Density and thermal expansion coefficients of liquid and austenite phase in lamellar cast iron

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Abstract: Volume change related defects formation mechanisms are an important detracting phenomenon in production of complex shaped cast components. Among different technical alloys, cast iron behaves in a complex manner due to the combined volume change of the formed phases. The liquid and the austenitic phase are contracting while the graphite phase is expanding during the solidification. The complex volume change in combination with complex casting shapes causes a considerable deviation from isotropy in the solidification domain. The mentioned difficulties are considered the main reason why an extensive research work is condensed in the literature within this topic. The multitude of reported experimental set up and the various efforts to interpret the volume change phenomena in terms of density and thermal expansion coefficients makes the results difficult to compare from different sources. With these difficulties in mind, the present paper presents a broad experimental series and measures unidirectional linear deformation of an industrially spread lamellar cast iron alloy system (Fe-C-2Si) using the push-rod based dilatometer technique. The measurements are divided into two major groups with respect to the liquid iron deformation over the liquidus temperature line, and the austenite deformation below the solidus temperature line. The obtained results are interpreted as thermal expansion coefficients, density variation slopes, and density data at the liquids and solidus temperature. The obtained results are compared with literature data and with calculated values by the Thermo Calc software.

Key words: density; thermal expansion coefficient; dilatometer; cast iron; Fe-C-2Si; CALPHAD

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As part of moving towards a more sustainable production of diesel engines for heavy vehicle applications, the ability to predict casting defects has become ever so important. One such defect type is shrinkage porosity. In lamellar graphite iron, shrinkage porosity will form a network of voids, with entries at the surface of the cast component^[1]. In diesel engines, shrinkage porosity defects may cause leakage between the fuel and cooling channels and will also result in decreased mechanical properties. The mechanisms behind the formation of shrinkage porosity are many and complex, however, one of them is the change in volume and density of the material during solidification.

In order to model the solidification process for cast components correctly, it is of essence to know how the material will actually behave. Although measuring the volume and density changes during solidification has proven quite a difficult task, there are some data available in literature. Lucas^[2] measured the liquid densities of a number of Fe-C alloys, with carbon contents ranging from 0wt.% to 4.27wt.%. Data from the measurements can be found in Fig. 1, together with the data from other sources. Kusakawa et al.^[3] have shown a linear relationship between melt density and temperature. Although it could not be seen that the carbon equivalent influenced the density to any greater extent, it was observed that the combination of carbon and silicon had an effect on density^[3]. Since these experiments were conducted on hyper-eutectic

lamellar and nodular irons, the density change was decreased below the liquidus temperature, due to the precipitation of primary graphite. It was also found that the graphite shape affected the amount of contraction-lamellar graphite to a lesser extent than nodular graphite [3].

Fig. 1: Density data found in literature [2-7]

In order to produce sound castings, often of complex geometry, the industry relies on various simulation software for the prediction and avoidance of defects. These computer programs employ databases with different material properties listed, such as density among the thermophysical properties. However, the need for a better understanding of how defects such as shrinkage porosity form has inspired the present experimental setup. Measurements of how the volume of the molten material changes with temperature can be made with the help of a conventional dilatometer. How the material behaves in the solid state can be investigated in the same way. When it comes to the two-phase areas, where liquid and solid phases co-exist, it is a bit more difficult to discern what is really measured. Hence, if the density values at the liquidus and solidus of the iron-carbon phase diagram could be defined, it would be a tool for predictions of density in the mushy zone.

The scope of the present work is to measure the thermal expansion coefficient and calculate the resulting density of the liquid and austenite phase in materials aiming to produce lamellar cast iron. Specifically, the density of the liquid and austenite phase will be focused along the liquidus and austenite temperature line as a function of the carbon content. The intended measurement method will use the standard unidirectional push-rod based dilatometer. The obtained results will be compared to literature data and simulated data by Thermo Calc software designed to calculate thermophysical properties. Literature results from different authors cover results obtained from isolated chemical compositions and different experimental and interpretation methods. The setup of the present investigation will allow information about the density of the liquid and austenite phase as a function of a wide chemical composition interval, derived from a coherent experimental and interpretation method.

