

Powder metallurgical nanostructured medium carbon bainitic steel: *in-situ* thermal stability studies

I. Lonardelli^{1,2}, M. Peet¹, W. van Beek and H.K.D.H. Bhadeshia¹

¹University of Cambridge, Materials Science and Metallurgy, Pembroke Street, Cambridge CB2 3QZ, UK

²University of Trento, Materials Engineering and Industrial Technologies, Via Mesiano 77, 38123 Trento, Italy

³Swiss-Norwegian Beamlines, ESRF, BP 220, 38043 Grenoble Cedex, France

Introduction

Carbide-free bainitic steels are representatives of a wide class of alloys in which interesting mechanical properties are obtained from relatively simple and cheap heat treatments. [1]. The final phase mixture consists of bainitic ferrite and thin film of retained austenite (Fig.1).

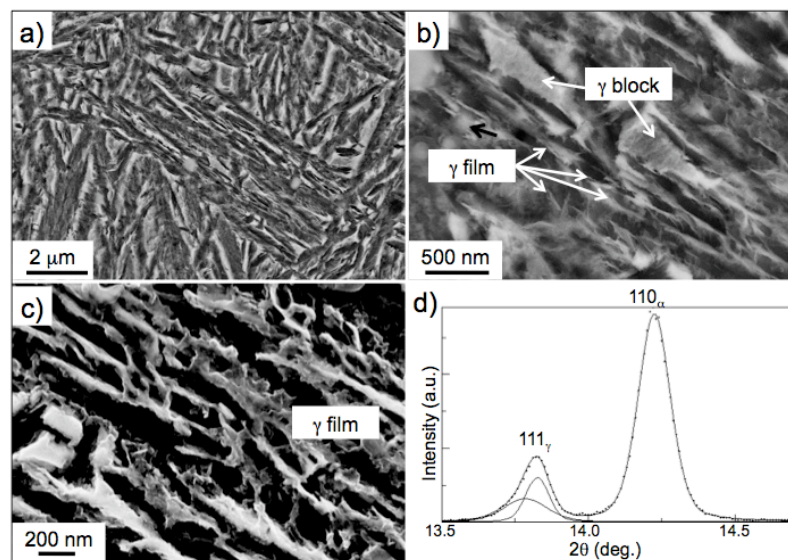


Fig.1. SEM micrograph of medium carbon-high silicon superbainitic steel.

There are circumstances in which the steel is subjected temporarily to elevated temperatures in excess of 400°C; for example the galvanizing treatment where the steel passes through a bath of a molten zinc-rich alloy or in aero-engine shafts in order to apply corrosion-resistant coatings. It is possible that the thermal stability of the austenite would not in these case be sufficient, leading to its decomposition into a thermodynamically more stable mixture of ferrite and cementite. Detailed examinations of the microstructure during heating and holding at high temperature is essential in order to understand how is possible to design a more stable steel.

Experimental procedure

Cylindrical samples of 1 mm diameter and 10 mm length were machined from the isothermally transformed material for the *in situ* continuous heating experiment. The experiment was carried out on the synchrotron facility at the Swiss-Norwegian Beam Line BM01, ESRF in Grenoble, France. During heating (5°C/min.) from RT to 650°C using a hot air blower, the sample was exposed to an X-ray beam of monochromatic wavelength $\lambda=0.502467$ Å and a beam size of 5 mm horizontal \times 0.8 mm vertical. The temperature was monitored with a thermocouple in contact with the sample during the entire experiment. A 2-circle diffractometer was available for high-resolution powder diffraction measurements. Each circle has a high precision encoder mounted directly on the rotation

