifications higher than 97%. This obstacle may restrict the use of these materials for applications where high magnetic properties are required since Ma et al. [9] proved that the highest magnetic performance is achieved with the highest density values. Accordingly, some thermal treatments such as hot isostatic pressing (HIP) could be used to decrease porosity and hence improve the magnetic response. In this sense, Qiu et al. [10] achieved fully densities in a nickel-base superalloy after applying for 3 h a HIP process at \( \sim1190 ^\circ \text{C} \) and a pressure of 120 MPa. In a recent study carried out by Martínez et al. [11], higher densifications were obtained in pure nickel powders via HIP than those obtained via a conventional hot-pressing process.

The interest in the wide possibilities of nickel and nickel alloys has grown over the years. In the recent review of Horke et al. [12] it is possible to find many studies related to these materials after being processed by MIM, but they are mainly based on their mechanical properties. On the other hand, the application of HIP in nickel [11] or nickel alloys [13] is also an issue of topical interest. However, these studies do not focus on magnetic properties but in the study of densification [14], microstructure [15], elongation [16] or strength and ductility [17] after HIP. There are few studies about the magnetic properties of nickel alloys, and none of the pure nickel, after the combined application of MIM and HIP. Thus, there is still room for exploring the application of these techniques for enhancing the magnetic properties of nickel.

In the search for optimizing pure nickel microstructural, mechanical and magnetic performance (by means of facilitating magnetic domain motion), the objective of this paper is twofold:

1. Execution of a HIP treatment after sintering to minimize the residual porosity of the pieces.
2. Selection of an adequate sintering atmosphere (\( \text{N}_2-5\%\text{H}_2, \text{N}_2-10\%\text{H}_2-0.1\%\text{CH}_4 \) or low vacuum) which decreases impurities.
2. Experimental Procedure

Commercially available pure carbonyl nickel powder (3–7 µm) was selected for the evaluations. The rounded morphology of the powder can be seen in Figure 1, which shows a Scanning Electron Micrograph (SEM) of the powder with a carbon content of 0.07 wt.% and an absolute density of 8.87 g/cm³ measured by means of an elemental analyzer LECO CS-230 and a helium pycnometer Micromeritics AccuPyc II 1340, respectively.

![Figure 1. Scanning Electron Micrograph (SEM) image of carbonyl nickel powder.](image)

The feedstock was prepared by mixing the nickel powder with a previously developed multi-component binder system consisting of paraffin wax (PW) and high-density polyethylene (HDPE) in equal proportions. The nickel powder content in the feedstock is 50% in volume based on previous research carried out by Herranz et al. [18] in which a feedstock with adequate fluidity was developed after different rheological studies and torque measurements. Mixing of the feedstock was performed at a temperature range of 170–180 °C using a ThermoHaake Rheocord 252p twin screw extruder. High homogeneity was pursued by extruding the feedstock twice.

Afterwards, the feedstock was granulated and molded into the shape of cylindrical bars using an injection molding machine (Arburg Allrounder 270S) with a 22 mm reciprocating screw and a Selogica feedback controller. The size of these test bars was 6 mm in diameter and 60 mm in length.

After the injection stage, the parts were debound with a combination of solvent debinding followed by thermal debinding. For solvent debinding, the parts were fully immersed in heptane for 5 h at 60 °C. Thermal debinding was carried out by heating the samples in a nitrogen atmosphere and using a thermal cycle designed from thermogravimetric analysis results with a maximum temperature of 440 °C.

The initial sintering conditions were selected in accordance with a previous study of Romero et al. [8] in which sintering temperatures between 1300 °C and 1360 °C and sintering holding times between 1 and 20 h were considered. Parts were sintered at 1325 °C for 4 and 12 h in N₂-5%H₂ atmosphere. For a porosity reduction, these parts were additionally subjected to a treatment of hot isostatic pressing (HIP) at 1050 °C for 3 h and a
pressure of 180 MPa under an Argon atmosphere. The pressure was maintained during the heating and cooling phases (both at a rate of 1 °C/min).

