Note

Effect of Solute Silicon on the Lattice Parameter of Ferrite in Ductile Irons

Fei HUYAN,^{1)*} Richard LARKER,²⁾ Per RUBIN³⁾ and Peter HEDSTRÖM¹⁾

1) Dept. Materials Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden. 2) Indexator Rototilt Systems AB, Box 56, 922 21 Vindeln, Sweden.

3) Rubin Materialteknik, Gullhönenvägen 13, 975 96 Luleå, Sweden.

(Received on July 25, 2013; accepted on September 25, 2013)

The effect of solute silicon on the ferrite lattice parameter has been investigated using X-ray diffraction in cast ductile irons (DI) with nominal Si contents between 2.50 and 4.56 wt%. It was found that silicon changes the ferrite lattice parameter by $-0.00185 \text{ \AA}$ per wt% Si. This contraction coefficient is three times larger than the most commonly used Si coefficient in the literature. Since substitutional solution by silicon contracts the ferrite lattice while the interstitial solution by carbon expands the lattice, the Si contraction coefficient found will have a significant effect on subsequent evaluation of the carbon content in austempered Si-alloyed ductile irons and steels.

KEY WORDS: iron alloys; X-ray diffraction (XRD); silicon; ferrite lattice parameter.

It has recently been shown that increasing the Si content in ferritic ductile irons (DI) to about 3–4 wt% is a cost-efficient and effective way to further improve the mechanical properties by Si solution strengthening.^{1,2)}

The excellent mechanical properties of austempered ductile iron (ADI) and nanocrystalline bainitic steels are due to a fine dual-phase structure of acicular ferrite and retained austenite.^{3–5)} These structures are frequently denoted carbide-free bainite in steels and ausferrite in ADI. The alloys consist of rather high Si contents to suppress the carbide formation and e.g. conventional ADI contain about 2.5 wt% Si.

The distribution of carbon between acicular ferrite and retained austenite is a key issue for several reasons. First, there is a long-standing debate regarding the phase transformation mechanism of bainite and today there are two opposing theories. The diffusionless-displacive theory assumes the growth of bainite to be essentially martensitic,^{4,6)} whereas the diffusional theory assumes that the bainitic transformation is controlled by carbon diffusion.^{7,8)} Second, the carbon partitioning between ferrite and austenite affects the stability of the austenite. Higher carbon content lowers the martensite start temperature and thus stabilizes the austenite. Third, the proportion of the ferrite and austenite phases, which is vital for properties, can be estimated using the lever

rule and thus accurate carbon contents in the respective phase must be established. For instance, Chang⁹⁾ calculated the amount of retained austenite in ADI using the lever rule and found better agreement with experiments if the carbon content of ferrite was assumed high (0.37 wt% C) instead of the conventional low solubility of carbon in ferrite.

Carbon supersaturation of ferrite has also been reported experimentally. Peet *et al.*³⁾ found that the carbon content in the bainitic ferrite of a steel alloy 0.75C–1.63Si–1.95Mn–1.48Cr, isothermally treated at 200°C for 12 days, was $1.1 \pm 0.7 \text{ at\%}$ (about $0.23 \pm 0.15 \text{ wt\%}$) using atom probe tomography (APT). Caballero *et al.*⁴⁾ studied an Fe–1C–1.5Si–1.9Mn–1.3Cr steel, treated at 200°C for 48 h, and found the carbon content of bainitic ferrite to be $3.01 \pm 0.30 \text{ at\%}$ (about $0.62 \pm 0.06 \text{ wt\%}$) by X-ray diffraction (XRD), and $1.36 \pm 0.07 \text{ at\%}$ (about $0.28 \pm 0.02 \text{ wt\%}$) by APT.

XRD is widely used to evaluate the amount of solute elements in individual phases in steels. The method is based on the relationship between the ferrite lattice parameter (a_α) and the alloying content, e.g. in an Fe–C–Si–Mn alloy:

$$a_\alpha (\text{\AA}) = 2.8664 + 0.039 \times \text{wt\%C} - 0.0006 \times \text{wt\%Si} + 0.0006 \times \text{wt\%Mn} \quad \dots (1)$$

where 2.8664 Å is the lattice parameter for pure bcc iron,¹⁰⁾ and the concentration of each element is in weight percent.^{11,12)} The Si coefficient $-0.0006 \text{ \AA}$ per wt% Si suggested by Leslie¹²⁾ is widely used in the literature, e.g. in Refs. 4) and 13).^{4,13)}

Thus the carbon content of ferrite (C_α) can be calculated according to:

$$C_\alpha (\text{wt\%}) = (a_\alpha - 2.8664 + 0.0006 \times \text{wt\%Si} - 0.0006 \times \text{wt\%Mn}) / 0.039 \quad \dots (2)$$

Clearly, the determination of carbon content from XRD relies on the accuracy of the lattice parameter measurements and the accuracy of the coefficients. Different Si coefficients are found in the literature and e.g. Nieswaag and Nijhof⁴⁾ used a coefficient of $-0.00135 \text{ \AA/wt\%Si}$, while interpreting the work from Krishtal *et al.*¹⁵⁾ gives a coefficient of about $-0.00364 \text{ \AA/wt\%Si}$ up to 10 wt% Si.

