



## **AFFECT OF CEMENTITE PRECIPITATION ON THE EXTEND OF BAINITE REACTION IN ADI**

**Zdzisław Lawrynowicz**

*University of Technology and Life Sciences, Mechanical Engineering Faculty  
Department of Materials Science and Engineering, av. Kaliskiego 7  
85-789 Bydgoszcz, Poland, e-mail: lawry@utp.edu.pl*

### **Abstract**

*Presented paper demonstrates how the precipitation of cementite from ferrite or/and austenite in ADI may influence the extend of bainite reaction. Analytical calculations and experimental measurements of volume fraction of bainitic ferrite and volume of the untransformed austenite indicate that there is a necessity of carbides precipitation. A consequence of the precipitation of cementite from austenite during austempering is that the growth of bainitic ferrite can continue to larger extent and that the resulting microstructure is not an ausferrite but it is a mixture of bainitic ferrite, retained austenite and carbides. In case of this microstructure, the product of austempering reaction in ductile iron is rather bainite than "ausferrite". The results are discussed in the context of displacive mechanism of bainite transformation.*

**Keywords:** carbon diffusion, bainite transformation, cementite precipitation

### **1. Introduction**

The development of austempered ductile iron (ADI) is a major achievement in cast iron technology. The starting material for the production of ADI is the high quality ductile or nodular cast iron. In 1948 the invention of ductile iron was announced jointly by the British Cast Iron Research Association (BCIRA) and the International Nickel Company (INCO). By the 1950's, both the material, ductile iron, and the austempering process had been developed. By the 1990's, ASTM A897-90 and ASTM A897M-90 Specifications for Austempered Ductile Iron Castings were published in the US that consist the five Grades of ADI according to ASTM A897/897M.

The attractive properties of bainitic irons without carbides are related to its unique microstructure that consists of ferrite and high carbon austenite. Because of this microstructure, the product of bainitic reaction is often referred to as "ausferrite" rather than bainite [1-4]. The mixture of bainitic ferrite and untransformed austenite is an ideal combination from many points of view. Once the ausferrite has been produced, the components are cooled to room temperature. The cooling rate will not affect the final microstructure as the carbon content of the austenite is high enough to lower the martensite start temperature to a temperature significantly below room temperature. If the bainitic ferrite-austenite microstructure is held for long time periods, the blocks of high carbon austenite will eventually undergo a transformation to bainite, the two phase ferrite and carbide ( $\alpha + \text{Fe}_3\text{C}$ ).

The purpose of the present paper is to demonstrate how the precipitation of cementite from ferrite or/and austenite in ADI may influence the extent of bainite reaction.

## 2. Material and methods

The chemical composition of the experimental ductile iron is listed in Table 1. The concentration of alloying elements in the matrix is obtained from the chemical analysis. Ductile iron blocks were produced in a commercial foundry furnace. The melt was poured into a standard Y block sands molds (ASTM A-395), which ensured sound castings. Specimens austenitised at  $T_{\gamma}=950^{\circ}\text{C}$  for 60 minutes were rapidly transferred to a salt bath at austempering temperatures 250, 300, 350 and  $400^{\circ}\text{C}$ , held for 15, 30, 60, 120 and 240 minutes and then water quenched to room temperature. The microstructure of the as-cast material matrix contains 40% ferrite and 60% pearlite, however graphite nodules in material is 11.5%.

Tab. 1. Chemical composition of ductile cast iron ADI, wt-%

C	Si	Mn	P	S	Mg	Cr	Ni	Mo
3.21	2.57	0.28	0.06	0.01	0.024	0.036	0.098	0.015

The  $X$ -ray investigations were performed on the specimens heat treated after specific time of the isothermal bainite reaction at the given temperature. The total volume fraction of the retained austenite was measured from the integral intensity of the (111) $\gamma$  and (011) $\alpha$  peaks. The presence of high silicon content in ADI retards the formation of cementite in ferrite and austenite. Then, the measurements of carbon concentration in retained austenite were carried out by using  $X$ -ray diffraction. The carbon concentration was calculated from measured lattice parameter of the retained austenite. The  $2\theta$  values for austenite peaks were used to calculate the  $d$  spacing with Bragg's law and then the lattice parameters. The lattice parameter of austenite ( $a_{\gamma}$ ) is related to the known relationship between the parameter and the carbon concentration [2,3]:

$$a_{\gamma} \text{ (nm)} = 0.3573 + 0.0033 x_{\gamma} \quad (1)$$

where  $x_{\gamma}$  is the carbon concentration in austenite, in weight %.