With the aim of testing the influence of the sintering atmosphere, more parts were heated at 5 °C/min up to a sintering temperature of 1325 ± 25 °C for a sintering time of 1 h in three different atmospheres: N₂-5%H₂ with a higher gas flow than in the reference case studied by Romero et al. [8], N₂-10%H₂-0.1%CH₄ and low vacuum (10-2 mbar). When the optimum sintering temperature in each case was selected, the sintering time was extended for different holding times up to a maximum of 20 h to maximize the densification of the parts.

The characterization of mechanical, compositional, and microstructural properties of the sintered parts has been carried out. Density assessment has been obtained in accordance with the standard ISO 2738:1999 [19] by means of the Archimedes’ method of water displacement. The microstructure of the samples was observed on a Leica DR-IRM optical microscope. Measurement of residual carbon content was obtained in a LECO CS-230 instrument via the combustion method. Vickers microhardness (HV) measurements were obtained following the test standard ISO 4498:2010 [20] in a Future Tech micro-durometer by applying a load of 1 kg for 15 s in at least 7 locations on each sample. Finally, the magnetoelastic behavior of the nickel specimens was assessed by measuring the field-dependent elastic modulus according to a methodology developed by Morales et al. [21].

3. Results and Discussion

3.1. Effect of Thermal Treatment (HIP)

The effect of hot isostatic pressing has been studied on the sintered MIM parts with the objective of improving the magnetic performance of pure nickel parts processed by MIM. The selected conditions to sinter the samples were 1325 °C in N₂-5%H₂ atmosphere for 4 and 12 h of the plateau. These maximum and minimum sintering times were selected in accordance with a previous work of Romero et al. [8]. Times longer than 12 h do not produce any densification improvements, whereas sintering times less than 4 h provide unsatisfactory porosity levels. The HIP treatment was applied to both sample types.

3.1.1. Density

The effect of the sintering plateau on the relative density of the pieces before and after HIP treatment is shown in Figure 2. An increase in the relative density from 94.5% to 96.5% was observed when the sintering time is prolonged from 4 to 12 h without HIP treatment, whereas complete densification is almost achieved in both cases after applying the HIP treatment: 99.2% and 99.5% for the cases of 4 and 12 h of sintering plateau, respectively. Density is one of the key factors affecting magnetic domain motion, so this increase of densification is expected to produce a great improvement of nickel magnetic properties.

3.1.2. Microstructure

The evolution of porosity is shown in the micrographs of the samples without etching (see Figure 3). Porosity decreases considerably by prolonging the duration of the sintering plateau from 4 to 12 h as can be seen in Figure 3a,b, respectively. The porosity of the samples subjected to the HIP treatment is almost imperceptible (see Figure 3c,d), and only minimal amounts of residual porosity are found. These results validate the selection of an appropriate HIP cycle.
Figure 2. Sintering plateau and HIP treatment effect on the value of relative density.

Figure 3. Optical micrographs of polished samples sintered in N\textsubscript{2}-5%H\textsubscript{2} at 1325 °C during (a) 4 h of plateau, (b) 12 h of plateau, (c) 4 h of plateau and hot isostatic pressing (HIP) treatment and (d) 12 h of plateau and HIP treatment.
To evaluate the effect of HIP treatment on the size and structure of nickel grains, the microstructures of the different samples after etching are displayed in Figure 4. Due to the high corrosion resistance of the nickel samples, the intensive etching process produces some oxides and new pores that can be observed in the micrographs.

Figure 4. Micrographs of samples sintered in N$_2$-5%H$_2$ at 1325 °C during (a) 4 h of plateau, (b) 12 h of plateau, (c) 4 h of plateau and HIP treatment and (d) 12 h of plateau and HIP treatment. The enclosed area in dashed lines illustrates the area equivalent to that magnified for samples without HIP.