axis. The experiment was performed in transmission geometry with an illuminated volume two orders of magnitude higher compared to a normal X-ray experiment in reflection. The detector has 6 fast counting chains so that 6 patterns can be collected simultaneously, with an offset of $2\theta = 1.1^\circ$, in order to reduce the total data collection time to a minimum. Diffraction spectra collected every 25°C interval during heating at $5^\circ\text{C}/\text{min}$, between room temperature to 650°C , were entered into the program MAUD (Materials Analysis Using Diffraction) and fit using the Rietveld procedure. A reference specimen of Si powder standard (NIST SRM-640c) was used to determine the wavelength of the incident beam (0.502466 \AA) and calibrate the instrument parameters for the integrations. The fractions of retained austenite and bainitic ferrite as well as the lattice parameters were evaluated using the 111, 200 austenite peaks and 110, 002 ferrite peaks. Line profile analysis was performed using Popa approach incorporated into the Rietveld algorithm to account crystallite size and microstrain ($\langle e^2 \rangle^{1/2}$) this latter quantity being proportional to the square root of dislocation density.

Results and discussion

Fig. 2 shows the experimental 2D plot that covering a broad range of diffracted Bragg angles during in-situ heating of the isothermally generated mixture of fine bainite and retained austenite, up to 650°C from room temperature, with a heating rate of $5^\circ/\text{min}$.

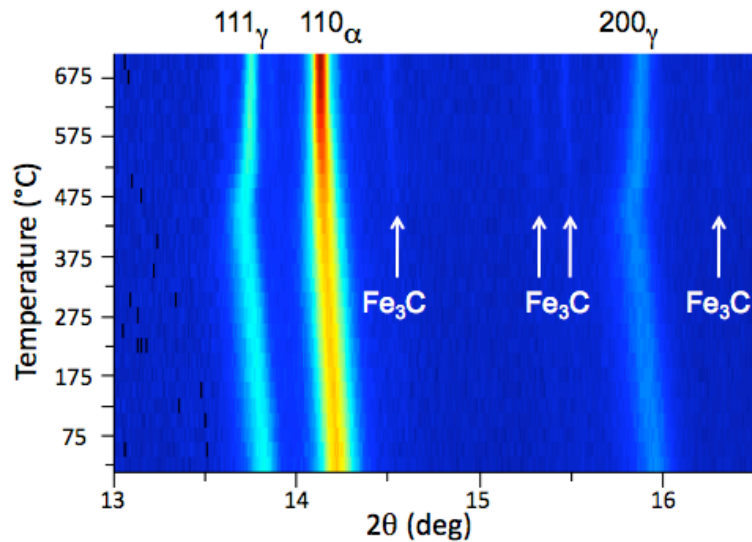


Fig. 2. Experimental 2D plot shows the qualitative evolution of retained austenite, bainitic ferrite and cementite during continuous heating using in situ X-ray synchrotron diffraction technique.

White arrows indicate clearly the cementite peaks that start to be detectable at 450°C . Note the changes in the position of the $\{111\}$ and $\{200\}$ austenite peaks at $400\text{--}450^\circ\text{C}$, with a sensible reduction of the lattice parameter up to 600°C . As already mentioned, the residual austenite peaks are affected by a strong asymmetry due to the gradient of the carbon content in the retained austenite network. The volume fraction of the blocky austenite is small and the thickness of the film austenite network varies between 15 and 100 nm (Fig. 1) with a consequent broad distribution of the carbon content as measured in a recent work by using atom probe tomography [2]. The changes in quantities of both the high carbon and low carbon austenite as well as the lattice parameters during the heating experiment are reported in Fig 3.

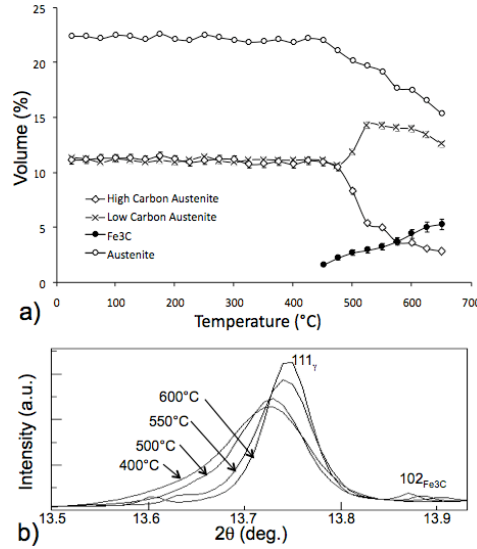


Fig. 3. Quantitative evolution of retained austenite and cementite during heat treatment (a). The 111 austenite peak profile changes during heating is also shown (b).

