Nanostructured bainitic steel obtained by powder metallurgy approach: structure, transformation kinetics and mechanical properties

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A PM approach is investigated in the context of extremely fine low temperature bainitic steels with a reasonable combination of ultimate tensile strength and uniform elongation. The strategy consists of three steps. First, ball milling is used for mechanical alloying and to create a large density of interfaces prior to sintering. In the second step, spark plasma sintering is used as a rapid consolidation process to retain a very fine and homogeneous structure after sintering. The isothermal heat treatment which leads to bainite can then be done at a low austenitisation temperature (860°C) for a few minutes, leading to a small initial austenite grain size. A fine grain size promotes the rapid transformation of the austenite into bainite. The characteristics of a nanostructured Fe–Ni–C bainitic steel obtained after mechanical alloying and nanostructuring of the powder, spark plasma sintering and final heat treatment are reported.

Bainitic and super-bainitic steels are representatives of a wide class of steels in which interesting mechanical properties are obtained from relatively simple and cheap heat treatments. These treatments are intended to achieve a particular mixture of two phases in which very fine ferrite platelets alternate with thin films of retained austenite. The scale of this structure implies a very large density of interfaces, making it very strong even though there are no carbide particles present. Furthermore, the onset of plastic instability can be delayed by the presence of austenite, which undergoes martensitic transformation during plastic deformation.

The cheap way of introducting austenite in the microstructure is by preventing the precipitation of iron carbides during bainitic transformation. The mechanism can be simply explained as follows: the carbon that is partitioned from bainitic ferrite then stabilises the austenite. Silicon and aluminium are commonly used to achieve this by affecting the chemical driving force for the precipitation of cementite from austenite.[1] The concept of a mixture of bainitic ferrite and retained austenite generated at exceptionally low homologous temperatures was recently developed, and this leads to platelets of bainitic ferrite (20–40 nm in thickness) embedded in a matrix of carbon enriched austenite.[2–4] This particular structure, which macroscopically is isotropic, is strong (~2 GPa) and tough (30–45 MPa $m^{0.5}$). However, the isothermal heat treatment required to generate this structure is conducted at around 200°C, where kinetics are slow and it can typically take 10 days to reach the desired degree of transformation. To reduce significantly the time required by accelerating the transformation kinetics, expensive elements such as cobalt or aluminium must be added to the alloy to enhance the free energy change accompanying transformation. However, recent experimental evidence has reinforced the fact that the martensite start temperature and the transformation rate of bainite are both correlated with parent austenite grain size.[5,6] Sintering is a mechanism by which fine austenite grains can be ensured and hence might represent a method of accelerating the super-bainite transformation.

In the work presented below, a nanostructured bainitic steel was obtained by a combination of three steps: mechanical alloying and nanostructuring, spark plasma sintering and heat treatment. The goal was to obtain a fine and stable microstructure before heat treatment in order to refine the austenite grain size due to austenitisation and hence accelerate the subsequent bainitic transformation.

Experimental procedure

The Fe–C–Si–Ni–Cr–Mo powder was obtained by mechanical alloying of elementary powders (Ni), master alloy powders (SiC as a source of carbon and silicon and FeSi powder as a source of Si), and a blend of pre-alloyed water atomised powders (CrL from Höganäs) according to the chemical composition reported in Table 1. The alloy was designed on the basis of the theory[4,7] that predicts the highest temperatures at which bainite (B_s) and martensite (M_s) can form in a steel of a given composition. These two temperatures constitute the upper and lower limits at which the austempering heat treatment can be done. However, more refined microstructures are obtained by reducing the transformation temperature but avoiding the martensitic transformation.[8]

Table 1 Chemical composition of experimental steel/wt-%

Fe	C	Si	Cr	Mo	Ni
bal.	0·73	1·82	1·47	0·23	4·12

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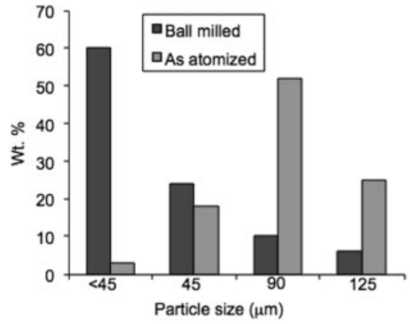