The microstructure consists of large coaxial grains and shows twinning inside the grains. Twins are formed by the reflection of one of the grains through a common plane. The crystal structure is the same, but they have different spatial orientations. This effect is very common in cubic close-packed metals such as nickel and the major part of the twin interface is parallel to {111} planes. Most theories on the mechanism of twin formation require the movement of a grain boundary for annealing twin grain nucleation, or are assigned to the nucleation and formation of new grains that take place during sintering. The formation of these twin boundaries would significantly reduce the grain boundary energy of powder during the sintering stage. Moreover, some studies suggest that the proportion of twins increased in impure nickel during grain growth whereas in pure nickel the proportion decrease [22]. In any case, recent studies demonstrated that twinning may have its own kinetics and could take place independently of grain growth [23]. Furthermore, the twinning activity may change as a function of sintering temperature and time [24] although it is not the aim of this paper to analyze these effects.

Variations in grain orientation cause the variation in the shade of the grains. The nickel structures exhibit large grains after the sintering cycle and huge grains after HIP treatment. The average grain size increases from 114 ± 4 µm to 164 ± 54 µm after extending the
sintering plateau from 4 to 12 h (Figure 4a,b), whereas grain sizes are increased significantly more after applying the HIP treatment in both sintering durations. Specifically, up to 884 ± 543 µm when the sample was sintered for 4 h (see Figure 4c), and even more when the sample was sintered for 12 h of the plateau (see Figure 4d). In this latter case, the length of the grains occupies the entire diameter of the sample (∼4.7 mm) and a width of ∼1282 ± 71 µm.

3.1.3. Mechanical Properties

Hardness increases with increasing densification of the sample, which occurs if either the duration of the sintering plateau is increased or if the HIP treatment is applied (see Table 1). Despite there being no notable differences in the hardness values after the HIP treatment (both initial densification values were similar), the greatest increase in hardness is obtained when the HIP is applied to the sample sintered for 4 h. This fact may be due to the excessive thickening of grains which occurs for samples initially sintered for 12 h.

Table 1. Microhardness values in the samples subjected to the different heat treatments.

| Microhardness (HV₁) | Sintering Plateau |        |        |
|---------------------|-------------------|--------|--------|
|                     | 4 h               | 12 h   |        |
| Pre-HIP             | 125 ± 7           | 131 ± 2|
| Post-HIP            | 143 ± 6           | 138 ± 8|

3.1.4. Magnetoelastic Properties

The variation of the elastic modulus as a function of the applied magnetic field is shown in Figure 5 for samples subjected to different heat treatments. The curves obtained show the same behavior with two distinguishable zones. The first trend corresponds to the variation of the magnetic field between 0 and ∼200 Oe, where rapid growth of elastic modulus is registered. When the intensity of the applied magnetic field increases, the growth of elastic modulus slows until saturation. This behavior has also been observed in the works of Morales et al. [25] on nickel and Morales et al. [26] on other ferromagnetic metals like iron and cobalt, and is consistent with the magnetic domain theory. The displacement of the domain walls is facilitated for low magnetic fields, whereas a high magnetic field saturates the sample in a single magnetic domain and an upper limit is attained.

In the demagnetised state (for \( H = 0 \) Oe), different values of elastic modulus are due to different densifications: the higher the density, the higher the elastic modulus, with the values converging around ∼190 GPa.

In the saturated state, longer sintering plateaus result in higher values of elastic modulus due to the increase in densification obtained in the samples. This fact is even more intensified when the HIP treatment is applied. These results clearly prove that the field-dependent elastic modulus is related to the closing of the porosity, because magnetic domain motion is facilitated when the magnetic field is applied.

The magnetoelastic behavior can be characterized by measuring the difference of elastic modulus between the saturated state and the demagnetized state. Results for the samples subjected to the different heat treatments are gathered in Table 2. The \( \Delta E \)-effect increases from 7% to 8.1% when the longer sintering plateau (12 h) is used since this produces higher densifications. Indeed, reduction of porosity when HIP treatment is applied increases \( \Delta E \)-effect up to 8.7% for a sintering time of 4 h, or up to 9.6% for a sintering time of 12 h. In this latter case, complete densification is accompanied by a huge grain size which also facilitates magnetic domain motion.
Figure 5. $\Delta E$ of the samples sintered in $N_2\cdot 5\%H_2$ at 1325 °C during 4 and 12 of plateau without and with HIP treatment.

