Abstract

Fe-1.4C-0.65Si-0.85Mo ultrahigh carbon steel was produced from Höganäs Astaloy 85 Mo HP base iron, fine graphite and silicon carbide powders mixed with polypropylene glycol. Liquid phase sintering in 10%H₂-90%N₂ at 1300°C resulted in density increase from ~6.8 g·cm⁻³ to ~7.7 g·cm⁻³ and a microstructure comprising fine pearlite and grain boundary cementite networks. Austenitisation, isothermal quench/autotemper at M₁₀₀% temperature followed by cooling to room temperature produced a crack-free martensitic microstructure. To obtain ferrite plus fine spheroidised carbides, the material was annealed for 3 hours at 750°C. To attain full density and well-distributed submicron carbides, specimens were warm forged at 700-750°C. Microstructures and hardness values are presented for all stages of processing.

Keywords: spheroidised ultrahigh carbon steel, densification, liquid phase sintering, forging

INTRODUCTION

Powder Metallurgy ultrahigh carbon steels, UHCSs, have been investigated especially by Sherby et al. [1-4] and latterly by Abosbaia et al [5-7], utilising liquid phase sintering. Numerous technical problems such as graphite segregation during mixing, porosity, and microcracking during quenching had to be solved and their detailed solutions are reported elsewhere [6, 8]. Graphite was bound to the surfaces of the base powder by a judicious use of polypropylene glycol 50% diluted with ethanol. In order to optimise the sintering cycle, ThermoCalc modelling (Fig.1) was employed [5-7]. The heating profile was modified to allow early dissolution of carbon to ensure escape of porosity-producing gases as they form during heating. By controlled cooling from the quenching temperature (micro)cracking was avoided. Annealing at 750°C produced a spheroidised plus ferrite microstructure. To attain full densification and further grain refinement (aiming at a structure amenable to superplastic forming) warm forging was used. This paper deals with the detailed microstructural features and hardness resulting from each step of the processing cycle.

EXPERIMENTAL PROCEDURES

Höganäs Astaloy Mo85HP was used as the base iron powder. 1.45 wt.% carbon was introduced as fine Grafitwerk UF4 graphite (of 99.5% purity) and silicon was added as fine <9 µm silicon carbide powder. Microstructural observations of initially sintered specimens, using liquid paraffin as a binder, showed excessive porosity, Fig.2. As the evolving gas must be formed either from reduction of oxides or from adsorbed water
vapour, via the water-gas reaction: \( \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \), from \( \sim 500^\circ\text{C} \), therefore graphite was dried by heating to \( 120^\circ\text{C} \) overnight in a vacuum oven.

Turbula powder mixing was performed as follows: the base and silicon carbide powders were dry mixed for 20 minutes. Then 0.5 cc of polypropylene glycol, diluted to 50% by methanol, was carefully added to 100 g of powder and mixing resumed for 20 minutes - in order to coat the metal powders with polypropylene glycol. The mixing was then stopped, graphite powder added and mixing re-started in order to 'glue' the graphite to the base powder particles. Metallographic specimens were die compacted, generally at 600 MPa. Green and sintered densities were measured using physical calculation for \( \rho \): green densities were \( \sim 6.8 \, \text{g.cm}^{-3} \).

Sintering was carried out in nearly full semi-closed steel containers [9] pushed into a mullite tube furnace, with pure (99.9%) alumina paper placed between the bottom of the container and the samples - to ensure no diffusion of carbon between sample and container. Each container had a labyrinth seal, but no additional oxygen getter material. The furnace atmosphere was nitrogen plus 10% hydrogen, with a gas flow of \( \sim 500 \, \text{cm}^3 \, \text{min}^{-1} \) and an inlet dew point no worse than \(-60^\circ\text{C}\).

Noting that self diffusion of \( \text{Fe} \) in \( \text{Fe} \) is approximately 100 times greater in the alpha than in the gamma phase and that time is also a strong variable, the heating profile was chosen so as to minimise time spent in the alpha temperature range. To determine best heating profile four sets of experiments were performed with first hold at 600, 730, 750, 900°C for 20 minutes before increasing the temperature to \( 1100^\circ\text{C} \) and holding for 2 hours in each case. The results can be seen in Figs.3a-d. The chosen profile set the heating rate at \( 20^\circ\text{C}/\text{min} \) and a \( 900^\circ\text{C} \) first hold of 10 minutes. This ensured that graphite could begin to go into solution in the austenite and leave pores for escape of any gases produced, simultaneously with minimisation of \( \text{CO}_2/\text{CO} \) production and any alpha phase sintering. The temperature chosen to ensure carbon and silicon diffusion and homogenisation was \( 1100^\circ\text{C} \), with a hold of 2 hours. Finally at \( 5^\circ\text{C}/\text{minute} \) temperature was raised for sintering at \( 1300^\circ\text{C} \) for 30 minutes, followed by slow-cooling, Fig.4. At this temperature, ThermoCalc prediction, Fig.1, was for nearly 20% liquid phase [6].

A simple quenching heat treatment to produce a martensite plus retained austenite structure resulted in microcracking [5,6,8], where large volume change and hence build up of internal stress had occurred, Fig.5a. An isothermal quench into a fan assisted oven preheated to \( 130^\circ\text{C} \) proved necessary. This temperature is dictated by the martensite start temperature, \( M_s \), of \( \sim 180^\circ\text{C} \) and the \( M_{(10\%)} \) temperature of \( \sim 130^\circ\text{C} \) [5,6]. To promote auto-tempering of the martensite laths, this isothermal quench was for 2 hours, which also reduced internal stresses before the compacts were removed from the oven, and allowed further transformation on cooling to room temperature, [5,6], Fig.5b. The crack-free hardened specimens were then given a spheroidising treatment of 3 hours at \( 750^\circ\text{C} \) to produce a ferrite plus sub-micron carbide structure, soft enough to allow a modest amount of resizing for dimensional control purposes, Fig.6. Tensile testing was carried out on these spheroidised specimens, typical fractographs can be seen in Figs.7a and 7b.

