

# Spheroidisation of Hypereutectoid State of Nanostructured Bainitic Steel

D. Luo<sup>a</sup>, M.J. Peet<sup>a</sup>, S. W. Ooi<sup>a</sup>, P. Yan<sup>a</sup>, Z. Yin<sup>b</sup>, H.K.D.H. Bhadeshia<sup>a</sup>

<sup>a</sup>*Materials Science and Metallurgy, University of Cambridge, UK*

<sup>b</sup>*Guangxi University, Nanning, Guangxi, P. R. China*

---

## Abstract

Nanostructured bainite is extremely resistant to severe tempering making it difficult to reduce its hardness sufficiently to allow certain processing prior to heat treatment into its final state. An attempt is therefore made to introduce the divorced pearlite reaction that relies on the presence of pro-eutectoid cementite in the austenite in order to produce a microstructure containing spheroidal cementite particles simply by continuous cooling from the two phase austenite and cementite field. It is demonstrated that dramatically reduced hardness values can be achieved using this method.

*Keywords:* nanostructured bainite, hypereutectoid steel, spheroidisation, cementite, softening heat treatments

---

## 1. Introduction

Strong steels sometimes need to be formed into shapes prior to the hardening heat-treatment. For example, bearing components are extremely hard in their final states ( $\approx 650$  HV) but steel has to be supplied to the manufacturer with a hardness that is less than about 235 HV in order to enable cold and warm forging operations and certain coarse machining operations that do not lead to excessive tool wear [1, 2]. Bearing steels are particularly susceptible to inclusions incorporated at the solidification stage [3, 4] - it is well known that in such alloys, the size and shape of inclusions are a function of the nature of deformation prior to hardening [5–7].

Nanostructured bainite [8] consists of a mixture of bainitic ferrite and austenite that is so fine, that the density of interfaces is comparable to that obtained by severe plastic deformation [9], leading to an extraordinary combination of properties in a material that can be large in all three dimensions and is now produced in the thousands of tonnes. The structure is generated solely by solid-state phase transformation at rates that are slow enough to avoid any rapid cooling or mechanical treatments. The fine scale also results in hardness values of about 650-700 HV, and in the context of bearing components, would require a softening heat treatment to permit easy manufacturing operations.

Attempts at tempering the nanostructure demonstrated vividly its resistance to tempering [10–12]. The carbon-rich austenite films between the slender bainite plates decompose during tempering and deposit a large fraction of carbide particles at the interfaces that are then effectively pinned. Since much of the strength of the bainite comes from its fine scale [13, 14], and since the carbides prevent the structure from coarsening, it becomes incredibly difficult to soften the material. Indeed, its resistance to tempering is comparable to secondary hardening steel of similar composition [10, 15]. There is another difficulty, the upper limit to the tempering temperature is limited to below about 750°C because of the formation of austenite at higher temperatures. It took 48 days of tempering at 708°C to reduce the hardness to about 250 HV, which is completely impractical from a commercial point of view. Exotic processes have been proposed for the spheroidisation of high carbon steel involving severe plastic deformation using equal channel angular processing before annealing [16] but such processes are impractical to adopt for general use.

Nanostructured bainitic steels contain a relatively large concentration of silicon, typically 1.5 wt%. It has been suggested that silicon retards the spheroidisation process in high carbon steel during isothermal annealing [17], making it all the more imperative to develop suitable softening processes for the nanostructured bainite.

Conventional bearing steels rely on the presence of proeutectoid cementite to stimulate the formation of *divorced* rather than lamellar pearlite when the austenite ( $\gamma$ ) is cooled. In the divorced eutectoid [18–26], the ferrite ( $\alpha$ ) and cementite ( $\theta$ ) transformations are no longer directly coupled at the transformation front with austenite, but as the  $\alpha/\gamma$  interface advances during cooling, the proeutectoid cementite particles that already exist, simply absorb the excess carbon and grow bigger, leading to a final, soft microstructure consisting of spheroidal cementite particles in a matrix of ferrite. The continuous cooling process associated with the divorced eutectoid reaction is relatively rapid and the resulting structure usually has about half the hardness of lamellar pearlite.

Returning now to the problem of softening nanostructured bainite, all previous studies have been conducted on specimens that are heat-treated to produce a single phase fully austenitic state, followed by transformation into bainite or pearlite. The purpose of the present work was to see if the divorced eutectoid concept could be exploited in order to produce a soft, spheroidised  $\theta + \alpha$  mixture by continuous cooling from the  $\gamma + \theta$  phase field.