Table 2. $\Delta E$ in the samples subjected to the different heat treatments.

| Sintering Conditions | Magnetic Field (Oe) | E (GPa) | $\Delta E$ (GPa) |
|----------------------|---------------------|---------|-----------------|
| 4 h                  | 0                   | 182.63  | 7.04            |
|                      | 2000                | 195.49  |                 |
| 4 h + HIP            | 0                   | 191.01  | 8.73            |
|                      | 2000                | 207.68  |                 |
| 12 h                 | 0                   | 189.91  | 8.11            |
|                      | 2000                | 205.32  |                 |
| 12 h + HIP           | 0                   | 190.02  | 9.60            |
|                      | 2000                | 208.32  |                 |

3.1.5. Final Pieces

After the HIP treatment, high quality and high brightness pieces, which have not lost their shape and do not exhibit surface defects or damage, have been obtained (see Figure 6). Similar contractions have been registered in the pieces regardless of the sintering time used. Thus, a contraction of 20.1% in length and 21.3% in diameter has been recorded with respect to the dimensions of the green parts.

Remarkable magnetic results have been obtained in the samples which underwent a combination of sintering and HIP. Magnetic performance has improved with the application of HIP up to 20% in comparison to nickel processed by MIM in the work of Romero et al. [8], and 2.4 times compared to conventional processing techniques studied by Morales et al. [25,26]. However, it should not be forgotten that the application of HIP treatment makes the processing of parts more expensive and complicated. For this reason, other ways of improving magnetic performance that are simpler, cheaper, and more feasible at an industrial level are explored. In this sense, the study of sintering treatment is further investigated by considering new sintering atmospheres.

3.2. Effect of Sintering Atmosphere

3.2.1. Density Effects

Density has been proven to have a great impact on the magnetic properties of soft magnetic materials. Thus, influences of the sintering temperature, time, and atmosphere on the density of the MIM nickel test bars have been studied in detail in the following
sections. The atmospheres chosen were high-gas flow N$_2$-5%H$_2$, N$_2$-10%H$_2$-0.1%CH$_4$ and low vacuum.

![Sample after HIP treatment.](image)

Figure 6. Sample after HIP treatment.

Relative density as a function of temperature is represented for the pure nickel bars sintered for 1 h under different atmospheres in Figure 7. In all cases, a significant increase in the densification occurs between 1300 and 1325 °C. For higher temperatures, melted zones were detected on the surface of the sintered pieces in all the atmospheres used. This behavior is in accordance with the phase diagram of Ni-C, which can be consulted in ASM Handbook [27]. This phase diagram reveals that at the carbon content of the brown parts (2.6 wt.%) the formation of the liquid phase takes place at a lower temperature due to the eutectic point at 1326.5 °C between both species. For this reason, a maximum sintering temperature of 1325 °C has been selected in all cases to avoid the uncontrolled melting of the parts. At this sintering temperature, similar relative density values (around 93.5%) have been obtained after sintering in the selected atmospheres for 1 h.

![Relative density as a function of sintering temperature at 1 h of holding time under N$_2$–5%H$_2$, N$_2$–10%H$_2$–0.1%CH$_4$ and low vacuum atmospheres.](image)

Figure 7. Relative density as a function of sintering temperature at 1 h of holding time under N$_2$–5%H$_2$, N$_2$–10%H$_2$–0.1%CH$_4$ and low vacuum atmospheres.

The dependence on the sintering time at 1325 °C under all the sintering atmospheres can be seen in Figure 8. Experimental evidence shows that, for all the considered cases,
the longer the sintering time is, the higher the densification results. However, it can be observed that minimum density changes are obtained with sintering times longer than 12 h at this temperature. For this reason, the optimal sintering time has been fixed at 12 h in all cases. The relative density value after 12 h at 1325 °C is 96.5% in sintering under N\textsubscript{2}–5%H\textsubscript{2} atmosphere, and 95.7% in sintering under N\textsubscript{2}–10%H\textsubscript{2}–0.1%CH\textsubscript{4} or low vacuum atmospheres.