1 Sieve analysis of powder before and after ball milling

The powder was milled for 6 h in a planetary ball mill (Fritch Pulverisette 6). During milling an on/off sequence was used to prevent the system overheating. The 0·73 wt-% of carbon added as SiC hinders cold welding between particles and powder adhesion to the jar. The ball milling was carried out in an AISI D2 steel jar having a volume of 500 mL using 100Cr6 steel balls with a diameter of 10 mm. Powder batches of 100 g were processed with a balls to powder ratio of 10 at a speed of 350 rev $\min^{-1}$. Before milling, the jar was sealed and kept under a low vacuum atmosphere.

After milling the powder was loaded into a graphite die and consolidated in a spark plasma sintering (SPS) apparatus. SPS is a pressure assisted high temperature sintering method wherein a pressing die and the sample (also conductive in this case) are heated by a pulsed dc current. The heating rate was 100 K $\min^{-1}$ up to 600°C. Heating from 600 to 950°C was performed at 50 K $\min^{-1}$. A reduced soaking time of 1 min was used. A maximum pressure of 60 MPa was applied above 600°C as indicated in previous studies.[9] The pressure was removed during cooling, whereas the vacuum was maintained at 2 Pa for the entire sintering process. Heat treatments were done under vacuum below 650°C; above this temperature a back-fill atmosphere of 100 mbar Ar–H_2 (90/10 vol.-%) was adopted. Forced cooling to the austempering temperature (and after that to room temperature) was carried out at 8 bar absolute pressure of nitrogen.

Structural investigations were performed on both as sintered and austempered samples. After grinding and polishing, the surface of each sample was etched with nital (5%) or nital–picral.

Scanning electron microscopy (SEM) and X-ray diffraction were used to characterise the samples after austempering. SEM investigations were also performed on fracture surfaces after tensile testing. Tensile testpieces were produced directly by sintering dog-bone shaped specimens. The gauge length over which elongation was measured was 12·5 mm and the cross-section of the sample was 4·5 × 5 mm.

Results and discussion

Energetic ball milling of the as atomised and blended powder was effective in mechanical alloying and nano-structuring of the final powder. The particle size distribution of the powders before and after milling is shown in Fig. 1. After ball milling the powder is strongly reduced in size, with most particles below 45 μm. However, the presence of a significant fraction of powder above 90 μm suggests that the coarser powder did not complete the refinement process (high angle grain boundary formation and thus fragmentation).

XRD analysis confirms a ferritic microstructure, and no peaks characteristic of Ni or SiC were detected, indicating that the alloying elements (nickel, silicon and carbon) are dissolved in the matrix. The average isotropic crystallite size was estimated as ∼35 nm. The oxygen content in the as atomised and blended powder was estimated as 0·14–0·18 wt-% whereas a level of 0·36 wt-% was measured in the milled powder. The significant increase of oxygen content can be attributed to the very fine particle size of the nickel (<10 μm) and SiC powders (50 nm) which tend to adsorb and trap a significant amount of air and humidity on the particle surface. The ball milling process itself also tends to refine the size of the particles, increasing significantly the total amount of surface available for oxygen absorption. When the powder is exposed to the atmosphere a passivation process occurs.

The bulk samples showed a good degree of densification after SPS consolidation of the ball milled Fe–C–Ni steel, reaching a relative density of 98·9%. It is worth noting that in this very rapid sintering process (13 min heating to 950°C followed by 1 min soaking) reduction of oxides by a standard carbon/oxide reaction would not be expected to take place. Even at higher soaking temperatures (or during high temperature vacuum heat treatment) the oxide reduction takes place only in the presence of open porosity in which the reduction products can be eliminated.

A typical microstructure after SPS at 950°C is shown in Fig. 2. The sample is not fully martensitic, with 7 vol.-% of residual austenite (white regions). Some micrometre sized pores are visible (arrows) as well as homogeneously distributed fine oxides.