## 2. Experimental method

Two arc melts were made using a master alloy from previous work, both of which have an increased carbon concentration to make it easier to introduce proeutectoid cementite (Table 1). The alloys were homogenised at 1200°C for 2 days while sealed in quartz tubes containing a partial pressure of argon. Although nanostructured bainitic steels with carbon concentration as high as 0.98 wt% have been studied in the past [10, 27], the austenitisation temperatures were always selected to ensure that all the cementite was in solution.

Equilibrium phase diagrams were calculated using MTDATA [28] and TCFE database. The calculations accounted for all of the solutes present in the steel; the phases permitted were austenite, ferrite, cementite and  $V_4C_3$  - the latter is not plotted on Fig. 2 because of its very small fraction.

Many of the heat treatment experiments were conducted using a Thermecmaster Z thermomechanical simulator with cylindrical specimens 8 mm in diameter and 12 mm in length. Transformation-start temperatures were interpreted using the offset method [29]. The specific heat treatments used in this study are illustrated in Fig. 1 and are routinely used [23, 30, 31] for the spheroidisation of ordinary bearing steels such as the classical 52100 alloy [2]. The ‘fast’ treatment [23] is based on basic research that recognised the temperature range over which the divorced eutectoid reaction occurs in the 52100 steel studied was in the range 722-690 °C and that slow cooling over that range as in the ‘slow’ version is not necessary.

Scanning electron microscopy was carried out on a field-emission gun scanning electron microscope,

### 3. Results and Discussion

Divorced pearlite is favoured when the cementite particle-spacing is small and the cooling rate is slow [22, 23, 25]. This is important because it is these cementite particles that consume the carbon that is partitioned into the austenite by the ferrite as it grows independently in the reaction described as the divorced eutectoid. In consuming the carbon, the particles coarsen so that the final, soft microstructure after the reactions are completed consists of spheroidal particles of cementite dispersed in ferrite.

In ordinary bearing steels (1C1.5Cr) the amount of proeutectoid cementite present at the austenitisation temperature of 840 °C is typically 3-4 wt% [2]. The alloys listed in Table 1 were designed to achieve cementite quantities within this range under the same conditions. Although the exact compositions intended were not achieved when the melts were manufactured, the phase diagrams shown in Fig. 2 indicate that at 840 °C, the Alloy A and B should under equilibrium conditions contain 3.62 wt% and 4.76 wt% of cementite, respectively. Fig. 3 shows samples of the two alloys quenched following austenitisation at 840 °C for 1 h, illustrating the dispersion of carbide particles present in the austenite before it begins to transform.

A number of experiments were done for the slow version of the spheroidising treatment (Fig. 1) was interrupted by quenching when the sample reached 815, 750 or 740 °C in order to verify the divorced eutectoid reaction. The reaction can of course only occur when ferrite formation becomes possible, which under equilibrium conditions is 770 °C (Fig. 2). Not all the observations are presented here for the sake of brevity, but Fig. 3c,d show the progress of the eutectoid reaction by the ferrite-austenite interface advancing, existing cementite particles coarsening by absorbing the partitioned carbon, and smaller carbide particles disappearing.

Fig. 4 shows the structures obtained and Table 2 summarises the data. It is evident that the required low level of hardness of about 250 HV can best be achieved using the slow version of the spheroidising process. The changes that occur during cooling are interesting. The variations in hardness seen above 770°C are due only to the precipitation of more cementite on cooling to the quench temperature, with the remaining matrix undergoing martensitic transformation although retained austenite will also be present. The hardness therefore remains high before the onset of the divorced eutectoid.

The hardness values of the partially treated samples quenched from various temperatures is of course a function of the microstructure that forms during quenching. For sample A, quenching from 815°C led to the formation of some bainite in addition to martensite, leading to the small hardness decrease, and for reasons that are not clear, the bainite was not present in the 750°C sample. Significant softening only occurred with the onset of the divorced eutectoid reaction (740°C). In the case of Alloy B, quenching from 740°C led to the untransformed matrix changing into lamellar pearlite, leading to the dramatic drop in hardness.