The matrix carbon concentration,  $x_{\gamma}^m$ , of the ductile iron was also determined experimentally with Dron 1.5 diffractometer using  $\text{CoK}\alpha$  radiation on specimens austenitised at  $950^{\circ}\text{C}$  for 60 minutes and quenched to ambient temperature. It was found that after quenching from austenitising temperature  $950^{\circ}\text{C}$  the calculated carbon content in matrix is  $x_{\gamma}^m = 1.044\% \text{C}$  and measured carbon content is  $x_{\gamma}^m = 1.05\% \text{C}$  thus, the measured value was taken for further calculation.

## 3. Results and discussion

When the matrix of ADI only consist of ausferrite, thus:

$$V_{\gamma} + V_{\alpha} = I \quad (2)$$

and the permitted fraction of bainite ( $V_\alpha$ ) can be determined from Lever rule applied to the  $T_0$ <sup>1</sup> curve, Fig. 1.

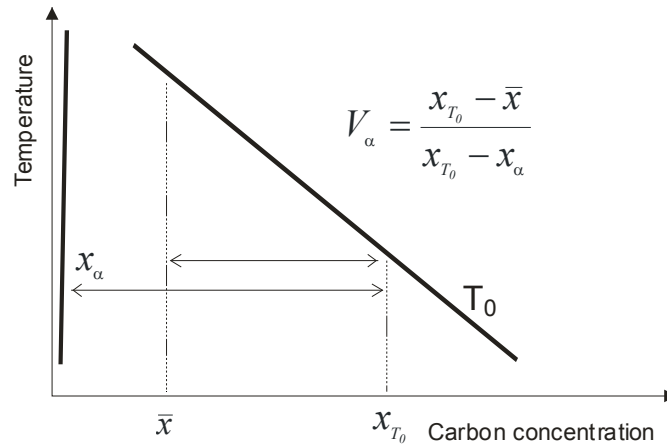


Fig. 1. Application of the Lever-rule to the  $T_0$  curve allows the estimation of the permitted fraction of bainite ( $V_\alpha$ ) at any temperature (where for 950°C  $\bar{x} = 1.05$  wt.% C  $x_\alpha = 0.03$  wt.% C)

The maximum volume fraction of retained austenite ( $V_\gamma$ ) will then equal  $1 - V_\alpha$ . In case of carbides precipitation the maximum volume fraction of bainitic ferrite ( $V_\alpha$ ) can be calculated using the following equation [4]:

$$V_\alpha = \frac{x_{T_0} - \bar{x}}{x_{T_0} - x_\alpha - x_C} \quad (3)$$

where  $V_\alpha$  is volume fraction of bainitic ferrite,  $\bar{x}$  is the average carbon concentration in the matrix of the alloy,  $x_\alpha$  is the paraequilibrium carbon concentration in the bainitic ferrite (0.03 wt. %),  $x_{T_0}$  is the carbon concentration of the austenite corresponding to the  $T_0$  curve,  $x_C$  is the amount of carbon, which is tied up as carbides (cementite). Thus, the maximum volume fraction of bainite taking into account cementite precipitation can be calculated using the relationship (3).

It is seen in Fig. 2 that precipitation of cementite leads to an increase of volume fraction of bainitic ferrite. Carbides locally reduce the carbon content of the parent austenite and increase the driving force for further ferrite growth.

The measured volume fraction of retained austenite, bainitic ferrite and carbon concentrations in residual austenite are shown in Tab. 2. Comparison of the calculated (Fig. 2) and measured (Tab. 2) fraction of bainite indicate that during bainite transformation in ADI must be intensive cementite precipitation.

Cementite can precipitate from supersaturated bainitic ferrite and also from austenite. The growth of bainite is probably diffusionless but any excess carbon in the supersaturated ferrite soon

<sup>1</sup> The  $T_0$  temperature can be defined [5-8] such that stress free austenite and ferrite of the same composition (with respect to both the interstitial and the substitutional alloying elements) are in metastable equilibrium. Thus any displacive transformation involving a full supersaturation of carbon (i.e. bainitic ferrite would then inherit the carbon content of the parent austenite) can occur only below the appropriate  $T_0$  temperature. Strain energy would have effect of shifting curve to lower carbon concentration,  $T_0'$  curve [9]. The  $T_0'$  line accounts for 400 J/mol of stored energy in the bainite. If this energy is reduced by plastic deformation of the surrounding austenite then a higher volume fraction of bainite should be able to form.

afterwards partitions into the residual austenite or precipitates within bainitic ferrite in the form of carbides [7-10]. When the process of carbon partitioning into the residual austenite is rapid relative to that of carbide precipitation, the transformation product is called “upper bainite”, whereas “lower bainite” is obtained when some of the carbon supersaturation is relieved by precipitation within the bainitic ferrite [8,9,11].