Since the carbon content is vital in ADI and the Si coefficient is necessary to evaluate the carbon content from XRD, the purpose of the present work is to evaluate the Si coefficient in DI with Si contents relevant for conventional and Si solution strengthened ADIs.

Three ductile iron ingots with different bulk Si content were cast. The low cooling rate during casting was assumed to give a similar low carbon content of the ferrite in the three alloys. The nominal Si contents were 2.50, 3.36 and 4.56 wt% (denoted as 2.5Si, 3.4Si and 4.5Si respectively), and the carbon equivalent values $(\text{wt\%C} + \text{wt\%Si}/4 + \text{wt\%P}/2)$ were between 4.25 and 4.35 wt%. All DIs were alloyed with approximately 0.2 wt% Mn, and the fraction of other elements was kept low. The cast DIs were cut to a size of $8 \times 5 \times 3 \text{ mm}^3$. The samples were mounted in phenolic powder resin and mechanically polished to mirror finish. The microstructure was characterized using Light Optical Microscopy (LOM) LEICA DMRM after etching with 2% Nital. The Si content of ferrite was examined using Energy Dispersive X-ray Spectroscopy (EDX) in a Scanning Electron Microscope

* Corresponding author: E-mail: huyan@kth.se

DOI: <http://dx.doi.org/10.2355/isijinternational.54.248>

(SEM), Hitachi S3700N. The XRD measurements were performed in a Bruker D2 Phaser with Cu anode. Prior to the DI investigations, a reference silicon powder was used for calibration of the instrument. The lattice parameter of the silicon powder was found to be 5.43148 ± 0.00037 Å by using the Nelson-Riley¹⁶⁾ method. This is in good agreement with pure Si reported as 5.43123 ± 0.00008 Å.¹⁷⁾

The XRD measurements were performed using increments of 0.024° in 2θ . The scan speed was set to 1 s per increment between 40 and 80° , and 3 s between 80 and 105° . The Cu $K_{\alpha 2}$ and background were subtracted from the data using the software EVA, and thus the X-ray wavelength is 1.5406 Å. The software Origin 8.6.0 was used for least-square fitting of a Pearson VII function to find peak centers. The Nelson-Riley (N-R) function¹⁶⁾ was calculated for each peak by

$$N-R = \cos^2\theta / \sin\theta + \cos^2\theta / \theta \dots\dots\dots (3)$$

where θ is the peak center. The lattice parameter of ferrite was finally determined by a linear fitting of N-R versus a_α using the least-square method.

Observed with LOM, the 3.4Si and 4.5Si DIs constitute of ferrite and nodular graphite (Fig. 1), while the 2.5Si DI also contains a small fraction of pearlite.

Four peaks from the ferrite phase are obtained from XRD between 40 and 105° . Figure 2 depicts a diffraction pattern with the peaks (110), (200), (211) and (220) indicated for the 3.4Si sample. The lattice parameters calculated from the d-spacing of each peak is then plotted versus the corresponding Nelson-Riley values. Figure 3 shows such a plot for alloy 3.4Si DI, and the extrapolated value at N-R=0 is

Fig. 1. Microstructure of the 3.4Si DI using LOM.

Fig. 2. X-ray diffraction pattern for the 3.4Si DI.

the determined a_α for this alloy. The extrapolated a_α and the Si contents measured using EDX are plotted in Fig. 4, and the Si coefficient is determined to be -0.00185 ± 0.00018 Å/wt% Si from the linear fit.

The carbon contents of ferrite (C_α) are then calculated using Eq. (2) but with different Si coefficients. The results are presented in Table 1. Applying the Si coefficient determined in the present work, the carbon contents of ferrite are calculated to be in the range of 0.043 – 0.060 wt%. A calculation using Thermo-Calc with database TCFE7 shows slightly lower values with equilibrium carbon contents in ferrite between 0.018 and 0.020 wt% at 820°C for 2.35 – 4.63 wt% Si. The relatively small difference between experiments and calculations may be due to the accuracy of measurements but also e.g. the C coefficient used. Nonetheless, the results confirm that the carbon content of ferrite is low and comparable in the three DIs after casting.

The Si coefficient determined in the present work should be compared with previously reported coefficients for Si. It is obvious that the coefficients in the literature are rather different. One reason for this is that alloys with different sili-

Fig. 3. Lattice parameter of ferrite versus Nelson-Riley function for the 3.4Si DI.

Fig. 4. Lattice parameter of ferrite versus silicon content. Note that some error bars are very small and covered by the squares.

Table 1. Composition, lattice parameter and carbon content of ferrite in cast DIs.