![Figure 8](image.png)

**Figure 8.** Relative density as a function of sintering time at 1325 °C under different sintering atmospheres.

### 3.2.2. Microstructure

The behavior of porosity when different sintering times at 1325 °C are used (from 1 to 12 h) is similar for all the tested sintering atmospheres. Longer sintering times lead to a lower number of resulting pores. Figure 9a–d shows this trend in the case of sintering under N\textsubscript{2}–10%H\textsubscript{2}–0.1%CH\textsubscript{4} atmosphere and four different sintering times (1, 4, 8 and 12 h). In addition, the pores present in the microstructure are spherical in shape and appear isolated. These results provide support for those obtained from the density measurements, and they are consistent with the expected advantages of the use of PIM techniques collected by German [28].

The significance of microstructure in the properties of metals and alloys is widely recognized. The microstructures obtained from optimal sintering conditions under all sintering atmospheres are shown in Figure 10a–c. In view of the above, the microstructures are similar in all cases without remarkable differences. The structure consists of a nickel solid solution in the form of a polycrystalline metal. The nickel structures exhibit twinned and substantial coaxial grains due to the prolonged duration of the sintering cycle and the FCC structure. Similar microstructures consisting of coaxial and faceted grains with many annealing twins have been found in the bibliography, where the authors have sintered pure nickel or nickel alloys with a high percentage of nickel under different atmospheres. In this regard, the sintering of pure nickel under hydrogen atmosphere was carried out by Johnson and Westcot [29] and the sintering of superalloy 625 under high vacuum atmosphere by Özgün et al. [30]. Many black marks appear from the pitting oxidation suffered by etching,
3.2.3. Carbon Content and Mechanical Properties

Interstitial impurities have a critically negative effect on magnetic performance as different authors have demonstrated. Bidulskýa et al. [31] verified this fact by adding to an iron alloy different amounts of an aluminum alloy and evaluating different magnetic parameters such as the core loss, the remanence and the coercivity. Ma et al. [32] achieved in a Fe-Ni-Mo alloy the best magnetic performance in terms of permeability, saturation induction and coercive force, decreasing the level of impurities using longer sintering times and higher sintering temperatures. Thus, the minimization of impurities to the lowest possible level will always be beneficial. Thermochemical reactions in the MIM process are fundamental to carbon control, which could act as an impurity. These reactions of oxidation-reduction and decarburization–carburization are typical and dominant, as has been widely discussed by Palermo and Malas [33]. Furthermore, German [34] described the relevance of carbon control as a discriminant parameter in the MIM industry.

Figure 9. Optical micrographs of samples sintered at 1325 °C under N₂-10%H₂-0.1%CH₄ atmosphere for sintering times of (a) 1 h, (b) 4 h, (c) 8 h, and (d) 12 h.
In this study, the level of carbon is reduced when sintering times are extended under all atmospheres. In the case of sintering under N$_2$-10%H$_2$-0.1%CH$_4$ atmosphere, the decarburization has been most pronounced, as seen in a reduction beyond the carbon content of the starting powder (0.07 wt.%) after longer sintering times. A higher amount of hydrogen in this atmosphere favors, even more, the reduction reaction and decarburization process. This fact can be seen in Table 3 in which the carbon content after different sintering times under N$_2$-10%H$_2$-0.1%CH$_4$ atmosphere has been recorded.