#### 4. Conclusions

Ordinary isothermal tempering has been shown in the past to be ineffective in reducing the hardness of nanostructured bainite consisting of mixtures of bainitic ferrite and carbon-enriched austenite, to a level adequate for some manufacturing operations. It has been demonstrated in this work that the same nanostructured steel can be softened by exploiting the divorced eutectoid reaction, in a heat treatment where the starting state is not fully austenitic, but the austenite contains proeutectoid cementite particles. On cooling below the eutectoid temperature, the particles simply absorb the excess carbon rejected by ferrite, thus suppressing the formation of lamellar pearlite and leaving a final microstructure of coarse cementite spheroids in a ferritic matrix. The resulting hardness, achieved in heat treatments of 10 hours or less, has a hardness of only 250 HV.

The process can be applied by austenitisation of ordinary nanostructured bainitic steels in the two phase austenite and cementite field, or if it necessary to use greater austenitisation temperatures, then by appropriately increasing the carbon concentration of the steel.

The relatively large carbon concentration of the nanostructured bainite studied here is not in fact exceptional; the properties of such alloys have been documented in the past [32, 33]. The distinction of the present work is in controlling the austenitisation conditions to be within the cementite and austenite two-phase field, so that the proeutectoid cementite particles can be exploited to facilitate the divorced eutectoid reaction. Subsequent heat treatments to form the nanostructured bainite can start either from the fully austenitic state, or permit the presence of some proeutectoid cementite. The properties of nanostructured bainite containing spheroidised cementite particles have never been characterised and are the subject of current research.

**Acknowledgments:** The authors are grateful to Professor A. L. Greer for the provision of laboratory facilities at the University of Cambridge.

Table 1: Chemical compositions (wt%) of the alloys studied. The  $Ac_1$  and  $Ac_3$  temperatures represent the lowest temperature at which austenite begins to form, and the temperature at which it stops forming, at a heating rate of  $10^\circ\text{C s}^{-1}$ .

	C	Si	Mn	Cr	Mo	Ni	Co	V	$Ac_1/^\circ\text{C}$	$Ac_3/^\circ\text{C}$
A	0.85	1.75	2.15	1.39	0.24	0.03	1.42	0.1	805	821
B	0.94	1.78	2.20	1.42	0.24	0.03	1.45	0.1	817	840

Table 2: Hardness of samples produced by interrupting the spheroidising process and quenching to ambient temperature. The process begins at  $840^\circ\text{C}$ .

	Slow process quench temperature				Complete slow process	Complete fast process
	$840^\circ\text{C}$	$815^\circ\text{C}$	$750^\circ\text{C}$	$740^\circ\text{C}$		
A	$788\pm 17$	$638\pm 15$	$797\pm 11$	$705\pm 21$	$252\pm 5$	$269\pm 4$
B	$810\pm 14$	$777\pm 7$	$728\pm 19$	$271\pm 9$	$255\pm 4$	$292\pm 9$

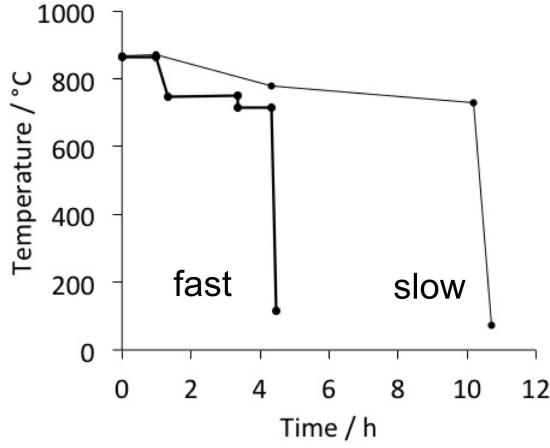


Figure 1: Two different spheroidisation treatments, in both cases beginning with 1 h austenitisation at  $840^\circ\text{C}$ . The ‘slow’ version then involves cooling to  $750^\circ\text{C}$  at  $25^\circ\text{C h}^{-1}$ , from there cooling to  $690^\circ\text{C}$  at  $10^\circ\text{C h}^{-1}$  and air cooling from  $680^\circ\text{C}$  [30, 31]. The ‘fast’ version is due to [23], involving cooling to  $722^\circ\text{C}$  at  $500^\circ\text{C h}^{-1}$ , holding for 2 h, cooling to  $690^\circ\text{C}$  and holding for 1 h, followed by air cooling.