The lattice parameter changes due to the thermal expansion was calculated using the following equation:

$$a^T = a^{298} [1 + e(T - 298)] \quad (1)$$

where T is the temperature in K , and a is the lattice parameter of austenite and ferrite. The thermal expansion coefficient for austenite and ferrite considered was $e_g = 2.065 \times 10^{-5} K^{-1}$ and $e_a = 1.244 \times 10^{-5} K^{-1}$ respectively. From a quantitative point of view (Fig. 3 a), the austenite starts to decompose above 450°C, with cementite that starts to grow from the carbon enriched austenite. This assumption is supported by the evolution of diffraction pattern during heating (Fig. 3 b), where the changes in peak shape and peak position of 111 austenite are clearly recognized. However, the change in lattice parameter of the high carbon enriched austenite is above 400°C (Fig. 4 a) and between 400°C and 450°C there is a sort of incubation period in which the carbides are not detectable and no decomposition of retained austenite is observed.

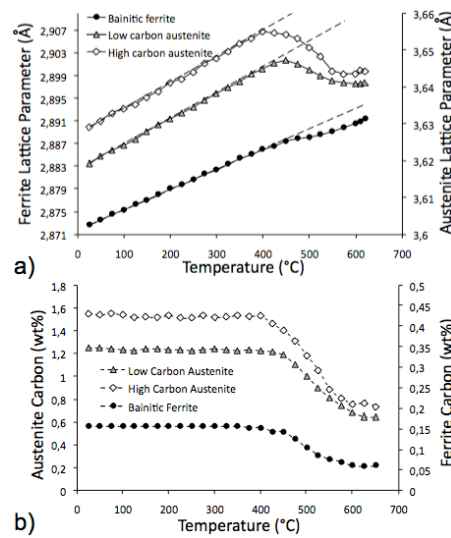


Fig.4. Lattice parameter of austenite and bainitic ferrite as a function of temperature (a). The evolution of carbon content with the temperature is shown in (b).

The super-saturated ferrite lattice start to deviate from the linear thermal expansion between 400°C and 425°C. Above 450°C up to 525°C relevant structural changes are detected from the lattice parameter as well as from the quantitative analysis. Particularly, the decomposition takes place only in a small amount of retained austenite network and the residual austenite has a significantly smaller carbon content. This can be quantitatively observed as a decrease in the high-carbon retained austenite but surprisingly, although the overall quantity of austenite decreases (Fig. 4a), there is an increase in percent of the austenite with less carbon at temperatures close to 500°C. This must be due to a redistribution of carbon through homogenisation, rather than the growth of austenite, which is not possible from a thermodynamic point of view. At 525°C, about 0.2 ± 0.008 of the volume fraction of retained austenite survives, but decomposition then proceeds with a noticeably increasing rate due to cementite formation. Above 600°C, the synchrotron X-ray determined retained volume fraction of austenite is 0.152 ± 0.006 . The calculated carbon content of bainitic ferrite and retained austenite during continuous heating is reported in Fig. 4b. The loss of carbon in austenite and supersaturated ferrite is clearly evident. Particularly, the amount of carbon in supersaturated ferrite appears to decrease substantially during tempering above 400°C, in contrast to a recent work in which the carbon in a superbainitic steel, was measured with atom probe tomography where the amount of material that can be examined is much more limited [2]. After formation of superbainitic microstructure, for the retained austenite becomes impossible to accommodate all the carbon that is rejected from the ferrite [3], and the enrichment in carbon of retained austenite is first controlled by diffusion in ferrite, but is later driven by diffusion in austenite [4]. During continuous heating, no further enrichment of carbon from supersaturated ferrite into austenite was observed. However, some considerations in terms of microstructural changes must be discussed. Fig 5a shows the average microstrain changes with the temperature.