1 Theoretical background

The temperature dependence of the density in the liquid state has been investigated by Steinberg [8] for a number of metals and semi metals. The temperature dependence of the density in the liquid state, Λ , at constant pressure, can be written as:

$$\Lambda = \left(\frac{\partial \rho}{\partial T} \right)_P \quad (1)$$

where ρ is density in $\text{g}\cdot\text{cm}^{-3}$ and T is temperature in K. Through the assumption that the fractional change in density between 0 K and the boiling temperature is constant, Steinberg arrived at the equation:

$$\Lambda = -\frac{\rho_m}{CT_b - T_m} \quad (2)$$

where ρ_m is the density at absolute melting temperature in $\text{g}\cdot\text{cm}^{-3}$, T_m is the absolute melting temperature in K, C is a constant and T_b is the boiling temperature.

Based on experimentally retrieved data, the conclusion has been drawn that the temperature dependence of the density for liquid metals is linearly related. Using Steinberg's formulas, Jimbo and Cramb [5] stated the equation:

$$\rho = \rho_m + \Lambda(T - T_m) \quad (3)$$

From experimental data and a least-squares treatment of these, the following equation was derived (based on Eq. 3):

$$\rho = (7.10 - 0.0732 \times \%C) - (8.28 - 0.874 \times \%C) \times 10^{-4} (T - 1823) \quad (4)$$

where T is the temperature in K and $\%C$ is the carbon content in wt.%. The liquid density thus varies with temperature and carbon content.

Interpolating the Equations of Jimbo & Cramb and Ogino [9], and taking silicon into account, Mills [4] arrived at the values found in Fig. 1.

From Fig. 1 it can be deduced that the density of an iron-carbon alloy depends on both the carbon content and the temperature. Kagawa et al. [10] came to the conclusion that the carbon equivalent could not be used to form a relationship between expansion and the chemical composition of lamellar graphite iron. However, to describe the expansion rate during the eutectic solidification, the modified carbon equivalent could be used, giving a linear function.

Cooling conditions will affect the fraction and type of phases that are formed in cast iron during solidification. Chen et al. [11] have shown that these different phases, which comprised the microstructure, will considerably influence the specific volume (i.e. the inverted value of density) of cast iron. It could also be said that silicon affects the solubility of carbon in austenite, thereby indirectly increasing the specific volume of austenite.

When it comes to carbon as an interstitial atom in the fcc lattice, it should fit into the limited octahedral space between the iron atoms. If the rigid sphere model is applied, atoms like these will expand the lattice if they are larger than the interstitial space. However, Ledbetter and Austin [12] found that dilatation is not only a matter of the size of the atom,

but possibly also about the strength of the bond between the different atoms. Comparing carbon and nitrogen as interstitials, it was found that although the nitrogen atom was smaller than the carbon atom, it expanded the iron lattice more than the larger-sized carbon atom did. Lucas^[12] has observed that an addition of 1% carbon to austenitic Fe-C will result in a change in specific volume between 2.2% and 3.9%. In liquid state, this change turned out to be less explicit (around 1%). The reason for this is due to a more yielding lattice in the liquid state. A change of slope of the curve specific volume vs. compositions was also noticed. This change occurred around 8at.% (approx. 1.7wt.%) and possible reasons were discussed. Among these, the ordering of the atoms, the variation in lattice parameter with temperature and the tendency of carbon to create vacancies that it will occupy, could be mentioned. Olsson^[13] has also discussed the influence of carbon in the liquid of Fe-C alloys and the conditions prevailing when carbon is expanding the lattice and when it does not. These observations regard liquid Fe-C alloys, where the lattice structure is replaced by short range order. The theory states that carbon in low-carbon alloys will distribute in a way that it is non-expanding, thereby the density increases. With increasing of the temperature, these non-expanding positions will also increase in number. Thus, at low carbon contents, the carbon atoms would place themselves in such interstitial positions that they would not expand the iron lattice. The solubility limit could be expressed by a temperature dependent exponential function. At values above the solubility limit, carbon will start to expand the lattice.