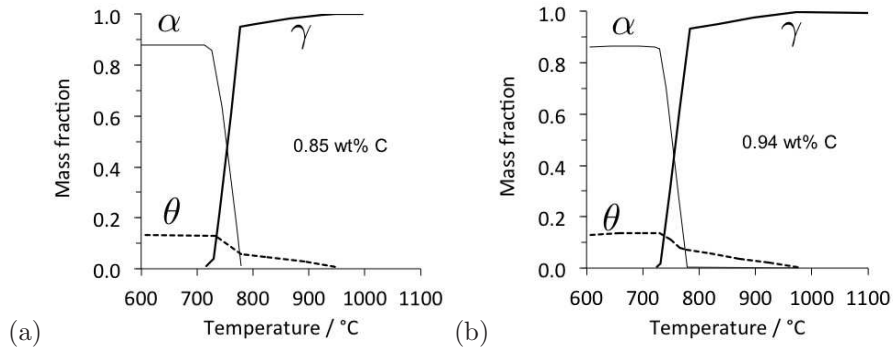


Figure 2: Calculated equilibrium phase fractions. (a) Alloy A. (b) Alloy B.

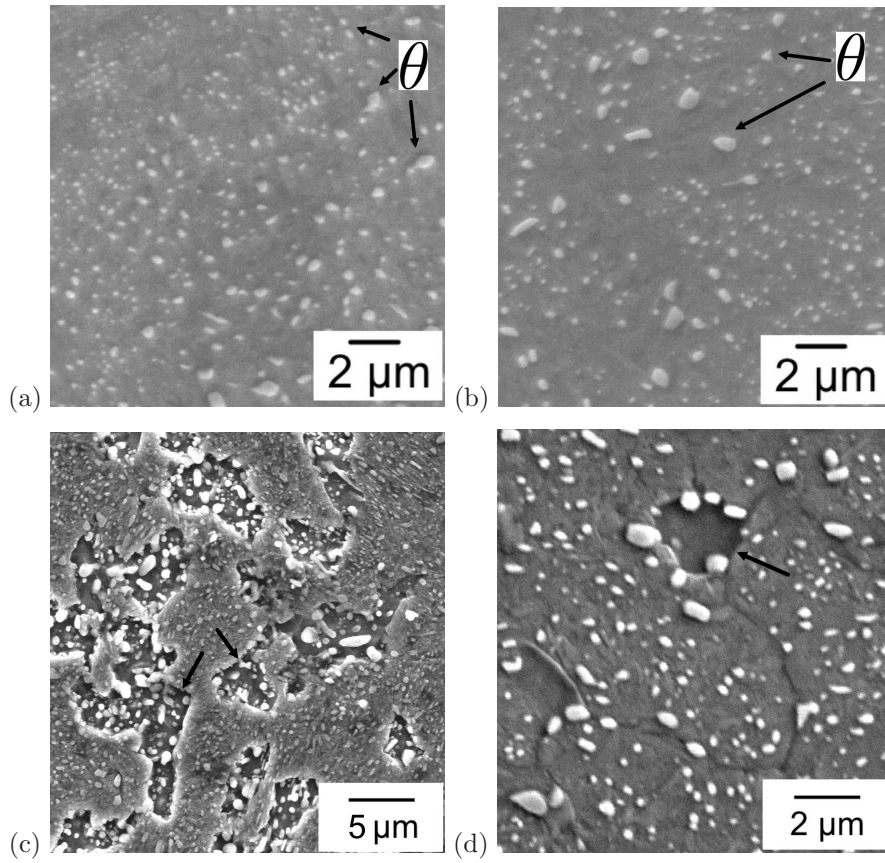


Figure 3: Microstructures at stages of the slow spheroidisation treatment. (a) Alloy A quenched from 840°C, 1 h. (b) Alloy B quenched from 840°C, 1 h. (c) Alloy A quenched from 740°C. (d) Alloy B quenched from 750°C. In (c,d) the arrows indicate the divorced eutectoid transformation front.