Two types of forging experiments were subsequently carried out. In one, the specimens were heated to the working temperature in argon for 30 min and forged, 1 or 2 strikes, on a screw press between flat plates heated to \( 200^\circ\text{C} \), Figs.8a, b respectively. The second set of experiments was carried out on a Gleeble HDV-40 machine at TUBA, Freiberg [7]. The specimens were heated in argon to \( 700^\circ\text{C} \) and then forged at strain rates of \( 10^{-3}, \, 10^{-2}, \, 10^{-1} \) and 1 s\(^{-1}\) (recorded) \( \sim 1.15 \) natural (logarithmic) strain, Fig.9a, b.

Polished metallographic specimens were etched in 2% Nital and examined either using a Reichert MeF3 optical microscope or a JEOL 6400 scanning electron microscope.
equipped with a Kevex Sigma-32 microanalysis system. Hardness tests, on as-sintered and heat-treated specimens, were carried out on a Vickers machine, generally with a 10 kg load (HV 10).

RESULTS

Fig.1. ThermoCalc generated phase diagram for Fe-0.85Mo-0.6Si-0 to 3C alloy.

Fig.2. Porous gas sintered specimen. Hold 600°C - 15 min, hold 900°C - 2 hours, heat to 1300°C - hold 1 hour. No graphite drying, liquid paraffin binder.
Fig. 3. Porosity developed due to CO₂/CO generation during the early part of the heating cycle with 1ˢᵗ hold at 600-730-750-900°C (clockwise from top left) for 20 min then to 2ⁿᵈ homogenisation hold at 1100°C for 2 hours. Dried graphite employed.

Fig. 4. Dense gas sintered specimen. Dry graphite, polypropylene glycol binder. Fast heat to 900°C hold 20 min, hold 2 hours at 1100°C to homogenise, sinter 1300°C for 30 min. Sintered density >7.7 g.cm³.
Fig. 5. (a) Crack free isothermally quenched/autotempered martensitic structure, to be compared with (b) oil quenched microcracked martensitic structure.

Fig. 6. Spheroidised microstructure obtained by holding quenched, crack free specimen at 750°C for 3 hours.

Fig. 7a. SEM fractograph of spheroidised material, original magnification x1000.

Fig. 7b. Tensile fracture surface, original magnification x5000.
Fig.8. Warm-forged spheroidised microstructures following (a) one strike and (b) 2 strikes at 750ºC. Original magnifications x2000.

Fig.9. Warm forged microstructure obtained by Gleeble compression at 750ºC at a strain rate of 0.001 s⁻¹. (a) Original magnification x2000, (b) Original magnification x5000.

Tab.1. Strengths and hardnesses for Fe-1.4C-0.6Si-0.85Mo samples; ρ > 7.7 g·cm³.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Yield Strength [MPa]</th>
<th>UTS [MPa]</th>
<th>Hardness HV 10 (± 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal (130ºC) Quench</td>
<td>Brittle</td>
<td>700</td>
<td>765</td>
</tr>
<tr>
<td>Spheroidised 750ºC</td>
<td>410</td>
<td>945 (16% strain)</td>
<td>211</td>
</tr>
<tr>
<td>Press: 1 Strike forged 750ºC</td>
<td>-</td>
<td>-</td>
<td>195</td>
</tr>
<tr>
<td>Press: 2 Strike forged 750ºC</td>
<td>-</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>Gleeble: 0.001 s⁻¹ strain rate</td>
<td>769</td>
<td>-</td>
<td>310</td>
</tr>
</tbody>
</table>

DISCUSSION

This work took a long time to come to fruition mainly because of the various problems of graphite drying and binding to the base powders to prevent both gas porosity and inhomogeneity. The process heating profile developed consisted of fast heating to
above the alpha-gamma transformation to 900°C, which helped to minimize harmful, pore
generating, gas production and promoted diffusion of graphite into austenite leaving
temporary connected porosity to help relieve any gas pressure. The hold at 1100°C for 2
hours enabled diffusion of silicon and carbon to produce a well homogenized compact
before raising to the sintering temperature of 1300°C, which produced ~20% of liquid in the
austenite + liquid phase region and promoted excellent densification. The Bayesian neural
network software of Capdevila et al. [10] proved invaluable in helping to understand how to
overcome the quench cracking problem. The use of the auto-tempering treatment at M(10%)
temperature proved to be the final stage of the process, which allowed production of crack-
free, dense, well spheroidised specimens ready for forging, which process has shown the
potential to produce stronger and more dimensionally accurate components. To be noted is
the excellent improvement in yield strength following Gleeble forging at 700°C with strain
rate of 10^{-3} \text{s}^{-1} to (recorded) ~ 1.15 natural (logarithmic) strain.

CONCLUSIONS

This work has shown that high density, ultra high carbon steels can be produced
with an excellent combination of properties: high strength coupled with excellent ductility.
These microstructures, hardness and strength can be further improved by correct use of
warm forging. To be attempted is search for combination of temperature and strain rate for
superplasticity.

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REFERENCES

[2] Sherby, OD., Carsi, M., Kim, WJ., Lesuer, RD., Ruano, OA., Syn, CK., Taleff, EM.,
1996, p. 1559
Progress, vol. 10, 2010, p. 59
vol. 8, 2008, p. 91
Metall., vol. 46, 2003, p. 165
2002, p. 894