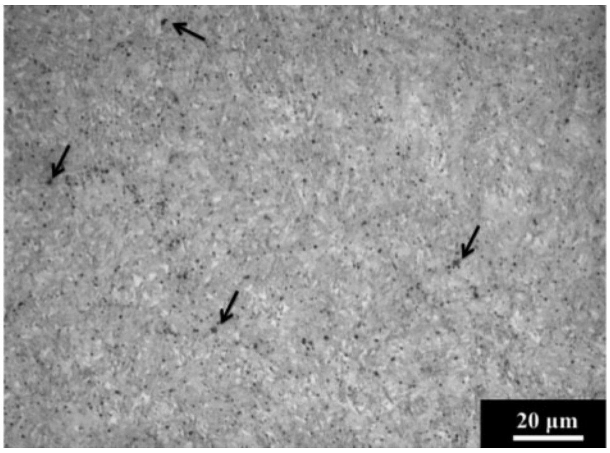
Before austenitisation and subsequent austempering the samples were heated to 1250°C for 10 min then quenched at room temperature to promote precipitation and growth of the oxides.

A subsequent austenitisation at 860°C for 10 min was performed, followed by austempering at 240, 260 or 280°C. Dilatometric investigations of the M_s temperature (after austenitisation at 860°C) have shown lower values (125°C) than predicted considering the chemical composition alone (197°C). Dilatometric curves for the bainitic transformation at the three temperatures and optical micrographs are displayed in Fig. 3.

As extensively reported in the literature, lower transformation temperatures produce a finer microstructure. Micro-hardness as a function of isothermal transformation temperature is shown in Fig. 3*e*.

However, the time required to initiate the transformation is affected by several factors. Chemical composition can change dramatically the time required to achieve the desired microstructure.[4] Other important factors are the transformation temperature and the initial austenite grain size.[4,5] Here, with an alloy with 0·73 wt-%C, the time required to initiate the transformation at 240°C was 10^4 s: dramatically smaller than that for steel of similar composition produced by conventional processes at the same temperature. As mentioned above, both M_s and the bainitic transformation kinetics depend on the initial austenite grain size. Here, the nanostructuring process ensured, even after heat treatment, that a fine austenite structure remained to reduce the time to initiate transformation.

Estimates of the quantities of retained austenite after austempering, obtained by X-ray diffraction analysis, are displayed in Fig. 4*a*. The increased austenite volume fractions measured for the samples heat treated at higher temperatures are attributed to the fact that less bainite can form at higher temperatures (Fig. 3*a*). Moreover, due to its high carbon content, the residual



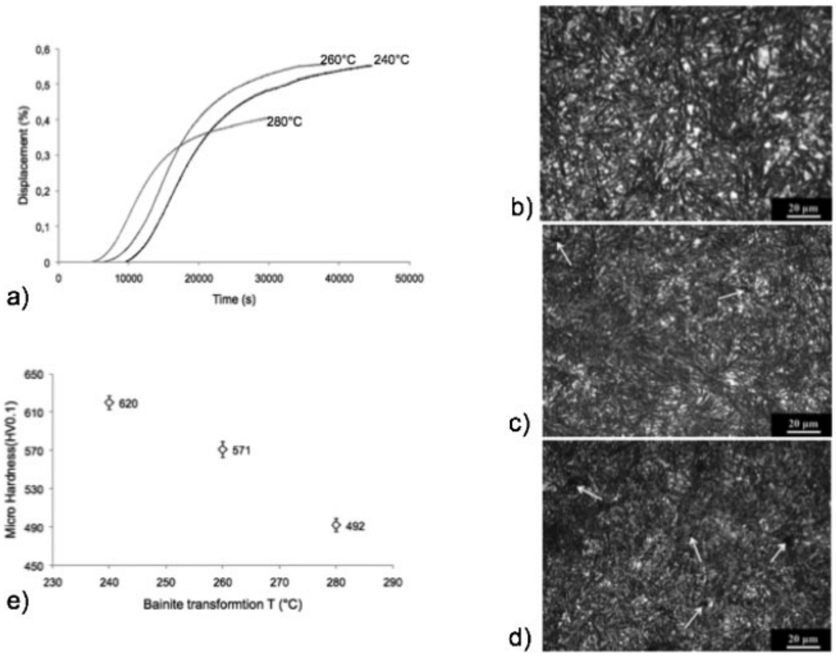
2 Optical micrograph of microstructure after SPS at 950°C for 1 min (arrows indicate micropores)

austenite cannot transform to martensite on cooling.