Sample	Si in ferrite (wt%)	a_α (Å)	C_α (wt%)		
			Present	Leslie	Krishtal
cast DI 2.5Si	2.35 ± 0.15	2.86438 ± 0.00010	0.057 ± 0.003	-0.019	0.16
3.4Si	3.53 ± 0.13	2.86167 ± 0.00048	0.043 ± 0.012	-0.070	0.21
4.5Si	4.63 ± 0.03	2.86031 ± 0.00036	0.060 ± 0.009	-0.088	0.27

con contents have been used. In the present work, the silicon content was between 2.50 and 4.56 wt%, which ranges from the typical ADI up to the silicon solution strengthened ADIs.⁵⁾ The silicon content in Leslie's work¹²⁾ was 0.7–2.96 wt% and it was mentioned that the relationship of silicon content versus lattice parameter was non-linear in this range. In the work by Krishtal *et al.*,¹⁵⁾ the silicon content was 4.7–16.0 wt%. Hence, part of the deviation between the Si coefficients in the present work and the literature is most likely related to the non-linearity of Si versus lattice parameter as well as the different ranges of silicon evaluated. Nonetheless, it is proposed that the Si coefficient in the present work should provide a good estimate of the lattice shrinkage for most high-Si steels and ADIs since the Si to lattice parameter relationship appears linear in the associated range of Si.

The application of the proposed Si coefficient to determine the carbon content is clearly depending on the accuracy of the C coefficient as well as the accuracy of the lattice parameter determination. The C coefficient in Eq. (2) was taken from Ref. 11)¹¹⁾ and it should be noted that there are large uncertainties in this value due to the difficulty in determining low concentrations of C accurately. Another C coefficient can be extrapolated from an equation compiled by Bhadeshia *et al.*¹³⁾ A polynomial expression was used for C in the equation, however the relationship of lattice parameter and carbon content is quite linear up to higher than 0.1 wt% C, and the C coefficient is 0.030 Å/wt%C in this case. The equation has been widely applied to bainitic steels and by using it, the estimated carbon contents in the present work would be about 30% higher in the ferrite.

In conclusion, the ferrite lattice parameter in ductile irons was found to change by -0.00185 Å per wt% Si. This con-

traction of ferrite is three times larger than the most used Si coefficient in the literature and since substitutional solution by silicon contracts the ferritic lattice while the interstitial solution by carbon expands the lattice, it will have a significant effect on the determination of ferrite carbon content in *e.g.* high silicon austempered ductile iron and steels, evaluated by XRD.

The authors are thankful to KTH and AIMday for funding and to Mats Hillert for useful discussions.

REFERENCES

- 1) R. Larker: *China Foundry*, **6** (2009), 343.
- 2) EN 1563, 2011 Founding - Spheroidal Graphite Cast Irons, Comité Européen de Normalisation, Brussels, (2011).
- 3) M. Peet, S. S. Babu, M. K. Miller and H. K. D. H. Bhadeshia: *Scr. Mater.*, **50** (2004), 1277.
- 4) F. G. Caballero, M. K. Miller and C. Garcia-Mateo: *Acta Mater.*, **58** (2010), 2338.
- 5) R. Larker and P. Rubin: Proc. 6th Int. Quenching and Control of Distortion Conf., ASM, OH, (2012), 329.
- 6) H. K. D. H. Bhadeshia: *Bainite in Steels*, 2nd ed., Cambridge University Press, London, (2001).
- 7) A. Borgenstam, M. Hillert and J. Ågren: *Acta Mater.*, **57** (2009), 3242.
- 8) A. Borgenstam, P. Hedström, M. Hillert, P. Kolmskog, A. Stormvinter and J. Ågren: *Metall. Mater. Trans. A*, **42A** (2011), 1558.
- 9) L. C. Chang: *Metall. Mater. Trans. A*, **34A** (2003), 211.
- 10) S. J. Lee and Y. K. Lee: *Scr. Mater.*, **52** (2005), 973.
- 11) E. J. Fiasiska and H. Wagenblast: *Trans. AIME*, **239** (1967), 1818.
- 12) W. C. Leslie: *The Physical Metallurgy of Steels*, McGraw-Hill, New York, (1982).
- 13) H. K. D. H. Bhadeshia, S. A. David, J. M. Vitek and R. W. Reed: *Mater. Sci. Technol.*, **7** (1991), 686.
- 14) H. Nieswaag and J. W. Nijhof: MRS Proc., Vol. 34, eds. by H. Fredriksson and M. Hillert, Materials Research Society, Warrendale, PA, (1984), 411.
- 15) M. A. Krishtal, T. A. Sirenko, E. G. Titenskii and G. I. Naumov: *Met. Sci. Heat Treat.*, **12** (1970), 78.
- 16) J. B. Nelson and D. P. Riley: *Proc. Phys. Soc.*, **57** (1945), 160.
- 17) Standard Reference Material 640d, National Institute of Standards & Technology, Gaithersburg, (1987).