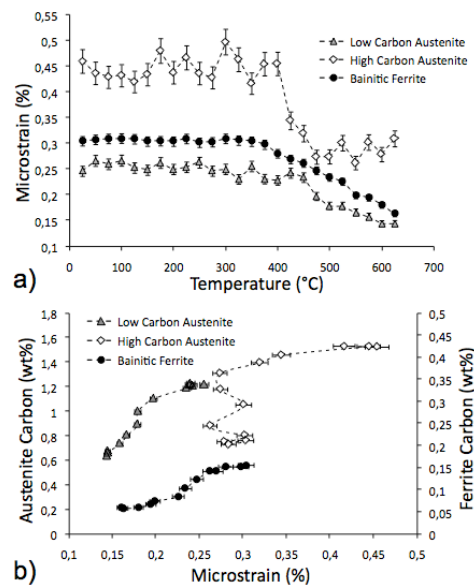


Fig.5. Microstrain evolution as a function of temperature (a), and austenite and ferrite carbon concentration as a function of microstrain (b).

In general, the annihilation of crystal defects can be detected by a decrease of the microstrain. In both retained austenite and supersaturated ferrite, the decrease of the defect density is concomitant with the loss of carbon and the formation of cementite that becomes quantitatively detectable at 450°C (black filled circles Fig. 3a). At 400°C a significant decrease of microstrain in supersaturated ferrite and, in high carbon enriched austenite can be explained as a dislocation annihilation. If the dislocation density decreases with increasing temperature, the carbon might be rejected from the

bainitic ferrite and film austenite. Fluctuations of carbon concentration detected in supersaturated ferrite were attributed to the presence of high-density defects regions in which high level of carbon can be trapped at dislocations and nanotwins. Carbon at defects has a lower energy than cementite, so cementite precipitation occurs when defects are annealed. This interpretation is consistent with our observations in which cementite is seen around 450°C (Fig. 3a) after recovery of microstrain (Fig. 5a). The ability of dislocations to trap the carbon atoms was originally suggested by Kalish and Cohen [5]. Recently, the carbon level of the Cottrell atmosphere in the vicinity of the dislocation were estimated to be 7.4 at.% [6] in agreement with a previous work in which Wilde *et al.* [7] observed a maximum carbon concentration within a dislocation atmosphere of 8 at.%. The relationship between defect density and carbon content in bainitic ferrite was also investigated by using laboratory X-ray diffraction [8]. Our experimental observations suggest that as reported in Fig. 5b, there is a correlation between dislocation recovery and changes of carbon in retained austenite as well as in bainitic ferrite during tempering. Between 400°C and 450°C a significant decrease of defect density occurs with a subsequent decreasing (450°C-500°C) in carbon content. This correlation is particularly significant in high carbon film austenite in which the size of the grains is well below 100 nm. At this level of size the full and partial dislocations originated during low temperature bainitic transformation will annihilate at the grain boundary during tempering.

References

- [1] E. Kozeschnik and HKDH Bhadeshia, *Mat. Sci. Technol.*, **24**, 343 (2008).
- [2] FG Caballero, MK Miller, AJ Clarke, C Garcia-Mateo, *Scripta Mater* **63**, 442 (2010).
- [3] S.A. Mujahid, HKDH Bhadeshia, *Acta Metall. Mater.* **40**, 389 (1992).
- [4] M. Hillert, L. Hoglund, J. Agren, *Acta Metall. Mater.* **40**, 1951 (1993).
- [5] Kalish D, Cohen M. *Mater Sci Eng* 1970; 6: 156.
- [6] FG Caballero, MK Miller, SS Babu, C. Garcia-Mateo, *Acta Mater.*, 2007, 55, 381.
- [7] Wilde J, Cerezo A, Smith GDW, *Scripta Mater* 2000; 43:39.
- [8] C. Garcia-Mateo, M. Peet, F.G. Caballero, HKDH Bhadeshia, *Mat. Sci. Technol.* 2004, 20:814.