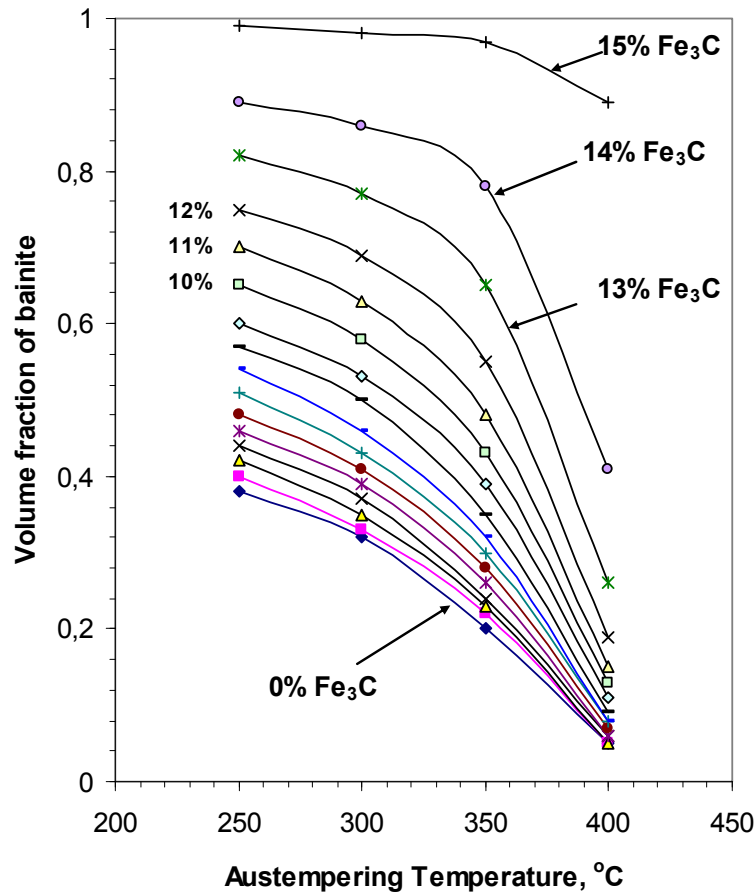


Fig. 2. Calculated the maximum volume fraction of bainite in investigated ADI taking into account cementite precipitation in the range from 0% to 15 wt. % Fe<sub>3</sub>C

Austenite is supersaturated with respect to cementite precipitation when  $x_\gamma > x^{\gamma\theta}$ , where  $x^{\gamma\theta}$  denotes carbon concentration at the extrapolated  $A_{cm}$  boundary. This means for the bainite reaction, that  $x_{T_0} > x^{\gamma\theta}$  since the growth of bainitic ferrite stops when  $x_\gamma$  reaches the value  $x_{T_0}$  given by the  $T_0$  curve of the phase diagram. A consequence of the precipitation of cementite from austenite is that its carbon concentration drops below  $x_{T_0}$ , so that the growth of bainitic ferrite can continue to an extent larger than would be otherwise possible (see Fig. 2).

The large discrepancies among calculated and measured volume fractions of bainite can be explained by intensive cementite precipitation during bainitic reaction. The thermodynamic restriction imposed by the  $T_0$  curve on the extent of bainite transformation can result in the formation of pools of retained austenite with a coarse, blocky morphology, Fig. 3.

Tab. 2. The measured volume fraction of retained austenite, bainitic ferrite and carbon concentrations in residual austenite

Austempering conditions		Austenitisation temperature, 950°C			
°C	Time, min.	Measured volume fractions of, %		Carbon concentrations of the residual austenite $x_\gamma$ , wt.%	
		retained austenite $V_\gamma$	bainitic ferrite, $V_\alpha$	$x_\gamma$ , calculated	$x_\gamma$ , measured
400	15	43.6	56.4	2.37	1.42
	30	38.3	61.7	2.69	1.50
	60	45.1	54.9	2.29	1.54
	120	44.7	55.3	2.32	1.54
	240	31.3	68.7	3.29	1.54
350	15	40.3	59.7	2.56	1.50
	30	38.1	61.9	2.71	1.50
	60	35.5	64.5	2.90	1.62
	120	36.3	63.7	2.84	1.58
	240	29.8	70.2	3.45	1.38
300	15	38.3	61.7	2.69	1.25
	30	32.2	67.8	3.19	1.54
	60	31.8	68.2	3.24	1.50
	120	25.1	74.9	4.09	1.62
	240	18.3	81.7	5.60	1.62
250	15	29.8	70.2	3.45	0.88
	30	29.8	70.2	3.45	1.02
	60	30.1	69.9	3.42	1.01
	120	24.2	75.8	4.25	1.25
	240	16.4	83.6	6.25	1.22

