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**THE INFLUENCE OF OXIDE PARTICLES IN STRENGTH AND DUCTILITY
OF BULK IRON WITH BIMODAL GRAIN SIZE DISTRIBUTION.**

C. CASAS¹, R. TEJEDOR¹, R. RODRÍGUEZ-BARACALDO², J. A. BENITO^{3,4*} and J.
M. CABRERA^{1,4}

¹ Department of Materials Science and Metallurgical Engineering, ETSEIB, Universitat Politècnica de Catalunya, Av. Diagonal 647, 08028 Barcelona, Spain.

² Department of mechanical engineering, Universidad nacional de Colombia, Bogotá, Colombia.

³ Department of Materials Science and Metallurgical Engineering, EUETIB, Universitat Politècnica de Catalunya, Comte d'Urgell 187, 08036 Barcelona, Spain,

⁴ Fundació CTM Centre Tecnològic de Manresa, Plaça de la ciència, 2, 08243 Manresa, Spain.

*Corresponding author.

E-mail address: Josep.a.benito@upc.edu

Tel. +34-934010946, Fax.+34-934010706

Materials Science Department, Pavelló E. ETSEIB.

Av. Diagonal, 647.

08028 Barcelona

Spain

Abstract.

The strength and ductility of bulk nanostructured and ultrafine grained iron with 0.39% oxygen in weight was determined by tensile tests. The samples were obtained by consolidation at 500 °C of milled iron powder. Heat treatments were designed to cover a wide range of grain sizes from 100 to 2000 nm with different percentages of coarse and nanostructured grain areas, which is defined as bimodal grain size distribution. Transmission electron microscopy was used to determine the diameter, volume fraction and location of oxides in the microstructure. The strength was analyzed following two approaches, the first one based on a high influence of oxides, a mixed particle-grain boundary strengthening model, and the second one based on simple grain boundary strengthening. The mixed model underestimated the strength of nanostructured samples whereas simple grain boundary model worked better. However, for specimens with bimodal grain size the fitting of the mixed model was better. In this case, the more effective particle strengthening is related to the dispersion of oxides inside the large ferrite grains. In addition, the bimodal samples showed an acceptable combination of strength and ductility. Again, the ferrite grains with oxides inside promoted strain hardening due to the increase in dislocation activity.

Keywords: mechanical milling, nanostructured materials, iron, oxide particles, strength, ductility.

Introduction

The development of nanocrystalline (NC) and ultrafine-grained (UFG) materials with good strength/ductility balance is one of the main topics in current structural materials research. In the case of NC and UFG iron and steels several processes based in the severe plastic deformation of the ferrite grains has been used. Mechanical milling and in particular ball milling of iron has been extensively used to produce nanostructured powders that rendered NC and UFG bulk materials after a consolidation process [1-5]. The presence of an oxide layer in the powder before milling caused that some oxygen content was detected in the bulk consolidated samples. Moreover, depending on the milling media some carbon content has also been reported [5,6]. This means that in the analysis of the mechanical properties of the consolidated ball-milled iron, the presence of finely dispersed particles in the nanostructure must be taken into account.

Generally, the yield strength of industrial iron and low carbon steel had been evaluated by a classical Hall-Petch relationship $\sigma_y = \sigma_0 + k_y \cdot D^{-1/2}$ [7,8] and the increase of strength related mainly to grain boundary strengthening. For Armco iron and low carbon steels, the grain size dependence of yield strength has been shown by the high values of the Hall-Petch coefficient k_y , between 550-600 MPa· $\mu\text{m}^{1/2}$ [9,10].

In recent times the role of particles in strength of ball-milled iron has been investigated and a new model has been proposed [11]. In this approach, the contribution of grain boundary strengthening is reduced when the grain size gets below 2 μm and then a large percentage of the strength is related to the contribution of particles. We can define it as a mixed particle-grain boundary strengthening model. The major contribution of particles in the NC range would be produced when they would be finely dispersed inside the ferrite grains instead of being located at grain boundaries. At the same time, advances in thermomechanical processing have allowed to obtain UFG irons in which

the precipitation of carbides and oxides has been suppressed [12]. In these UFG and industrial irons, a high dependence of grain boundary strengthening of ferrite with carbon solute has been shown. It has been reported that the presence of only 60 ppm of solute carbon changes the Hall-Petch coefficient k_y associated for pure iron from around $150 \text{ MPa} \cdot \mu\text{m}^{-1/2}$ to $600 \text{ MPa} \cdot \mu\text{m}^{-1/2}$ [13]. Applying these values for k_y the Hall-Petch relationship seems to be obeyed in industrial irons for grain sizes below $1 \mu\text{m}$ and even at $0.2 \mu\text{m}$ [14-15]. Therefore, we can say that this is an approach for the strength of NC and UFG iron based on a simple grain boundary strengthening.

The increase in strength produced in the NC and UFG irons after grain refinement is generally accompanied by a fall in the ductility. Under compression, together with a high values of strength, a moderate ductility has been found even for average grain sizes close to the NC range [3,16-18]. It must be noted that, in these cases, the strain hardening declined as the grain size was refined, being virtually zero below 300 nm . At the same time, shear banding was clearly the main mode of deformation as the grain size reached the UFG range [3,17,19].

Nowadays, different Severe Plastic Deformation (SPD) techniques are used to obtain UFG iron from relatively pure materials as Armco iron or Interstitial-free steels (IF) [20]. In the case of UFG iron obtained by Equal-Channel Angular Extrusion (ECAE) the resulting microstructure consists on elongated grains with a cellular dislocation substructure [21,22]. This microstructure has the tendency of shear banding and the related strong shear localization have been identified as the main cause of the low ductility found in tensile tests. The same problem has been observed in UFG irons produced by High Pressure Torsion (HPT) and Accumulative Roll Bonding [23-26] in which the high strength is accompanied by a low uniform deformation. In this case, the elongated and aligned structure resulted in a high mechanical anisotropy that led to a

limited fracture toughness in certain orientations [23]. The use of heat treatments after SPD deformation of UFG iron helps to improve the total elongation of the samples and even strain-hardening regions without an important reduction in strength, but the total increase in uniform elongation is small [24,27,28]. On the other hand, the presence of carbon and the cementite formation seems to be effective since UFG steels processed by caliber warm rolling have shown tensile elongation with Lüders band formation and subsequent strain hardening when the carbon content was above 0.15 wt% forming globular cementite particles [29].