Phase transformations are governed by the change in free energy^[14]. For a unit volume of a substance, the Helmholtz free energy can be expressed comprising internal energy, pressure, volume, temperature, and entropy. The entropy is a measure of the amount of disorder in a system, in a crystal structure, the entropy is low, and in a gas, the entropy is high^[15]. Disorder in the solid, crystal state comes from the thermal vibrations of the atoms at the lattice points^[14]. In the liquid state, disorder also results from structural disorder. The thermal energy at higher temperatures will increase the occurrence of vacancies in the lattice structure until the long-range order is dispersed and replaced by a short-range order. Hence, the liquid has no fully ordered structure of the solid state, but it is not as chaotic as the gaseous state. This change from ordered crystal structure to less ordered structure will, in most materials, entail an increase in volume. Likewise, the arrangement of atoms into a crystal structure taking place during solidification will, in most cases, mean a decrease in volume. Looking closer at the formation of disordered systems into ordered ones, the bonds to the nearest neighbour must be investigated. In solids, these bonds will point in specific directions, but in liquids, it is equally probable that the nearest neighbour would be found in any direction^[16]. Structures of liquids are therefore represented by distribution functions that will give the probability of the existence of a given number of atoms at certain positions. Investigations of undercooled metallic melts have shown that an icosahedral structure is present in these melts, more pronounced at the

lower temperature^[17]. This structure could also be found in melts above the liquidus temperature. It was also found that the icosahedral structure presented in melts, forming fcc and bcc structure in the solid state.

Even though the occurrence of melting and solidification are situated at the same positions in the phase diagram, they are two different processes. So is, for instance, undercooling a phenomena at solidification, but as heating above the melting temperature, a solid metal will not remain in the solid state^[18]. It has also been suggested that thickness and structure of a melting interface is different from a solidifying one.

2 Experimental procedure

As previously mentioned, there are many methods for measurements of material expansion and contraction.

An extensive overview of the problems related to volume change measurement in lamellar cast iron was published by Svidró and Diószegi^[19] where they pointed out the importance of the measurement method and the strong anisotropic deformation property of the solid phase in lamellar cast iron. The standard linear push-rod dilatometer intended for use in the present work have a detracting property when the deformation in solid state is investigated, depending on the degree of anisotropy of the investigated alloy. Based on the considerable anisotropic property of cast iron alloy, many different experimental setups were created to measure the expansion and dilatation of cast iron where the push-rod dilatometer method is an apart group used for investigating cast iron. In the Results section below, Table 5 shows the measurement methods for the referenced papers, together with the type of alloy tested.

According to the scope of the present work for the calculation of the density at the liquidus and solidus temperature two different experimental series were produced.

For the liquidus line, a series of samples with carbon contents ranging from 2 to approx. 4wt.% and with a silicon content around 2wt.% were cast. (The level of silicon used in these experiments is close to the one existing in cast iron used for diesel engines.) Other elements were to be kept to a minimum.

For the solidus line, another series was cast with carbon contents ranging from 0.5 to 2wt.%. As in the previous series, the silicon level was around 2wt.% with as little as possible of other elements.

2.1 Materials for investigation of melt density

Eight grey cast irons with different amounts of carbon were cast and poured in quick cups for thermal analysis and in steel moulds for samples. The different melts were prepared in a Minac induction furnace from pig iron with additions of ferrosilicon and ferro-flakes to adjust the carbon and silicon contents. Coins were taken from each melt for spectral analysis. The chemical composition of the grey cast iron is listed in Table 1.