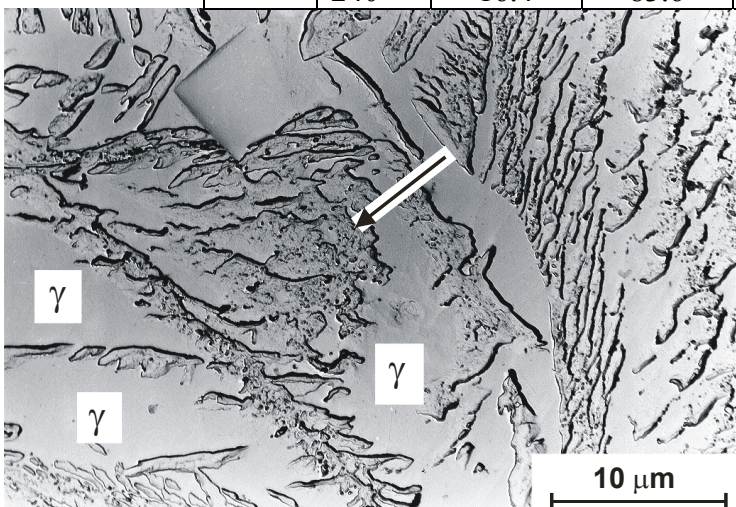


Fig. 3. Carbon replica taken from sample austenitised at 950°C and austempered at 400°C for 120 min. This replica reveals the presence of carbides inside of bainite (arrowed) and shows large pools of blocky retained austenite

Because of the inhomogeneous distribution of carbon and other solutes in the matrix after transformation to bainite the retained austenite is enriched to a greater extent in the immediate vicinity to bainite platelets or in the region trapped between the platelets and in the eutectic cell boundary (Fig. 3) while other region contains relatively poor carbon [12]. The above effect can be exaggerated in ADI, since cast iron is usually extremely segregated. Martensite is usually found to be in the cell boundary which solidified last [13]. It indicates that the austenite in cell boundary is less enriched with carbon, and therefore is thermally unstable.

#### 4. Conclusions

The following conclusions were reached:

1. Analytical calculations and experimental measurements of volume fraction of bainitic ferrite and volume of the untransformed austenite indicate that there is a necessity of carbides precipitation.
2. A consequence of the precipitation of cementite from ferrite or/and austenite during austempering is that the growth of bainitic ferrite can continue to larger extent and that the resulting microstructure is not an ausferrite but is a mixture of bainitic ferrite, retained austenite and carbides.

#### References

- [1] Chang, L.C., *Carbon content of austenite in austempered ductile iron*, Scripta Materialia, vol.39, No 1, pp. 35-38, 1998.
- [2] Pietrowski, S., *Nodular cast iron of bainitic ferrite structure with austenite or bainitic structure*, Archives of Materials Science, vol. 18, No.4, pp.253-273, 1997. (in Polish)
- [3] Guzik, S.E., *Austempered cast iron as a modern constructional material*, Inżynieria Materiałowa, nr 6, pp.677-680, 2003. (in Polish)
- [4] Takahashi, M., Bhadeshia, H.K.D.H., *A Model for the Microstructure of Some Advanced Bainitic Steels*, Materials Transaction, JIM, 32, pp. 689-696, 1991.
- [5] Ławrynowicz, Z., *Transition from upper to lower bainite in Fe-Cr-C steel*, Materials Science and Technology, 20, pp.1447-1454, 2004.
- [6] Ławrynowicz, Z., *A discussion on the mechanism of bainite transformation in steels*, Technology and Materials, Gdańsk, Politechnika Gdańska, 4, pp.149-155, 2006, (in Polish)
- [7] Ławrynowicz, Z., *Mechanism of bainite transformation in Fe-Cr-Mo-V-Ti-C steel*, International Journal of Engineering, 12, pp.81-86, 1999.
- [8] Christian, J.W., *Theory of transformations in metals and alloys*, 778, Oxford, Pergamon Press, 1965.
- [9] Bhadeshia, H.K.D.H., *Bainite in Steels*, Institute of Materials, 1-458, London, 1992.
- [10] Shiflet, G.J., Hackenberg, R.E., *Partitioning and the growth of bainite*, Scripta Materialia, 47, pp.163-167, 2002.
- [11] Bhadeshia, H.K.D.H., *Diffusion of carbon in austenite*, Metal Science, 15, 477-479, 1981.
- [12] Kutsov, A. at al., *Formation of bainite in ductile iron*, Materials Sci. and Engineering, A273-275, pp.480-484, 1999.
- [13] Bhadeshia, H.K.D.H., Christian, J.W., *Bainite in Steels*, Metallurgical Transactions A, 21A, pp.767-797, 1990.