One of the strategies to obtain NC and UFG metals with better tensile plasticity developed in recent years has been the bimodal grain size distribution. The structures containing nanostructured and coarse grained zones in which the grains are micrometric in size have been suggested to prevent failure by shear localization [30]. The nanostructured matrix grains impart high strength whereas coarse grains help the structure to induce strain hardening mechanisms that stabilize the tensile deformation. By this way the material retained much of its strength recovering part of its ductility before SPD. Bimodal structures has been obtained by different techniques, such as annealing of copper after ECAE processing [31], hot consolidation of milled and unmilled powder blends of Al-7.5 Mg [32], Fe-Cr alloys [33] and Oxide Dispersion Strengthened (ODS) ferritic steels [34] and also by consolidation of milled iron in a Spark Plasma Sintering (SPS) equipment [5,17]. It should be noted that in the bimodal structures obtained by blends of milled and unmilled powders, a banded structure is formed due to the easy deformability of coarse-grained particles [35]. On the other hand, the structure obtained after annealing of ECAE samples after annealing or by consolidation of only milled iron results on a more equiaxed structure. Finally, in the cases were the presence of dispersed oxides in iron and iron alloys were investigated

[5,17,34], the strain hardening observed in tensile tests was related to the presence of macroscopic ferrite grains capable of storing dislocations together with the presence of finely dispersed oxide particles.

Mechanical milling of pure iron and subsequent warm or hot consolidation has been one of the main techniques to obtain bulk samples of NC and UFG iron and steels with a homogeneous grain size distribution [2-4,16,18]. However, porosity and lack of bonding between powder particles in the consolidated specimens by these techniques has been pointed out as the main causes for the brittle behavior observed, especially in tensile tests.

In this context, the aim of the present paper was to produce pure iron with a bimodal grain size distribution from mechanically milled powder and investigate its mechanical response by hardness and tensile tests to find a good combination of high strength and ductility. At the same time, microstructural observations were carried out to investigate the size, volume fraction and location of oxide particles in the ferritic matrix. This microstructural features were used to calculate a predicted yield strength following the two strengthening models mentioned before. These predicted yield strengths were compared with the experimental ones in order to evaluate the influence of oxide particles on the strength in the NC and UFG ranges.

Materials and Methods

Commercial pure iron powder with a particle size between 75 and 160 μm was mechanically milled to obtain a nanostructured iron powder. MM was carried out for 17 hours in a planetary ball mill with stainless steels vials and hardened steel 100Cr6 balls with 10 mm diameter under Ar gas atmosphere. The ratio balls-powder was 27:1. The average particle size of the milled powder was around 80 μm and microhardness was

evaluated in the powder by Vickers indentations with a load of 0.1 N. The powder had a hardness of 8.1 ± 0.7 GPa and a mean crystallite grain size of 26 ± 10 nm as determined by X-ray diffraction using a modified Williamson-Hall method [36].

The milled powder was consolidated using a two-step process. The first process consisted in a cold compaction of the powder at 1300 MPa. The powder was not taken from the mould after cold compaction. The second step was a hot static compaction at a fixed pressure of 850 MPa held for 1 hour at 500 °C. The specimens were 1 mm in height and 10 mm in diameter. Additionally, some specimens were heat treated under an Ar atmosphere between 650 °C and 775 °C during 0.5 hours to attain different grain sizes. The final chemical composition (mass%) was 0.03 for C, 0.39 for O, 0.94 for Cr, 0.53 for Ni and 0.017 for P (Fe balance). Specimens for tension tests were cut from the consolidated samples using wire electrical discharge machining. The samples were 0.8 mm wide, 0.8-1 mm thick and 2 mm of gage length. Tensile tests were conducted in a Deben tensile machine at an initial strain rate of $1.7 \cdot 10^{-3} \text{ s}^{-1}$. The elongation was calculated from the gauge length and the displacement measured by tensile machine. The hardness of consolidated samples was evaluated by Vickers indentations on the upper and lower flat surfaces of the cylinders applying a load of 1.96 N. At least 15 measures were done for each specimen. The cylinders were grinding and finally polished with diamond suspension of 6 μm grain size.

The density was determined by the Archimedes method with water as a liquid medium.

Microstructural analysis and determination of ferritic grain size was performed by scanning electron microscopy (SEM) using a JEOL JSM6400 microscope equipped with an Energy Dispersive X-Ray Spectroscopy (EDS) system (Oxford Inca X-sight) and by transmission electron microscopy (TEM) using a Philips CM30 microscope operating at 300 kV. For the preparation of TEM samples, the consolidated pieces were

ground on 600-grit silicon carbide to a thickness of 250 μm and then were cut into discs of 3 mm in diameter. Finally, the samples were electrochemically thinned on a Struers Tenupol II using 6% vol HClO_4 and 94% vol CH_3COOH at room temperature. The analysis of grain size was performed from SEM and TEM images with a BUEHLER image analyzer software. In the cases of the as-consolidated and the heat treated at 650°C samples, bright field and dark field images obtained by TEM were combined to clearly identify the contour of the grains. In order to differentiate areas of nanograins from areas of coarse grains in bimodal structures, grains with diameter lower than 500 nm were considered as nanograins, whereas larger grains were computed as coarse grains. Finally, the examination of the size and distribution of oxides was performed by TEM dark-field images on the same samples used by the determination of the grain size of ferrite. For every type of treatment, at least ten micrographs were examined and more than 100 clearly identified oxide particles were counted. For the calculation of the volume fraction of oxides an apparent diameter was determined for every oxide identified and the foil thickness of the studied areas was measured using the extinction contour method [37].

To study the amount of subgrain boundaries and high angle boundaries in the strength of the as-consolidated specimens, the microstructure of some samples consolidated at 500 °C were characterized by Electron Back Scattered Diffraction (EBSD). The samples were mechanically polished with 2500 grit SiC paper until 0.02 μm colloidal silica suspension following standard metallographic procedures. The EBSD measurements were performed using a JEOL JSM-7001 F Field emission Scanning Electron Microscope (FE SEM) using the Oxford Instruments HKL channel 5 software package. A step size of 0.15 μm was used and misorientations below 3° were not considered in the post processing data procedure.

Results.

- Microstructure

All the consolidated samples showed high relative densities above 98% with respect to the density of pure iron. The microstructure of the consolidated samples and its evolution with heat treatments at different temperatures can be observed in Fig. 1. The average ferritic grain size, the volume fraction of coarse grains together with the particle size of the oxides and its volume fraction present in every sample are listed in Table 1. The TEM bright field micrograph of the as-consolidated samples at 500 °C (Fig. 1A) shows that the ferrite grain size is in the NC regime. Grains are equiaxed and randomly oriented according to the continuous diffraction rings of ferrite in the expanded Selected-Area Diffraction (SAD) pattern of Figure 2A. Inside the first ring of $\text{Fe}\{110\}$ a weak ring is clearly visible. The value of interplanar spacing associated to that ring agrees well with the highest intensities of FeCr_2O_4 and Fe_3O_4 . The three-dimensional atom probe (3DAP) analysis in [5] has shown that O and Cr in MM annealed iron form oxide particles in the grain boundaries so the presence of FeCr_2O_4 in the present samples is very likely. The examination of these oxides dissolved in the ferrite matrix by TEM dark-field images (Fig. 2B and 2C) showed that they were mainly located in the grain boundaries and some of them dispersed inside ferrite grains, being very difficult in some cases determine the exact situation due to overlapping of ferrite grains. In these as-consolidated samples at 500 °C, the oxides are very small in size, with an average grain size of 15 ± 10 nm.