Table 1: Chemical compositions in wt.%, uncompensated liquidus temperature and maximum temperature used in the experiments for the grey iron alloys. The liquidus temperatures are from logged data, and on cooling these temperatures are lower than actual temperature, due to position of the thermocouple

Samples	C	Si	Mn	P	S	CE	T_{liq} (°C)	T_{max} (°C)
C400	3.8	1.74	0.53	0.025	0.017	4.39	1,147	1,276
C375	3.63	1.68	0.38	0.023	0.013	4.20	1,167	1,278
C350	3.38	1.91	0.45	0.02	0.02	4.02	1,197	1,304
C325	3.11	1.82	0.48	0.02	0.02	3.72	1,238	1,370
C300	2.95	1.85	0.38	0.02	0.02	3.57	1,252	1,365
C275	2.74	2.11	0.46	0.02	0.03	3.45	1,283	1,380
C250	2.43	1.8	0.44	0.02	0.03	3.04	1,319	1,410
C225	2.33	1.73	0.43	0.02	0.03	2.91	1,336	1,435

For the dilatation experiments, a conventional push-rod dilatometer from Netzsch (DIL 402C) was used. The cast material was cut into pieces 12.00 ± 0.05 mm long and a diameter of 6.40 ± 0.02 mm. The pieces were ground to exhibit a smooth surface. The cast iron samples were put in an aluminium oxide crucible, basically a hollow cylinder with one piston at each side to contain the sample. Lubrication, in the form of graphite powder, had to be used in order to extract the samples from the crucible after the experiment. The crucible, prepared with a sample, was then put in the measurement chamber of the dilatometer, with one end positioned against a flat, rigid surface and the other end in contact with the pushrod. The load that the pushrod exerted on the piston was set to 40 cN. Before the sample was placed in the chamber, it was made sure that the pistons and the sample ran smoothly within the encasing cylinder to minimize the occurrence of false detection data due to some part getting locked in one position.

The temperature program for each alloy was chosen based on data from the cooling curves obtained at the casting. The maximum temperature for each alloy was set within a range of 90 to 130 °C above the liquidus temperature, see Table 1. Prior to the investigation of the alloys, the temperature program was run with an aluminium oxide standard, to establish a baseline. All the experiments were carried out in helium atmosphere. The gas purity was $\geq 99.999\%$ and the chamber was evacuated and filled three times before the start of the temperature program. A slight overpressure was generated at the last filling of the chamber, in order to monitor any leakage. The heating and cooling rates were both set to $8\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, with an isothermal time of 30 min at the maximum temperature.

The registered data for each run was plotted in a graph using the Proteus software, provided by Netzsch. Additional evaluation was made using MATLAB. The temperatures stated in this paper are the logged temperatures from the measurements. Due to the position of the thermocouple, the actual temperature in the sample on cooling will be somewhat higher than the logged temperature.

Since there were severe problems with gas evaporating from the molten samples, disturbing the measurements, an addition of

approximately 0.02wt.% aluminium had to be made to all of the grey iron alloys before testing.

2.2 Materials for investigation of austenite density

The steel samples were produced in a similar way as the cast iron samples. Six alloys, of varying amounts of carbon, were cast in furan sand moulds. Two different sand moulds were used, a closed cavity and an open one. The closed mould cavity was shaped as bars of $\Phi 15$ mm with a length of 100 mm. The cavities of the open mould were shaped as cylinders, slightly conical, with a bottom diameter of 50 mm and a top diameter of 55 mm, with a height of 140 mm. The alloys cast as bars were directly machined into dilatometer samples and the alloys cast as cylinders were first sawed into bars, then machined into dilatometer samples. It was discovered that the alloys cast as bars contained a large degree of shrinkage porosity. Samples taken from the quick-cups were used for thermal analysis. Coins for spectral analysis were taken and the chemical composition of the alloys is listed in Table 2.

The temperature program for the steel samples was based on previous trials when the metal would start to deform, as well as of a calculated phase diagram. The maximum temperature used in the experiment was selected to reach below deformation temperature but high enough to be in the vicinity of the solidus temperature. The selected temperatures can also be found in Table 2. The steel samples were tested without the crucible, the isothermal time at maximum temperature was therefore reduced to 20 min. A calibration standard, aluminium oxide standard, was used in this part as well, in order to establish a baseline. The load from the pushrod was also reduced, to 25 cN. Heating and cooling rates were kept the same, $8\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