**Table 3.** Carbon content and microhardness in samples sintered under N$_2$-10%H$_2$-0.1%CH$_4$ atmosphere.

| Sintering Time (h) | Carbon Content (%) | Microhardness (HV$_1$) |
|-------------------|--------------------|------------------------|
| 1                 | 0.1554 ± 0.0036    | 88 ± 5                 |
| 4                 | 0.0973 ± 0.0018    | 102 ± 7                |
| 8                 | 0.0289 ± 0.0009    | 98 ± 6                 |
| 12                | 0.0071 ± 0.0012    | 89 ± 2                 |

The average carbon content and microhardness values, after optimal sintering processes at 1325 °C for 12 h under all sintering atmospheres are shown in Table 4. The use of reducing atmospheres with higher hydrogen content and an adequate gas flow, results in lower carbon contents. A lower decarburization process occurs, and the highest amount of carbon is registered after the sintering process under a low vacuum atmosphere, because this atmosphere is less reactive.
Table 4. Effect of the sintering atmosphere on the carbon content and microhardness.

| Atmosphere        | C (%)          | HV1  |
|-------------------|----------------|------|
| N₂-5%H₂           | 0.0992 ± 0.0020| 129 ± 2 |
| N₂-10%H₂-0.1%CH₄  | 0.0071 ± 0.0012| 89 ± 2  |
| Low Vacuum        | 0.2696 ± 0.0100| 140 ± 4 |

The microhardness values follow a trend depending on the final carbon content obtained due to the interstitial solid solution hardening. Higher carbon content leads to obtaining the highest hardness value of 140 ± 4 HV₁ for sintering under low vacuum, and the lowest carbon content to the lowest hardness value of 89 ± 2 HV₁ for sintering under N₂-10%H₂-0.1%CH₄. Medium carbon content gives rise to medium hardness values of 129 ± 4 HV₁ for sintering under N₂-5%H₂ atmosphere.

3.2.4. Magnetoelastic Properties

The variation of field-dependent elastic modulus (ΔE-effect) is shown in Figure 11 for specimens sintered at 1325 °C for different sintering times and under the different sintering atmospheres.

The same two growing trends have been recorded as in the previous case: a more pronounced growth of the elastic modulus between 0 and 200 Oe, and a less pronounced growth for higher field strengths. The magnetic domain theory that is widely described in the research developed by Morales et al. [25,26] can explain this behavior.

In general, for each sintering atmosphere, longer sintering times result in higher values of elastic modulus both in the demagnetized and in the saturated state. In the demagnetized state, because of the increase in the densification of the parts; in the saturated state, because the lack of pores favors magnetic domain motion and therefore magnetomechanical performance.

Same sintering times do not imply similar elastic modulus values since other factors, such as the different sintering atmospheres or carbon content, may affect this analysis. To compare results in all the atmospheres and conditions, ΔE-effect for the sintered specimens at 1325 °C for 1, 4, 8 and 12 h are shown in Table 5.

The use of reducing atmospheres produce remarkable increases in the ΔE-effect: N₂-5%H₂ atmosphere with high gas flow (~9–10%) and N₂-10%H₂-0.1%CH₄ (~10–10.5%). The lowest ΔE-effect has been recorded after sintering under a low vacuum (~4.5%). These results are consistent with the fact that impurities such as residual carbon worsen the magnetoelastic behavior of magnetic materials. In fact, sintering under less reducing atmospheres leads to final parts which maintain a high carbon content even for longer sintering cycles, hence they show a considerably lower ΔE-effect.

The more reducing atmosphere N₂-10%H₂-0.1%CH₄ seems to produce a faster decarburization effect than N₂-5%H₂. When sintering under N₂-5%H₂ atmosphere with high gas flow, it is necessary to extend the cycle for up to 12 h to obtain the highest ΔE-effect and the lowest carbon content, whereas under N₂-10%H₂-0.1%CH₄ the maximum ΔE-effect can be achieved when the sintering cycle is only four hours. It should be emphasized that the final carbon content is similar in the samples sintered under N₂-5%H₂ for 12 h and under N₂-10%H₂-0.1%CH₄ for only 4 h, which could confirm these findings and the relevant role played by the residual carbon content in the magnetic response.