It is interesting to note that the values of the volume fractions of these oxides (V_{fO}) detected inside the ferritic matrix and exposed in Table 1 go from 0.15% to 0.48%. The theoretical value for V_{fO} according the total mass percentage of oxygen found in the

samples (0.39%) would be approximately 2.1%. This difference can be explained partially by the fact that a number of oxides are located in the surfaces of the powder particles and not inside them, as it has been shown in other cases of consolidation of dry milled powders [38]. Fig.3 shows a SEM micrograph in which a joint between former powder particles of a sample heat treated at 725 °C can be observed. In this figure are included the corresponding maps obtained by EDS analysis for different elements present in the materials. It can be seen that the signals for chromium and oxygen coincide well, indicating the presence of oxide particles of iron and chromium, as in other works about ball-milled iron containing both elements [5,17,39].

The EBSD studies of the as-consolidated samples at 500 °C rendered that in the microstructure high-angle boundaries were predominant and the relative frequency of low angles boundaries were around 15-18% in all the cases analyzed. The presence of low angles boundaries can be clearly observed in the EBSD image in Fig. 4, but the majority of grains are well differentiated by high angle boundaries. The calculated average grain size from the EBSD studies was 97 nm, virtually identical to the value obtained from TEM measurements.

After a heat treatment at 650 °C, the microstructure was still homogeneous with a small increase in average grain size. The location of oxides in Fig. 2C was very similar to that of the as-consolidated samples, with a strong presence of oxides at the grain boundaries, although the presence inside the grains is also important. When the samples were heat treated at 660 °C and 675 °C some coarse grains appeared (Fig. 1C and 1D) occupying a volume fraction below 10% in both cases. At the same time little increase was found in the average size of oxides presented in the microstructure, since in the case of the samples heat treated at 675 °C, the calculated size was 20 ± 11 nm. Again, these oxides were located mainly on the grain boundaries.

The increase in temperature at 700 and 725 °C gave rise to an increase of the volume fraction of coarse grains (Fig. 1E), but not to a large increase of its size since the average values maintained between 2 and 3 μm . The heat treatment also affected the nanograin areas since at these temperatures a moderate increase of the average values was observed. With regard the size and distribution of oxides in these samples, it has to be noted that the growth in size was little, since the average size was 25 ± 14 nm in the case of heat treatment at 725 °C. However, these oxides were not only located on the former grain boundaries, but also inside the new large ferrite grains developed during heat treatment. In Fig. 2D, some of these oxides can be observed. Originally, these oxides were mainly located on the grain boundaries of the nanocrystalline ferrite, but were trapped inside ferrite grains after the movement of grain boundaries during heat treatment.

At 775 °C, although there are still fine-grained areas (Fig. 1F), its average grain size was well above 500 nm, and therefore the samples were not considered to be in the UFG regime. The distribution of oxides was very similar to the 700 and 725 °C heat treated samples.

- Tensile tests

Figure 5 shows the tensile strain-stress curves for the consolidated and heat-treated specimens. The as-consolidated samples showed a brittle behavior. They failed at very low stresses (77 MPa), although the relative density of the compacts was higher than 98%. The fragile behavior is confirmed in the fracture surfaces of these samples (Fig. 6A) in which the contour of the former powder particles are easy to identify. It is worth mentioning that the same samples but in compression tests were fairly good both in

strength and ductility, since compressive stress was 1922 MPa and compressive strain arrived to 32% [16].

Additional heat treatment at 650 °C had no strong effect in grain size, but the bonding between the powder particles was improved since the Ultimate Tensile Strength (UTS) was increased to 1920 MPa. Practically no plastic deformation was observed. For the samples heat treated at 660 °C, in which the growing of coarse grains was detected, the tensile strength was 1720, with no effect in ductility of these small coarse grain areas. The improving in strength for both samples was reflected in a change of the fractography, since the fracture occurred mainly through the former powder particles, although there were areas of particle debonding (Fig. 6B). In some small zones (distinguished with an arrow in Fig. 6B) signs of dimple fracture can be observed, probably related to a plastic deformation located in coarse grain areas.

With heat treatments at 675 and 700 °C the volume fraction of coarse grains was increased to 7 and 21%, respectively. This increase in coarse grain areas was reflected in tensile tests. The UTS decreased in both cases, especially for 700 °C samples. However, for the two heat treatments, ductility was observed with a significant length of uniform deformation. Both samples are interesting, since for 675 °C samples the strength was good (1244 MPa) with a 4% uniform strain and for 700 °C the UTS decreased to 1028 MPa, but with a 15% total strain, being the percentage of uniform elongation closed to 9%. Unlike the as-consolidated samples, in the case of heat treatment at 700 °C, there was similarity with previous compression tests [16]. The UTS and compressive stress were close, and the material showed large ductility with a slight strain hardening in both tests.

For the heat treatments at higher temperatures (725 and 775 °C), the increase of the volume fraction of coarse grains and the average grain size of fine grain areas, gave rise

to a decrease in strength and an improvement of both ductility and uniform deformation. The comparison of tensile results with previous compression tests rendered in this case a very similar behavior in the two kinds of tests. The ductility of the samples resulted in the presence of ductile fracture zones, characterized by a large deformation of powder particles and an important number of dimples (Fig. 6C) and gave rise to a large area reduction of samples, as can be observed in Fig. 6D.

Discussion.