All of the samples were weighed in air and water before and after the experiment in order to calculate the density at room temperature, according to the following equation:

$$\rho_{\text{sample}} = \frac{m_{\text{a}} \times \rho_{\text{w}}}{m_{\text{a}} - m_{\text{w}}} \quad (5)$$

where m_{a} is the mass of the sample weighed in air, ρ_{w} is the

Table 2: Chemical compositions in wt.% and estimated solidus and maximum temperature used in the experiment for the steel samples

Samples	C	Si	Mn	P	S	CE	T_{sol} (°C)	T_{max} (°C)
C200	1.83	2.09	0.364	0.018	0.032	2.53	1,155	
C175	1.51	2.04	0.386	0.015	0.027	2.2	1,155	
C150	1.49	2.02	0.374	0.013	0.020	2.17	1,218	1,167
C125	1.14	1.89	0.379	0.007	0.025	1.77	1,241	1,231
C100	1.08	1.88	0.339	0.009	0.027	1.71	1,264	1,218
C080	0.973	2.01	0.353	0.008	0.021	1.65	1,304	1,268
C050	0.593	1.75	0.413	0.004	0.021	1.18	1,355	1,280

density of water, and m_w is the mass of the sample weighed in water.

2.3 Thermo-Calc

A well-known software for the calculation of thermophysical properties is Thermo-Calc, which is based on the CALPHAD method. The software calculates density and thermal expansion coefficients based on molar volumes [20]. The database of molar volumes is compiled of experimental data from measurements of lattice parameters and coefficients of thermal expansion. The molar volume can be calculated [20] according to:

$$V_m(T) = V_0 \exp\left(\int_{T_0}^T 3\alpha dT\right) + \Delta V_m^{\text{magn}}(T) \quad (6)$$

where V_0 is the molar volume at the reference temperature T_0 , $\Delta V_m^{\text{magn}}(T)$ the magnetic contribution to the molar volume, 3α is the coefficient of thermal expansion for cubic elements of phases in the nonmagnetic state. The thermal expansion coefficient can be modeled using a polynomial:

$$\alpha = a + bT + cT^2 + dT^3 + eT^{-2} \quad (7)$$

The coefficients are evaluated from experimental data.

3 Results

Each dilatometer curve was analyzed in the Netzsch Proteus software for possible inflexion points, which, for the steel samples, would give a hint on where the austenite part of the curve would be located, and for the LGI samples, where the melt would be located. A graphic explanation can be found in Fig. 2(a) and (b).

For the grey cast iron samples in the liquid range, two different types of curves could be distinguished. The majority of the samples were categorized as Type-I curves, where no clear inflexion point at the presumed liquidus temperature could be distinguished. The Type-II curves, on the contrary, often had a clear inflexion point at the liquidus temperature and the slope of the curve in the molten area and in the two-phase area could differ quite markedly from the Type-I curves.

3.1 Thermal expansion coefficient, α

For the calculation of the α -values, data was exported from the Proteus software to MATLAB and used for calculating a similar curve in MATLAB, giving the change in length per initial length ($\Delta l/l_0$) vs. temperature (T). The first derivative

Fig. 2: (a) Dilatometer and temperature curves for a triple sample of alloy C050. The clear volume change displayed by the dilatometer curves signifies the solid-state transformation; (b) Phase diagram (generated in Thermo-calc) based on the chemical composition of sample C050

of that curve, i.e., Eq. (8) would be the coefficient of linear thermal expansion, α .

$$\frac{d(\Delta l / l_0)}{dT} \quad (8)$$

The thermal expansion coefficient of each curve in the series of samples tested in the austenitic range was calculated by a curve fitting model; the values were taken from the heating part of the program. The values of the thermal expansion coefficient in Tables 3 and 4 are the average values of the three tested samples of the same alloy. The calculations for the grey

iron samples were made by taking a moving average of the derivative. Focus in the liquid range was on the cooling part of the cycle and the values were taken from that area of the curves. It was found that the thermal expansion coefficient varied only slightly with carbon content. However, in comparison with the samples tested in the austenitic range, the values differed significantly from the values obtained for the liquid. The thermal expansion coefficients in the liquid range are listed in Table 3, and the ones in the austenitic range can be found in Table 4.