Two different morphologies of the retained austenite are visible in Fig. 4*b* and *c* (from the sample transformed at 280°C): very thin filaments of austenite (film austenite) between bainite lamellae, and islands ~2 μm in size (blocky austenite). A significant number of spherical oxides particles are also visible between and within the platelets. These oxides, which were formed during SPS consolidation and also during subsequent heat treatment at 1250°C, are thought to play a key rule by keeping the grain size stable by Zener grain boundary pinning.

Without the oxide particles the grains would undergo rapid grain growth during the heating phase of SPS or during heat treatment. In this sense, the oxide particles maintain a fine grained bulk matrix even above 1250°C. However, a large quantity of non-metallic oxides (mainly silicon and/or complex silicon oxides) is not desirable, because the material must have a good combination of strength and toughness and because the silicon is required in the matrix to prevent precipitation of cementite.

Fracture surfaces from the tensile test on the specimen transformed isothermally at 280°C are shown in Fig. 5. The fracture morphology is mainly ductile with some cleavage. Failure is due to micro-porosity (arrow 1) and de-cohesion at particles that were not sufficiently refined during milling (arrow 2). Sintering at a relatively low temperature (950°C) for a very short soaking time (1 min) resulted in a material that is not actually fully compacted. It is clear that during ball milling the powder must be better refined and that soaking time (temperature) during sintering must be increased to achieve full density. The tensile behaviour (Fig. 5*d*) is characterised by a yield stress of about 1210 MPa combined with a uniform plastic strain (4%) to failure at 1613 MPa.



3 *a* Dilatometer traces versus time during isothermal heat treatment at 240, 260 and 280°C; optical micrographs of bainitic microstructure obtained following transformation at *b* 280°C, *c* 260°C and *d* 240°C (white arrows indicate pores); *e* micro-hardness as function of transformation temperature

Conclusions

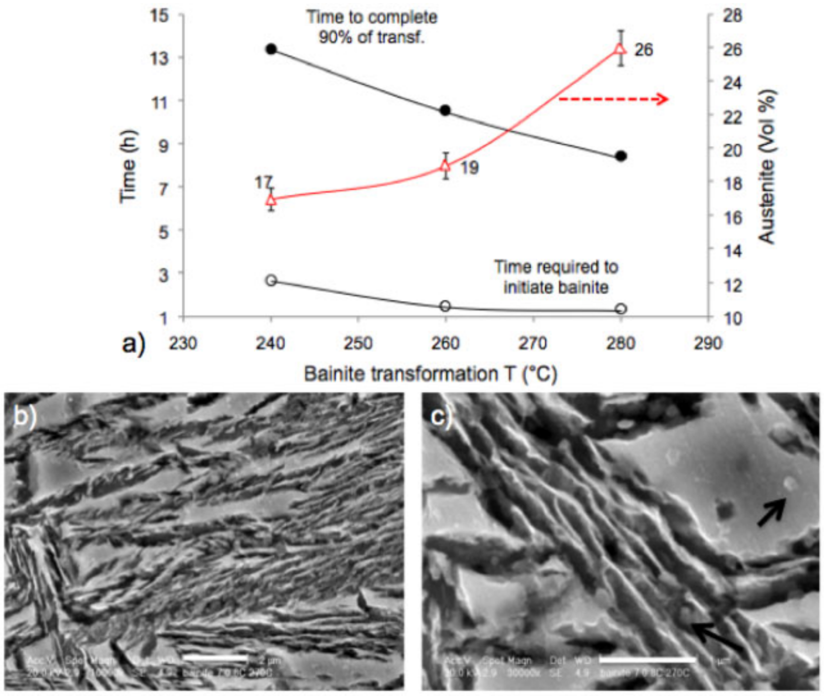
Ball milling is an effective method to produce a nanostructured alloyed steel powder. The high oxygen content (0·36 wt-%) can be mainly attributed to the very fine particle size of the Ni (4–10 μm) and SiC (50 nm) powders that tend to adsorb and trap a significant amount of air and humidity that cannot be removed with a conventional low vacuum process.