- Pinning effect from oxide particles in the consolidated samples

First is interesting to discuss about the development of the microstructures with heat treatments on the consolidated samples. The grain growth with temperature of the ball milled iron is delayed by the presence of the nanosized oxide particles detected in the microstructures [4-6]. The boundaries intersect with particles so an energy increase is needed to overcome these obstacles. The expected final grain size (D_{Z-S}) counting the effect of pinning particles has been calculated by the Zener-Smith equation:

$$D_{Z-S} = \frac{4d}{3Vf_o} \quad (1)$$

Where d is particle diameter and Vf_o is the volume fraction of oxides in the iron microstructure. The calculated values of D_{Z-S} are exposed in Table 1. For the samples near the nanostructured range or with a small percentage of coarse grain areas, the low heat treatment temperature has not enabled to obtain a substantial growth, and the comparison with the final grain size estimated by Eq.(1) seems to be rather difficult. When the heat treatment temperature was 725 and 775 °C, the grain growth was more evident and although the bimodal grain size distribution was still present, these temperatures seem more appropriate to compare the real and the estimated final grain size. For the samples heat treated at 725 and 775 °C, in which the zones with grain

below 500 nm were half of the total or they have simply disappeared, the calculated value from the Zener-Smith equation would be 22.2 and 7.9 μm , respectively. The value for the samples heat treated at 725°C is very far from the grain size of the coarse grain zones, around 2.9 μm . It is, nevertheless, important to note that in these samples the volume fraction of oxides calculated from TEM images was very low comparing with the rest. Since all the consolidated samples have been obtained from the same powder, it would be expected that V_{fO} for the samples treated at 675 °C would be higher and the final grain size more in line with experimental values. With respect to the final grain size in the 775 °C samples (7.9 μm), it was closer to the mean grain size calculated from the coarse grains areas (4.2 μm), but there is a difference between both values. In order to explain this discrepancy, the present results in particle size and volume fraction of the oxides have been compared with other studies on ball-milled iron [6,40] and it seems that the particle size of the oxides presented here fits well with their observations. Moreover, the fact that the particle size and distribution of the dispersed oxides not change remarkably during the heat treatments is also in accordance with their observations. The difference could be explained by the fact that the volume fraction of oxides determined from the matrix is clearly below the calculated value from the total oxygen content. This was also discussed in the work of Beliakov et al. [40], where the value of the total volume fraction of oxide was larger than the determined from TEM micrographs, taking into account the oxygen % in mass. In our case, with a 0.39% O, the total V_{fO} would be around 2.1%, far above the experimental values. As was exposed in Fig.3, a large amount of the oxides were located in the bonding surfaces between the former powder particles. These oxides are in some way dragging out the grain growth of the whole structure and though it is difficult to calculate their effect, the final grain size would be more accurate taking them into account.

- Contribution to strength from particles and grain boundaries

Before starting with the analysis of the influence of grain boundaries and small oxide particles on the strength of ball-milled iron, two considerations will be done. The first one is related to the strength values that will be used. Due to the brittle behavior of nanostructured samples in tensile tests, it is interesting to take into consideration the hardness and compression tests carried out at samples with identical heat treatments. This is because these tests are not as sensitive to porosity and bonding defects as tensile test. Therefore, the yield strength calculated from the tensile test, the values of hardness tests and the yield strength obtained from compression tests [16] are displayed together in Table 2. The hardness values have been converted to yield strength by $H_V = 3\sigma_y$. The correlation between the three tests was in general good, especially for samples with low grain size very close to nanocrystalline range and for samples in which the high heat treatment temperature allowed the overall growth of ferrite grains. However, for intermediate stages, at the beginning of the development of the bimodal structure, differences are larger. The main reason for this would be probably some differences in grain size, especially in the volume fraction of coarse grains, since at this stage the repeatability of the microstructures is more difficult.

The second consideration is related to the study of the misorientations between the ferrite grains in the consolidated samples. This study must be made since the exponent associated to the grain size in the calculation of the influence of grain boundaries could be affected [41]. For low angle boundaries (LAB), in which the misorientation is below 15° , the exponent associated is -1, whereas for high angle boundaries (HAB), the exponent would be -0.5. The EBSD studies carried out in the as-consolidated samples at 500°C show that the microstructure consists mainly in high angle boundaries. Low time

milling (below 20 h) is associated with sub-grain structures after rolling consolidation at 700 °C [1]. However, the results obtained here after a warm compaction at 500 °C are closer to those obtained for a powder ball-milled for 20 hours and annealed [42]. In this case, high-angle boundaries were also predominant. Therefore, in the calculation of the strengthening due to grain boundaries the exponent associated to the grain size will be - 0.5.

Now we will try to analyze for the present iron bulk specimens the contribution to the yield strength (σ_y) of friction stress (σ_0), grain boundaries (σ_{gb}) and oxide particles (σ_p). For this, the two approaches mentioned in the introduction are followed. The first one, proposed by Lesuer et al. [11] based in a mixed particle-grain boundary strengthening, will be called mixed-model. The second one, following the studies from Takaki et al. [13,14,43] based mainly in grain boundary strengthening will be called grain boundary model. For both cases, the calculated yield strength (σ_{yC}) is based in the addition of the different factors, as indicated in Eq.(2),

$$\sigma_{yC} = \sigma_0 + \sigma_{gb} + \sigma_p \quad (2)$$

The types of microstructure defined in both models are different from the obtained by cold rolling or typical SPD processes. In the latter cases, the structure is divided by lamellar boundaries oriented in the deformation direction which are HAGB and interconnecting cell dislocation boundaries which are LAGB [21,23]. Moreover, in the SPD microstructures, the volume fraction of LAGB is far greater than the one defined in the exposed models and also in the microstructure of the present ball-milled and consolidated iron in Fig. 4 [38,44]. These differences in the microstructure are the reason why the additional term related to the dislocation strengthening in the cell boundaries is not added to Eq.(2) [45]. The microstructures analyzed in both models are not oriented and have limited presence of LAGB. Particularly, in the mixed-model,

only long-time milled samples were taken into account in order to avoid those structures with high proportion of LAGB. In the same way, for the iron microstructures obtained in the present work and exposed in Fig. 1 seem to be more suitable to follow the same analysis than in both models, including the fact that the percentages of LAGB are small and the absence of dislocation cells in all the consolidated samples.

In the first approach, the *mixed model* based in the work of Lesuer et al. [11] great influence is given to the strengthening produced by oxide particles scattered in the ball-milled iron matrix. According to Lesuer et al, the friction stress (σ_0) has been taken as 28 MPa for an interstitial-free iron. In this calculation of the friction stress, no effect of interstitial or substitutional elements was added, since it was supposed that the particle strengthening was the main contribution to strength and others variables contributed little to the yield strength [11,46].