The field-dependent elastic modulus for specimens sintered in optimum conditions (at 1325 °C for 12 h) under all the considered atmospheres is shown in Figure 12 and Table 6. Since acquired densities in optimum conditions are very similar in all cases, the main differences can be attributed to different carbon content. In the demagnetized state, values obtained under reducing atmospheres such as N₂-5%H₂ or N₂-10%H₂-0.1%CH₄ are similar, but clearly lower than the value obtained in low vacuum, where the highest residual carbon content was found. Nevertheless, in the three cases the elastic modulus reaches a similar value in the saturated state.
Figure 11. ∆E-effect after sintering at 1325 °C for holding times of 1 h, 4 h, 8 h and 12 h under (a) N$_2$-5%H$_2$, (b) N$_2$-10%H$_2$-0.1%CH$_4$, and (c) low vacuum.
Sintering under reducing atmospheres promotes the decarburization of the samples and decreases the elastic modulus at the demagnetized state, but the lack of residual carbon content allows magnetic domains to rearrange easily, which dramatically increases elastic modulus in the saturated state, and therefore ΔE-effect.

Table 5. ΔE-effect as a function of the atmosphere and the holding times for samples sintered at 1325 °C.

| Atmosphere          | Sintering Time (h) | ΔE (%) |
|---------------------|--------------------|--------|
| N₂-5%H₂             | 1                  | 6.39   |
|                     | 4                  | 7.00   |
|                     | 8                  | 8.80   |
|                     | 12                 | 10.03  |
| N₂-10%H₂-0.1%CH₄    | 1                  | 8.89   |
|                     | 4                  | 10.61  |
|                     | 8                  | 9.57   |
|                     | 12                 | 10.15  |
| Low Vacuum          | 1                  | 4.46   |
|                     | 4                  | 4.76   |
|                     | 8                  | 4.17   |
|                     | 12                 | 4.34   |

The maximum ΔE-effect is obtained for the minimum level of impurities. Such is the case when sintering under the more reducing atmospheres, i.e., N₂-5%H₂ or N₂-10%H₂-

![Figure 12. ΔE-effect of specimens sintered at 1325 °C for 12 h in different atmospheres.](image)

Table 6. ΔE-effect as a function of atmosphere used in the samples sintered at 1325 °C for 12 h.

| Atmosphere          | Field (Oe) | E (GPa)  | ΔE (%) |
|---------------------|------------|----------|--------|
| N₂-5%H₂             | 0          | 183.27   | 10.03  |
|                     | 2000       | 201.66   |        |
| N₂-10%H₂-0.1%CH₄   | 0          | 182.29   | 10.15  |
|                     | 2000       | 200.78   |        |
| Low Vacuum          | 0          | 194.41   | 4.34   |
|                     | 2000       | 202.96   |        |

The maximum ΔE-effect is obtained for the minimum level of impurities. Such is the case when sintering under the more reducing atmospheres, i.e., N₂-5%H₂ or N₂-10%H₂-
0.1%CH₄ (and especially this latter). In these cases, the ΔE-effect is 10.03% and 10.15%, respectively. The selection of better gas flow conditions (increasing the flow) and the use of more reducing atmospheres have made it possible to further improve the meritorious results obtained in the previous study of Romero et al. [8], in which the maximum ΔE-effect was ~8%. Remarkably, these values are up to 2.5 times higher than ΔE-effect measured when nickel samples are conventionally processed.

Taking into account these results, the best atmosphere from a magnetoelastic point of view is N₂-10%H₂-0.1%CH₄ since it achieves a high elastic modulus at the saturated state (200.78 GPa) along with a high ΔE-effect (~10%). N₂-10%H₂-0.1%CH₄ also makes it possible to obtain similar results using lower sintering times.

3.2.5. Final Pieces

A comparison between green, brown, and sintered parts (in the same conditions under different atmospheres) is shown in Figure 13. Brown parts adopt this name due to their rust-colored appearance after the debinding stage, in which the binder is replaced with oxide bonds between the particles. The oxidation process can be expedited when a preliminary solvent debinding stage is used, as has been done in this case.

Figure 13. Images of the geometry samples after each processing step (green state, brown state and sintering state under different atmospheres).