Table 3: Thermal expansion coefficients of liquid lamellar graphite iron

Samples	C (wt.%)	CE (wt.%)	Measured α (cooling)	Temperature interval measurement (°C)	α Thermo-Calc	Temperature interval Thermo-Calc (°C)
C400	3.8	4.39	1.04×10^{-5}	1,202–1,276	9.14×10^{-6}	1,170–1,260
C375	3.63	4.20	1.08×10^{-5}	1,200–1,278	9.80×10^{-6}	1,170–1,260
C350	3.38	4.02	1.08×10^{-5}	1,190–1,300	1.05×10^{-5}	1,200–1,290
C325	3.11	3.72	1.07×10^{-5}	1,252–1,358	1.10×10^{-5}	1,240–1,330
C300	2.95	3.57	1.06×10^{-5}	1,261–1,364	1.14×10^{-5}	1,260–1,350
C275	2.74	3.45	1.05×10^{-5}	1,267–1,380	1.21×10^{-5}	1,290–1,380
C250	2.43	3.04	1.07×10^{-5}	1,305–1,410	1.30×10^{-5}	1,320–1,410
C225	2.33	2.91	1.06×10^{-5}	1,340–1,434	1.32×10^{-5}	1,340–1,430

Table 4: Thermal expansion coefficient (α) for the samples in austenitic range

Samples	C (wt.%)	CE (wt.%)	Measured α (heating)	Temperature interval measurement (°C)	α Thermo-Calc	Temperature interval Thermo-Calc (°C)
C050	0.593	1.18	2.20×10^{-5}	939–1,267	1.74×10^{-5}	1,130–1,270
C080	0.973	1.65	2.20×10^{-5}	918–1,254	1.61×10^{-5}	1,200–1,240
C100	1.08	1.71	2.17×10^{-5}	951–1,204	1.55×10^{-5}	1,170–1,210
C125	1.14	1.77	2.20×10^{-5}	974–1,218	1.53×10^{-5}	1,050–1,167
C150	1.49	2.17	2.95×10^{-5}	1096–1,153	1.44×10^{-5}	1,050–1,170

From the data in Table 3, it can be deduced that there exists a linear relationship between the coefficient of thermal expansion and the carbon equivalent in the liquid state. This is valid both for the current measurements and for the data calculated by Thermo-Calc.

The thermal expansion coefficient in the austenitic range seems to be quite stable except alloy C150. This may be because of the difficulties of measuring since the austenitic interval is smaller with a higher carbon content.

3.2 Density, ρ

The calculations of the density for all of the alloys are based on the assumption of material isotropy. Thus, the axial expansion could therefore be set as proportional to the expansion of the diameter, i.e.

$$\frac{\Delta l}{l_0} = \frac{\Delta d}{d_0} \quad (9)$$

where Δl is the change in length, and Δd is the change in diameter from the initial length, l_0 , and the initial diameter, d_0 .

The length and the diameter of the sample at an arbitrary temperature, T , can be expressed as

$$l(T) = l_0 + \Delta l(T) \quad (10)$$

and

$$d(T) = d_0 + \Delta d(T) \quad (11)$$

The density of a cylindrical sample (at an arbitrary temperature) can be written as

$$\rho(T) = \frac{4 \times m_a}{(d(T))^2 \times \pi \times l(T)} \quad (12)$$

where m_a is the mass of the sample (in air), for the samples tested in the austenitic range, measured before the experiment and for the samples tested in the liquid range, measured after the experiment.

For the samples tested in the austenite range, the measured curves had to be extrapolated up to the solidus temperature before the calculations of the density values. As these samples were tested without the encasing cylinder, material isotropy was assumed, and the calculations followed the pattern described by Equations [9-12].