In Eq. (3) each contribution is developed.

$$\sigma_{yC} = \sigma_0 + k_y \cdot D^{-1/2} + B \cdot [D_s]^{-1/2} \quad (3)$$

For σ_{gb} , the value of D corresponds to the average grain size taking into account fine and coarse grain zones (displayed in Table 1) and the value of $k_y=260 \text{ MPa} \cdot \mu\text{m}^{1/2}$ has been also taken from Lesuer et al. For σ_p , the value of B was taken as $395 \text{ MPa} \cdot \mu\text{m}^{1/2}$ [11] and D_s is the surface to surface interparticle spacing, calculated by Eq. (4) from the average particle diameter (d) and the volume fraction of oxides (Vf_o) calculated from the TEM micrographs for every heat treatment.

$$D_s = (3/2)^{0.5} \cdot \left(\left[\pi / (4Vf_o) \right]^{0.5} - 1 \right) \cdot d \quad (4)$$

In the second approach, the *grain boundary model*, the main influence of the strength in Eq. (3) is related to grain boundary strengthening. For the determination of σ_0 and σ_{gb} the influence on the ferritic matrix of some substitutional and interstitial elements has been taken into account [14,47]. With regard to σ_0 , the friction stress for coarse grained

pure iron free from impurity atoms is estimated at 40-50 MPa since good agreement was found between the values of pure iron and IF iron [14,47]. To this term, the additive effect of the impurity atoms in solid solution must then be added. The influence of chromium in the present samples is supposed to be very small, first because its additive term is low ($\Delta\sigma_0[\text{MPa}] = 7 \times (\text{wt.}\% \text{Cr})$) and secondly by the fact that chromium is combined with oxygen forming oxides all along the microstructure. Nickel has some influence in the solid solution of iron [48], and at 3 wt.% the proposed increment of the friction stress was around 50 MPa. With the Nickel content in the current iron samples the total increase of σ_0 could be estimated at 10 MPa. The last of the substitutional elements studied, phosphorus, has a strong tendency to enhance the friction stress of iron ($\Delta\sigma_0[\text{MPa}] = 250 \times (\text{wt.}\% \text{P})^{1/2}$) [14,47]. However, in the present samples the P content is low and some of it is expected to be segregated in the grain boundaries, therefore the maximum expected contribution of phosphorus to σ_0 would be around 30 MPa. On the other hand, the role of interstitial atoms, mainly oxygen and carbon, need to be discussed. In the case of oxygen, it has a very low solubility in ferrite, and it has been shown that it is combined with chromium and iron forming precipitates all along the microstructure. For these reasons no effect of oxygen is expected in the friction stress of iron samples. Finally, the presence of carbon atoms in solid solution can increase the friction stress in pure iron [43]. However, in several works about milling of iron and steels has been proven that carbon has a strong tendency to segregate at the grain boundaries [5,39,49,50]. Therefore, in the current samples, little carbon concentration is expected to be solved in the ferrite grains counting that the total carbon content is about 300 ppm. A further argument in favor of the low carbon solved in ferrite grains would be the fact that tensile tests have shown no yield point elongation, which is related in low-carbon steels to the presence of interstitial carbon [29,43]. In the

light of the results, the sum of all contributions to the friction stress of pure iron for the samples studied in this work seems to be very close to the value of 100 MPa proposed by Takaki et al. for low-carbon steels and UFG industrial irons [13,14,43]

The value of the Hall-Petch coefficient k_y , according with the dislocation pile-up model proposed by Hall and Petch [7,8] measures the contribution of grain boundaries to strength. In the works of Takaki et al. it has been shown that the Hall-Petch coefficient k_y for iron depends highly on the amount of solute carbon atoms segregated in grain boundaries [13,14]. While for pure iron the value of k_y is estimated around 100-180 MPa· $\mu\text{m}^{1/2}$, it increases with the presence of carbon. When the solute carbon content reaches 60 ppm, k_y is estimated to be in the 550-600 MPa· $\mu\text{m}^{1/2}$ interval, with no further rise with larger carbon content. In the present samples, in which a 0.03 % of carbon has been detected, it seems reasonable to take the most usual value of 600 MPa· $\mu\text{m}^{1/2}$ for k_y . This value is also very close for the value of k_y reported for Armco iron [9]. Finally, for the prediction of the strengthening related to dispersed oxides, a classical expression from Ashby-Orowan [51] will be used:

$$\sigma_p = \frac{Gb}{2\pi \cdot D_s} \ln\left(\frac{d}{2b}\right) \quad (5)$$

Where G is the Shear Modulus for ferrite (80.3 GPa) and b is Burgers vector (0,248 nm). D_s is the surface to surface interparticle spacing, calculated again by Eq. (4) [11]. The values for each contribution and the total strength obtained by both models are displayed in Table 3. Additionally, for direct comparison with experimental results, the average yield strength obtained by hardness, compressive and tensile tests of bulk specimens and the predicted strength by the two models are plotted together in Fig. 7. Along the experimental points a trend line has been drawn for better comparison and its slope has also been included. As in other cases in which the strength of consolidated

and heat treated samples obtained from ball milled iron with oxygen content has been plotted against grain size, the slope is clearly below $-1/2$ [11].

As can be seen in Table 3, in the mixed model developed by Lesuer et al. the weight of particle and grain boundary strengthening (σ_p and σ_{gb} respectively) in the present samples was almost the same in the nanostructured range. As the areas of coarse grains were increased, σ_{gb} declined and particle strengthening was the main responsible of the strength of samples.

Focusing the analysis in the as-consolidated samples and the heat treated samples at low temperatures (650 and 660 °C) in which there were no abnormal grain growth or it was very small, the calculated yield strength is below the experimental values. In the first two points, the difference is around 200 MPa, and it is clearly larger for the samples heat treated at 660 °C. However, in this last case we must consider that this difference is due to the fact that the small coarse grain areas affect significantly the grain size reducing σ_{gb} , but without affecting mechanical properties. In this case, it seems that it would be more accurate to use as a grain size the average value calculated in the nanometric areas, since these zones were clearly predominant. But independently of this last point, strength values by the mixed particle-grain boundary model seem to be slightly underestimated. It seems reasonable that the value chosen for friction stress (σ_0) in Eq. (2) could be changed to 100 MPa instead of 28 MPa and consequently the distance from the experimental values would be reduced, but in fact the trend would be no changed.

We now come to discuss about the samples with bimodal grain size distribution. As has been mentioned, when the heat treatment temperature was increased (675 and 700°C), abnormal grain growth was observed in ferrite whereas little increase was found in the particle size of oxides. Now, although the drop in σ_{gb} , the calculated strength in the

mixed particle-grain boundary model appears to fit better to the experimental values. Moreover, this trend is confirmed in the samples with higher volume fraction of coarse grains (heat treatments at 725 and 775 °C) since in these points the calculated values are very close or even higher than the experimental ones.

With regard with the model based on simple grain boundary strengthening, it is clear that the added contribution of oxide particles to strengthening is very low. In the nanostructured and ultrafine ranges in which no abnormal grain growth was observed or it was very low, the predicted strength is slightly higher or very close to the experimental values. In these ranges, this model seems to be a bit more accurate than the model based in the mixed strengthening. However, as the grain size increases and the volume fraction of large ferrite grains rises, the predicted values by grain boundary strengthening model are gradually getting away from the experimental strengths. When the average grain size is above 1 μm and coarse ferrite grains are easily found, the strength calculated using this model lies clearly below the observed values. Therefore, for the samples with bimodal grain size distribution, the mixed model based on particle-grain boundary strengthening works better than the simple grain boundary strengthening.