Spark plasma sintering is a powerful technology to sinter hard and nanostructured metal powder in a few minutes, while preserving a fine microstructure. However the sintering conditions must be optimised to obtain the fully dense material that is a prerequisite for high strength steel. This goal can be reached by increasing the sintering temperature to 1000°C and the soaking time to 3 min.

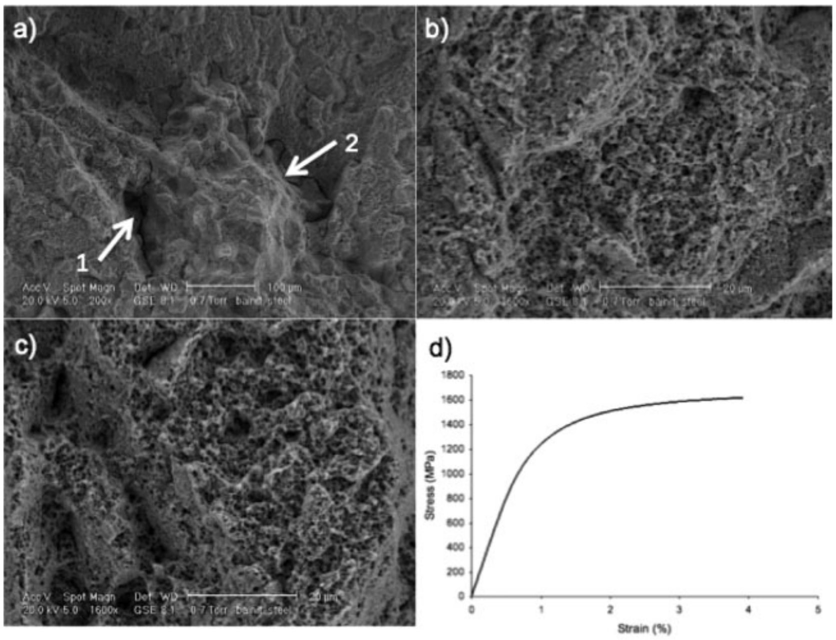
Austenitisation and austempering heat treatments performed on the as sintered specimens at 240, 260 and 280°C showed accelerated initiation of the bainite transformation (<3 h at 240°C). This result confirms that the PM approach can effectively accelerate the bainite transformation by reducing the starting austenite grain size (the transformation time predicted for conventional steels of similar compositions at the same temperature is ten times greater).

The sintered and heat treated microstructure shows thin bainite plates with films of retained austenite (a few nanometres in thickness) between them. A second, blocky austenite morphology is also present. Fine oxide particles are homogeneously dispersed in the matrix.

In tensile tests, the steel demonstrated a proof stress of 1210 MPa, UTS of 1613 MPa and elongation of 4%. The fracture morphology was mainly ductile, but reduced plasticity can be correlated with critical defects due to the presence of micro-pores in proximity to



4 *a* Volume fraction of retained austenite as function of isothermal transformation temperature and time to initiate and to complete 90% transformation as a function of temperature; *b*,*c* SEM micrographs (markers represent 2 and 1 μm respectively) of sample isothermal transformed at 280°C in which film and blocky austenite are clearly visible (arrows indicate oxide particles)



5 *a–c* fracture surfaces and *d* stress–strain curve of steel sintered at 950°C austempering at 280°C

large particles that had not been sufficiently refined during milling.

These results are intended as just a starting point to obtaining full density nanostructured bainitic steel by a PM approach.

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