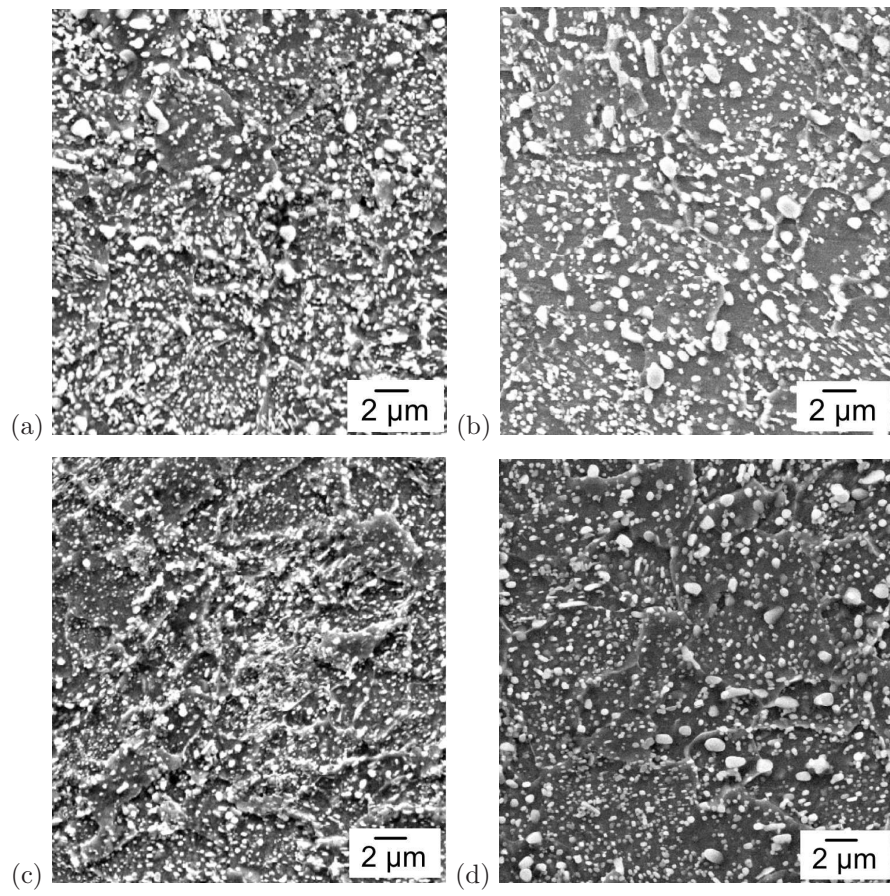


Figure 4: Micrographs following the spheroidisation heat treatments illustrated in Fig. 1. (a) 0.85C alloy, fast treatment, 269 HV; (b) 0.85C, slow treatment, 252 HV; (c) 0.94C alloy, fast treatment, 292 HV; (d) 0.94C, slow treatment, 255 HV.



## References

- [1] J. V. Lyons and M. J. Hudson. Machining properties of high-carbon chromium bearing steels. Technical Report Speical Report 94, Iron and Steel Institute, London, U.K., 1967.
- [2] H. K. D. H. Bhadeshia. Steels for bearings. *Progress in Materials Science*, 57:268–435, 2012.
- [3] W. Trojahn. Bearing steel quality and bearing performance. *Materials Science and Technology*, 28:55–57, 2012.
- [4] C. Bathias. Gigacycle fatigue of bearing steels. *Materials Science and Technology*, 28:27–33, 2012.
- [5] S. X. Li. Effects of inclusions on very high cycle fatigue properties of high strength steels. *International Materials Reviews*, 57:92–114, 2012.
- [6] K. Hashimoto, K. Hiraoka, K. Kida, and E. Costa Santos. Effect of sulphide inclusions on rolling contact fatigue life of bearing steels. *Materials Science and Technology*, 28:39–43, 2012.
- [7] P. Walker. Improving the reliability of highly loaded rolling bearings: the effect of up-stream processing on inclusions. *Materials Science and Technology*, 30:385–410, 2014.
- [8] F. G. Caballero, H. K. D. H. Bhadeshia, K. J. A. Mawella, D. G. Jones, and P. Brown. Very strong, low-temperature bainite. *Materials Science and Technology*, 18:279–284, 2002.
- [9] H. K. D. H. Bhadeshia. The first bulk nanostructured metal. *Science and Technology of Advanced Materials*, 14:014202, 2013.
- [10] C. Garcia-Mateo, M. Peet, F. G. Caballero, and H. K. D. H. Bhadeshia. Tempering of a hard mixture of bainitic ferrite and austenite. *Materials Science and Technology*, 20:814–818, 2004.
- [11] H. S. Hasan, M. J. Peet, and H. K. D. H. Bhadeshia. Severe tempering of bainite generated at low transformation temperatures. *International Journal of Materials Research*, 103:1319–1324, 2012.
- [12] F. Hu, K. M. Wu, T. P. Hou, and A. A. Shirzadi. Tempering stability of retained austenite in nanostructured dual phase steels. *Materials Science and Technology*, 29:947–953, 2013.
- [13] C. G. Mateo and F. G. Caballero. Ultrahigh-strength bainitic steels. *ISIJ International*, 45:1736–1740, 2005.
- [14] H. K. D. H. Bhadeshia. Large chunks of very strong steel. *Materials Science and Technology*, 21:1293–1302, 2005.
- [15] G. P. Contractor, E. G. Schempp, and W. A. Morgan. Carbide composition and microstructure during the quenching and tempering of a 5%CrMoV steel. *Trans. A. S. M.*, 54:208–219, 1969.