From the analysis of the both models, it seems that any of them fits perfectly along the range of grain sizes studied for the strength of the present ball-milled iron and two conclusions could be taken: the first one would be that the mixed model gives lower values than the experimentally observed in the nanocrystalline range and the second one would be that grain boundary strengthening alone cannot predict the strength of the samples when the bimodal grain distribution appears.

Validity of mixed-model in the nanometric range

On this particular subject, one of the plausible explanations would be that the present microstructure of the ball-milled iron is not exactly the same that it was taken in the development of the model [11]. In the proposed model, the microstructure consists in a mixture of two phases: “work-hardened” regions with large oxides (100 nm) in the grain boundaries and “transformed regions” in which the matrix consists on nanometric ferrite grains with ultra fine oxide particles dispersed inside the grains. This “transformed regions” would be the harder one and following the work of Lesuer et al. [11]. They would be obtained after at least 50 hours of milling. In the present case, the iron was milled only for 17 hours, far below the threshold value, and it could have some implications on grain boundary misorientations and the amount of oxide dispersions in the ferrite matrix. In the first point, milling below 50 hours would result in a microstructure in which low angle boundaries would be majority. However, as was discussed before, the microstructure represented in Fig. 4 was clearly dominated by high angle boundaries. In relation to the oxides in the ferrite matrix, maybe in the present powder milled for 17 hours the dispersion was not as effective as it was suggested in the model. The more milling time the more volume fraction of oxides solved in the matrix and this automatically would mean that for the long-time milled powder an increase of the contribution of σ_p would be expected. Finally, another factor to take into account would be the fact that the oxygen content in the present samples is rather small when comparing with the works of Belyakov and coworkers, since there mass percentages of 0.3, 0.8, 2 and 3% were used [1,40,42]. Again, more oxygen content and more milling time, would mean that the volume fraction of oxide particles inside ferrite matrix could be larger and the contribution of σ_p more important.

Another explanation would be that independently of the milling time and even oxygen content, the presence of the “transformed regions” with an important fraction of very fine oxide particles inside the nanometric ferrite grains was very difficult to obtain. These would mean that the oxides would be located preferentially in the grain boundaries no acting as real barriers to dislocation motion. Consequently, the absence of this “transformed regions” would play down the weight of σ_P in the strengthening of nanostructured samples and the predicted strength by the mixed model would be less. In the TEM images of Fig. 2B and 2C, although some particles were inside the matrix, most of them were located in grain boundaries. This fact has been also reported in different works about ball-milled iron [6,15] and there was evidence that after consolidation the interstitial atoms were located preferentially in grain boundaries of nanostructured ferrite grains [17,39], and sometimes no oxide particles were observed inside ferrite grains even in a long time milled iron [5]. Therefore, at least for ball-milled iron with low-oxygen content, similar to the one presented here or in the work of Srinivasarao et al [5], the strength related to oxide particles in the nanometric range could be less than predicted by Lesuer et al [11] due to the high concentration of oxide particles along the grain boundaries instead on inside the grains. In this context, it could be possible that the coefficients k_y for grain boundary strengthening σ_{gb} and B for particle strengthening σ_P in the mixed model would need a revision. To finish with this reasoning, it is interesting to note that at least in the nanometric range the use of the typical Hall-Petch model has a better fit even when no oxide contribution was added. This could mean that in ball-milled iron with low oxygen content and in the case that the oxide particles would be located preferentially in the grain boundaries, the strengthening could be related almost exclusively to the simple grain boundary strengthening with values of k_y around 550-600 MPa $\mu\text{m}^{1/2}$.

Unfortunately, here it is necessary to note the intrinsic difficulty in the measuring of oxides in samples with ferritic grain size on the border of the nanometric range. Then, it is reasonable to think that a moderate number of oxide particles with a few nanometers could have been not detected and that some of the locations of oxides were wrong due to overlapping effects. These uncertainties could lead to underestimate the real value of σ_p to a certain extent and some work has to be done to clarify the validity of the mixed particle-grain boundary strengthening model in the nanostructured range.

Failure of simple grain boundary strengthening in samples with bimodal grain size distribution.

We will discuss here the second question, the fact that the simple grain boundary strengthening clearly failed when the microstructure of the consolidated ball-milled iron was formed by the bimodal grain size distribution. Moreover, it is interesting to note that the distance between the observed and predicted values gradually increased as the percentage of coarse grain area was growing. It seems clear then that some strengthening apart from the one related to grain boundaries is acting. In this case, the strengthening from oxide particles seems to be the more plausible explanation and actually the mixed model is better adapted to the observed strength.

The mixed model works better since as the coarse grains zones are formed, the lack of mobility of oxides in comparison with grain boundaries causes that the oxides located in the ancient grain boundaries keep now inside the new coarse grains. Consequently, there is an increase of the volume fraction of oxides inside the grains. The presence of a dispersion of fine oxides in the ultrafine and coarse grains of ferrite was clearly showed in Fig. 2D in which the TEM image of a coarse grain was exposed showing a well defined network of little oxides. Moreover, the existence of a well defined network of

oxides inside ferrite has been showed before in recrystallized samples when the average grain size exceeds the low-ultrafine range [1,5,42].

Additionally, the rate of growth of the oxides with heat treatment temperature was very low, as reported in Table 1, and it is worth mentioning that even no growth has been reported in other studies [5,40]. Thus, when σ_P is calculated the values are high comparing with σ_{gb} . Therefore, the loss of strength due to grain growth is clearly compensated by particle strengthening

In a careful analysis of the mixed model fitting to the experimental values, it is evident that as the percentage of coarse grain areas increases, the predicted values are getting closer to the real ones. However, for the samples heat treated at 775 °C, the calculated strength is well above the experimental value. In the case of the heat treated samples at 725 °C, the predicted strength is close to the corresponding experimental value but we think that this value is affected by the low volume fraction ($V_{fo}=0.15\%$) of oxides calculated from TEM images. As was mentioned before, it is reasonable to think that V_{fo} in all the heat treated samples should be the same, since all the consolidated samples have been obtained from the same powder. If the average value for V_{fo} (0.34%) were introduced into the calculations for the 725 °C samples, the strength would also be clearly above the experimental strength. Therefore, the mixed model is capable to explain the loss of accuracy of the simple grain boundary strengthening, but it seems to overestimate the strength.