The marks in the center of the sintered pieces are due to the fixing used to evaluate the magnetoelastic properties. The surface appearance of the parts changed as a function of the sintering atmosphere used. A better surface quality and brighter appearance have been obtained using more reducing atmospheres (i.e., N₂-10%H₂-0.1%CH₄ and N₂-5%H₂) which favor the oxidation–reduction process in which H₂ is required. Thus, under these sintering conditions, the hydrogen component of the atmosphere reduces the metal oxides as shown in the following reaction for nickel (see Equation (1)). Subsequently, parts that were sintered in these atmospheres show better metallic appearance and brightness.
NiO(s) + H₂(g) ⇌ Ni(s) + H₂O(g) \hspace{2cm} (1)

A shrinkage between 19.0% and 19.7% in length and between 20.2% and 20.8% in diameter was recorded after the sintering stage, as can be seen in Table 7. The higher the density obtained after the process, the higher the registered shrinkage. The parts subjected to HIP treatment, that registered the maximum shrinkages, these differences are minimum since density values obtained after optimal sintering cycles varied only slightly less than 1%.

Table 7. Dimensional analysis of sintered parts with optimum densifications (sintered at 1325 °C for 12 h).

| Atmosphere          | Length (mm) | Shrinkage (%) | Diameter (mm) | Shrinkage (%) |
|---------------------|-------------|---------------|---------------|---------------|
| N₂-5%H₂             | 47.88 ± 0.01| 19.68         | 4.75 ± 0.01   | 20.83         |
| N₂-10%H₂-0.1%CH₄    | 48.28 ± 0.04| 19.00         | 4.79 ± 0.02   | 20.17         |
| Low Vacuum          | 48.05 ± 0.06| 19.39         | 4.77 ± 0.04   | 20.42         |

4. Conclusions

In this research, pure nickel components were produced via the Metal Injection Moulding technique. The influence of the HIP treatment and the atmosphere used in the sintering process has been carefully studied. The main results are:

• HIP treatment causes almost complete densification and enormous grain growth. Closing of porosity leads to a slight increase of hardness and facilitates magnetic domain motion. The best magnetic performance (ΔE~9.6% and 208.32 GPa of the saturated elastic modulus) has been obtained after HIP treatment on the sintered sample for 12 h of the plateau at the maximum temperature.

• An optimal sintering cycle consisting of a temperature of 1325 °C and 12 h of plateau time has been selected for the sintering process under all the atmospheres. Higher temperatures result in melted zones, and longer times do not improve density values. Under these conditions, the relative density values are between 95.7% and 96.5%, depending on the atmosphere used.

• Microstructure of the sintered components consists of large coaxial grains with twinning. Pores that appear in the microstructure are spherical in shape and are isolated.

• A large variation in the final carbon content is obtained depending on the sintering atmosphere. The higher the carbon content, the higher the microhardness values obtained.

• ΔE-effect increases for longer sintering times in the most reducing atmospheres due to lower carbon content. Values around 10% are achieved when an atmosphere of N₂-10%H₂-0.1%CH₄ or a high flow of N₂-5%H₂ are used. These values are remarkable because the obtained ΔE-effect not only is 2.5 times higher than those measured in conventionally processed nickel, but also slightly higher than those obtained after applying a secondary HIP heat treatment.

• Sintered parts suffer very close shrinkages. However, a better surface appearance, with higher brightness and metallic aspect, is obtained using the more reducing atmospheres.

Finally, it should be noted that selecting a suitable treatment and sintering atmosphere is an essential requirement to obtain the final properties which are sought. In this case, the best magnetic performance with ΔE~10% was obtained after a sintering process under N₂-10%H₂-0.1%CH₄ atmosphere at 1325 °C for 12 h, this being the best atmosphere from a magnetoelastic point of view. This result has been obtained without the need to apply other expensive secondary treatments such as HIP, but both strategies could be employed for maximizing magnetoelastic behavior.
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Abbreviations
The following abbreviations are used in this manuscript:

- MIM: Metal Injection Moulding
- HIP: Hot Isostatic Pressing
- SEM: Scanning Electron Micrograph
- PW: Paraffin Wax
- HDPE: High Density Polyethylene
- HV: Vickers microhardness

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