- [16] Y. G. Ko, B. W. Lee, J. S. Lee, D. Y. Choi, and D. H. Shin. Spheroidisation behaviour of 1.0 wt-% carbon steel processed by equal channel angular extrusion and annealing. *Materials Science and Technology*, 28:116–119, 2012.
- [17] K. H. Kim and J. S. Lee. On the microstructure and properties of Si-modified 100Cr6 bearing steels. *Materials Science and Technology*, 28:50–54, 2012.
- [18] K. Honda and S. Saito. On the formation of spheroidal cementite. *Journal of the Iron and Steel Institute*, 102:261–267, 1920.
- [19] J. H. Whiteley. The formation of globular pearlite. *Journal of the Iron and Steel Institute*, 105:339–357, 1922.
- [20] I. G. Uzlov, V. V. Parusov, and I. I. Dolzhenkov. Mechanism and kinetics of the transformation of austenite to divorced pearlite. *Metal Science and Heat Treatment*, 22:366–367, 1980.
- [21] T. Oyama, O. D. Sherby, J. Wadsworth, and B. Walser. Application of the divorced eutectoid transformation to the development of fine-grained, spheroidized structures in ultrahigh carbon steels. *Scripta Metallurgica*, 18:799–804, 1984.
- [22] J. D. Verhoeven and E. D. Gibson. The divorced eutectoid transformation in steel. *Metallurgical & Materials Transactions A*, 29:1181–1189, 1998.
- [23] J. D. Verhoeven. The role of the divorced eutectoid transformation in the spheroidization of 52100 steel. *Metallurgical & Materials Transactions A*, 31:2431–2438, 2000.
- [24] V. V. Basabe, J. J. Jonas, and C. Ghosh. Formation of deformation-induced divorced eutectoid pearlite above the Ae1. *Advanced Materials Research*, 409:829–834, 2011.
- [25] A. S. Pandit and H. K. D. H. Bhadeshia. Divorced pearlite in steels. *Proceedings of the Royal Society A*, 468:2767–2778, 2012.
- [26] Z. X. Yin and H. K. D. H. Bhadeshia. Divorced eutectoid transformation in high Mn bearing steel. *Advanced Materials Research*, 634–638:1798–1802, 2013.
- [27] A. Al Hamdany, D. Al Fattal, T. A. Jabbar, and H. K. D. H. Bhadeshia. Estimation of the fracture toughness of tempered nanostructured bainite. *Materials Science and Technology*, 28:685–689, 2012.
- [28] NPL. MTDATA. Software, National Physical Laboratory, Teddington, U.K., 2006.
- [29] H.-S. Yang and H. K. D. H. Bhadeshia. Uncertainties in the dilatometric determination of the martensite-start temperature. *Materials Science and Technology*, 23:556–560, 2007.
- [30] L. E. Heron. Spheroidise annealing of steel tube for bearings. *Metallurgia*, 80:53–58, 1969.

- [31] W. Hewitt. The spheroidise annealing of high carbon steel and its effect on subsequent heat treatment. *Heat Treatment of Metals*, 3:56–62, 1982.
- [32] C. Garcia-Mateo, F. G. Caballero, T. Sourmail, M. Kuntz, J. Cornide, V. Smanio, and E. Elvira. Tensile behaviour of a nanocrystalline bainitic steel containing 3 wt% silicon. *Materials Science & Engineering A*, 549:185–192, 2012.
- [33] F. Hu, K. M. Wu, and H. Zheng. Influence of Co and Al on bainitic transformation in super bainitic steels. *Steel Research International*, ? :DOI: 10.1002/srin.201200334, 2013.