- Strength and ductility in tensile test.

Once the influence of the ferrite grain size and the oxide particles on the strength of the consolidated ball-milled iron has been discussed, we can examine now the results from tensile test. For the as-consolidated state, the very low tensile strength found can be

attributed to a weak bonding between former powder particles. The aspect of the fracture in Fig. 6A in which the powder particles are well-defined confirms this fact. In the samples heat treated at 650 and 660°C, the bonding between particles has been clearly improved, since the strengths obtained are very similar to the yield strength calculated from hardness values. However, the samples in both states showed no ductility and the fracture examination gives no support to a particle debonding as in as-consolidated state. In this case in which the treatment temperature is well below the transition temperature A_{c1} , blocking of dislocations by carbon and oxygen atoms has been pointed out as explanation of the reduced plastic deformation [52]. However, the fact that the as-consolidated samples, in which this effect should be larger than in the heat treated samples, showed up to a 32% plastic strain during compression tests [16] takes strength to this argument. On the other side, some studies in Armco Iron deformed by HPT [23] showed that the fracture toughness of ultrafine grained iron obtained from bulk materials can be quite low as $15 \text{ MPa}\cdot\text{m}^{1/2}$. Then, can be expected that in the case of a ball-milled powder consolidated at no so high temperatures, the fracture toughness could also be low enough to cause brittle fracture in the presence of small artifacts, especially when high strengths are achieved.

In the case of the samples heat treated at 675 °C, the yield strength obtained by tensile tests is slightly lower than the expected from the hardness measurements. This can be due to small variations on the volume fraction of coarse grains between different samples which would have a marked influence on strength. The beginning of the growth of coarse grains is rather difficult to control and some differences can be expected at low temperatures. However, an increase in ductility with a clear presence of a uniform strain is observed. This combination of strength and reasonable ductility can be extended to samples heat treated at 700 and 725 °C. In these cases, no discussion has

been addressed to the post-necking elongation, since it could be affected by the thickness and gauge length of the tensile samples [53]. In the samples heat treated between 675 and 725 °C, the presence of relatively long periods of strain hardening between 4 and 10% agrees well with studies on Fe obtained by SPS of MM powder [5]. However, samples obtained from SPD processes [18,23,29] show a more reduced uniform elongation than MM samples in which bimodal grain size distribution has been observed, independently the gauge length used, even as small as 1 mm [24]. This difference, as exposed before [5], can be related to the bimodal grain size distribution obtained in MM processes. During heat treatments, and depending on the temperature, a volume fraction of coarse grains is formed. In these grains, dislocations can be generated and stored making uniform plastic deformation easier, whereas the remaining areas with nanocrystalline or ultrafine grains would be involved in giving strength to the whole.

Comparing the behavior of the present Fe samples with the tensile curves of the bulk iron made by SPS [5], two differences have been detected. The first one is the absence of Lüders band formation on the samples and the absence of yield point elongation phenomenon. The second one is the lower UTS values obtained in the present work although the percentage of volume fraction of coarse grains is similar than the reported in the bulk iron samples in the work by Srinivasarao et al [5]. In the first case, no peak yield stress was detected during the tests and careful observation of the tested samples gave no signals of Lüders or shear bands, which has been detected in tensile tests of ultrafine-grained Fe and low-carbon steels [18,54]. In the present case, the presence of C solved in nanocrystalline ferrite in tensile samples (0.03 wt%) is enough small and this could led to Lüders band formation. However, it must be pointed out that the Cr and O content in the present samples is nearly twice than in [5]. As has been exposed

before, the fine dispersion of nanometric oxides formed by Fe and Cr (Fig. 2D) are disposed inside the large ferrite grains acting as obstacles to dislocation motion. This situation would promote dislocation activity and strain hardening and, consequently, to increase the storing of dislocations.

Furthermore, the volume fraction of coarse grains in the present results seems to be slightly smaller than in [5], which means a larger content of the harder areas of ultrafine or nanocrystalline ferrite. In this sense, it must be pointed out that the presence of hard second phases is related to a diminution of Lüders band formation and an increase of work-hardening in tensile samples of UFG iron [54]. Therefore, it is possible that the combination of the two factors could restrict the free way of dislocations in the coarse grains and be the responsible of the absence of Lüders band formation.

To explain the lower values in the UTS of the present bulk iron samples with bimodal grain size distribution, it is interesting to recall the role of the areas with nanocrystalline or ultrafine grains. These areas act as a hard phase giving strength to the whole. This effect, according to grain boundary strengthening (σ_{gb}) in Eq. (2) is larger as the grain size decreases. If we look closely to the most representative points, the average grain size calculated for these areas is strong dependent with temperature. For the 675 °C samples, the hard phase has an average grain size of 160 nm, and for 700 °C, the values rises up to 310 nm. According to the data reported in the work of Srinivasarao et al., in the bimodal samples with similar percentage of coarse grain areas the mean grain size in the nanocrystalline areas was below 100 nm. Consequently, the present samples have a larger grain size and a smaller grain boundary strengthening, which means that lower strength values would be expected for the present samples comparing with the bulk iron made by SPS from milled iron powder [5].

Conclusions.

- The microstructure of iron samples obtained by consolidation of the initial ball-milled powders with 0.39 wt.% O at low heat treating temperatures (from 500 °C to 660 °C) was formed by ferrite with a grain size near the nanostructured range with fine oxides mainly located in grain boundaries. These bulk specimens rendered high tensile strength (1920 MPa) without ductility.
- The strength of these iron samples was not exactly predicted by mixed models in which the strength produced by particles plays an important role together with grain boundary strengthening. This may well be because the oxides were located in the grain boundary without giving additional strengthening instead of being inside the nanometric ferrite.
- The main reason for the low dispersion of oxides in ferrite was attributed to the low milling time and the low oxygen content. In this situation, models based in simple grain boundary strengthening for industrial irons rendered better results.
- In samples treated at higher temperatures (675 °C and above), abnormal grain growth produced a bimodal grain size distribution, in which zones with ultrafine grain size together with coarse grains containing a fine dispersion of oxides inside were observed. In these samples, the addition of strengthening from particles to the simple grain boundary strengthening is essential for a good prediction of strength.
- In the case of the samples heat treated at 675 °C the tensile results showed a drop of the strength to 1244 MPa but with 4% uniform elongation, and 1028 MPa with 9% total elongation when the temperature increased to 700 °C. The large uniform elongation found in these bimodal grained samples was probably due to the presence of

the small oxides formed by Cr and Fe with particle size around 20 nm and distributed inside large ferrite grains. These oxides provided a large number of defects promoting dislocation activity that stabilized plastic deformation and prevented the presence of shear bands or yield point elongation.

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LIST OF CAPTIONS.

Figure 1. Microstructures of iron samples with different heat treatment: TEM bright field images: A) as consolidated (SAD Diameter:1 μm); B) heat treated at 650 °C (SAD Diameter:1 μm); C) 660°C (SAD Diameter:1 μm); D) 675 °C (SAD Diameter:2 μm) and E) 700 °C (SAD Diameter:2 μm). SEM image: F) 775 °C.

Figure 2. Distribution of oxides. A) As-consolidated samples, SAD showing diffraction rings of Fe and Fe/Cr oxides. B) TEM dark-field/bright field image showing the distribution of small oxides in as-consolidated samples. C) TEM bright field image of a samples heat treated at 650 °C. D) TEM dark-field image that shows part of the oxide distribution in a coarse ferrite grain of samples heat treated at 725°C.

Figure 3. SEM and EDS analysis of a sample consolidated at 500 °C and heat treated at 725 °C in which a joint between former powder particles can be observed.

Figure 4. EBSD image of a consolidated specimen at 500 °C with no subsequent heat treatment. Black lines represents grain boundaries with misorientations large than 15°. White line represents subgrain boundaries with misorientation below 15°.

Figure 5. Tensile stress-strain curves for all the consolidated iron specimens.

Figure 6. SEM micrographs of the fracture surfaces for the tensile tested samples: A) as consolidated; B) heat treated at 660 °C; C) 725°C and D) 775 °C.

Figure 7. Comparison between the experimental values of yield strength (σ_y) with the values predicted (σ_{yC}) by the simple grain boundary strengthening model and by the mixed particle-grain boundary strengthening model.

Table 1

Consolidation procedure, grain size of ultrafine and coarse zones, volume fraction of coarse grain zones (Vf_{cg}) together with the total average grain size D . Particle size and volume fraction (Vf_o) of the oxides present in the studied samples. The final grain size (D_{Z-S}) calculated by the Zener-smith equation is also included.

Consolidation procedure	Grain size (nm)		Vf_{cg} (%)	Average grain Size D (nm)	oxides		D_{Z-S} (μm)
	fine	coarse			Particle size (nm)	Vf_o (%)	
HC 500°C	96	-	-	96	15 ± 10	0.48	4.1
HC 500°C + HT 650°C	115	-	-	115	16 ± 10	0.40	5.3
HC 500°C + HT 660°C	130	2200	4	210	25 ± 20	0.34	9.8
HC 500°C + HT 675°C	160	2750	7	340	20 ± 11	0.32	8.3
HC 500°C + HT 700°C	310	2000	21	660	23 ± 13	0.28	10.9
HC 500°C + HT 725°C	400	2900	47	1580	25 ± 14	0.15	22.2
HC 500°C + HT 775°C	700	4150	100	2000	25 ± 16	0.42	7.9

Table 2

Influence of heat treatment temperature on strength of consolidated samples. Hardness and yield strength obtained experimentally from hardness measurements σ_y (H), compression tests σ_y (C) from [16], and tensile tests σ_y (T). Finally, the average yield strength σ_y obtained from all the experimental values.

Consolidation procedure	$HV_{0.2}$ (GPa)	σ_y (H) (MPa)	σ_y (C) (MPa)	σ_y (T) (MPa)	σ_y AVERAGE (MPa)
HC 500°C	5.9 ± 0.2	1960	1850	-	1905
HC 500°C + HT 650°C	5.6 ± 0.3	1860		1850	1855
HC 500°C + HT 660°C	5.0 ± 0.3	1660		1700	1680
HC 500°C + HT 675°C	4.0 ± 0.4	1330		1170	1250
HC 500°C + HT 700°C	3.0 ± 0.2	1000	1100	920	960
HC 500°C + HT 725°C	2.5 ± 0.2	833	750	800	775
HC 500°C + HT 775°C	2.1 ± 0.1	700	650	720	685

Table 3.

Comparison of the experimental values of yield strength (σ_y) with the predicted values (σ_{yc}) from the mixed particle-grain boundary strengthening model and the simple grain boundary strengthening model. σ_{gb} : strength from grain boundaries and σ_p : strength from particles.

Consolidation procedure	σ_y AVERAGE (MPa)	Mixed model Particle-grain boundary			Simple model Grain boundary		
		σ_{gb} (MPa)	σ_p (MPa)	σ_{yc} (MPa)	σ_{gb} (MPa)	σ_p (MPa)	σ_{yc} (MPa)
HC 500°C	1905	860	860	1720	2010	48	2058
HC 500°C + HT 650°C	1855	795	785	1580	1869	43	1912
HC 500°C + HT 660°C	1680	590	600	1190	1401	29	1430
HC 500°C + HT 675°C	1250	470	660	1130	1127	33	1160
HC 500°C + HT 700°C	960	350	590	940	836	27	863
HC 500°C + HT 725°C	775	235	485	720	578	19	597
HC 500°C + HT 775°C	685	210	630	840	524	32	556

Fig.1. Microstructures of iron samples with different heat treatment: TEM bright field images: A) as consolidated (SAD Diameter:1 μm); B) heat treated at 650 $^{\circ}\text{C}$ (SAD Diameter:1 μm); C) 660 $^{\circ}\text{C}$ (SAD Diameter:2 μm); D) 675 $^{\circ}\text{C}$ (SAD Diameter:2 μm) and E) 700 $^{\circ}\text{C}$ (SAD Diameter:2 μm). SEM image: F) 775 $^{\circ}\text{C}$.

Fig. 2. Distribution of oxides. A) As-consolidated samples, SAD showing diffraction rings of Fe and Fe/Cr oxides. B) TEM dark-field/bright field image showing the distribution of small oxides in as-consolidated samples. C) TEM bright field image of a samples heat treated at 650 °C. D) TEM dark-field image that shows part of the oxide distribution in a coarse ferrite grain of samples heat treated at 725°C.

Fig. 3. SEM and EDS analysis of a sample consolidated at 500 °C and heat treated at 725 °C in which a joint between former powder particles can be observed.

Fig.4. EBSD image of a consolidated specimen at 500 °C with no subsequent heat treatment. Black lines represents grain boundaries with misorientations large than 15°.

White line represents subgrain boundaries with misorientation below 15°.

Fig. 5. Tensile stress-strain curves for all the consolidated iron specimens.

Fig.6 . SEM micrographs of the fracture surfaces for the tensile tested samples: A) as consolidated; B) heat treated at 660 °C; C) 725°C and D) 775 °C.

Fig.7. Comparison between the experimental values of yield strength (σ_y) with the values predicted (σ_{yC}) by the simple grain boundary strengthening model and by the mixed particle-grain boundary strengthening model.