The density calculations for the liquid samples build on the same assumption, however, in the case of radial expansion, these samples were confined by the container. The diameter of these samples at an arbitrary temperature in the molten state was therefore set to be the inner diameter of the aluminium oxide container at the same temperature (Thermal expansion of aluminium oxide is confirmed according to DIN 51045/89). Since the encasement of the samples in a cylinder meant that there initially would be a gap between the sample and the cylinder wall, the sample would at one point during melting collapse and fill up the whole cylindrical cavity, displaying a large and rapid decrease in length. In order to calculate the density of the melt, the volume of the sample, measured after the experiment, was set to be equal to the volume displayed at the end of the experiment. Regarding the density measurements, the slope of the curves of density versus temperature, exhibited by each sample, was calculated. An average value of the slopes of the samples of each alloy was taken, both in the liquid and the austenitic region. This would be equivalent to the temperature coefficient, Δ , described by Eq. (1).

A presentation of calculated slopes of the density curves in the liquid range, based on experimental data, compared with data from calculations in Thermo-calc can be found in Table 5, together with literature data.

Density values at the liquidus temperatures are shown in Fig. 3, together with data from calculations with Thermo-Calc and literature. For alloy C325, only two values were obtained, both are given in the figure. Density values from Ash & Saeger [21] and Benedicks et al. [7] were calculated from given liquidus temperatures. The values from Saunders et al. [6] were estimated based on liquidus temperatures calculated with Thermo-calc. Values given in the papers by Lucas [2], Kusakawa et al. [3] and Jimbo & Cramb [5] are also presented in the figure.

Fig. 3: Density at liquidus temperature. Data from measurements, calculations with Thermo-Calc and literature

The values by Lucas [2] give the impression that the higher the carbon content, the higher the density. This would be in line with the theory of carbon as an element that will occupy voids and hereby create a denser material. However, from a cast iron perspective, carbon will precipitate mainly as graphite and the common understanding is that this process will compensate for some of the solidification shrinkage. Another factor to take into account is that the liquidus temperature decreases as the composition of the alloy gets closer to the eutectic point, and that a lower temperature generally means a higher density. There is need to take into account that the alloys in Lucas' investigation were of a Fe-C composition and they did not contain silicon as an alloying element (i.e. did not contain silicon as an alloying element was also something to keep in mind). The density was also calculated for the samples in the austenitic range, as shown in Fig. 4.

Table 6 shows a comparison between the slope of the density curves from measurements and calculations in Thermo-calc.

Fig. 4: Density at solidus temperature, comparing with values calculated with Thermo-calc

4 Discussion

As density is a property that cannot be measured directly and the value read from a scale, calculations must always be involved in the pursuit of density data. This circumstance opens up the procedure to interpretations, which may influence the results to a smaller or larger extent. Looking at the results from the experimental measurements in comparison with the data obtained using Thermo-calc, the consistency regarding the alpha values (thermal expansion coefficient) is quite good. For the density values the similarity diverges are found. This may, however, not only be a question of calculation method but also a matter of experimental method.

Regarding the temperature data stated in the Tables, it must be kept in mind that these are values logged by the experimental equipment. Due to the position of the thermocouple - it is placed near either the outer container wall or the sample itself - the temperature in the centre of the sample will be higher than the logged temperature on cooling and lower on heating.

Since literature data is scarce, comparisons have in some

Table 5: Slopes of the density curves

References	Methods	Alloys	Temperature interval (°C)	Slope (kg·m ⁻³ ·°C)
Benedicks et al ^[7]	U-pipe	2.45wt.% C	1,465–1,410	-1.6199
		0.09wt.% Si		
		3.98wt.% C	1,225–1,400	-2.0835
		0.11wt.% Si		
		4.25wt.% C	1,205–1,345	-2.0525
		0.13wt.% Si		
Ash & Saeger ^[21]	Pycnometer (graphite crucible)	3.10wt.% C	1,264–1,455	-0.8001
		1.69wt.% Si	1,315–1,455	-0.7158
		3.76wt.% C		
Lucas ^[2]	Max. Bubble pressure	2.10wt.% Si	1,200–1,500	-0.7536
		Fe-C		
		4.27wt.% C	1,200–1,500	-0.7548
		4wt.% C		
		3.5wt.% C	1,300–1,500	-0.7409
Kusakawa et al ^[3]	Pycnometer (silica crucible)	3wt.% C	1,300–1,500	-0.7942
		3.7–3.8wt.% C	1,358–1,475	-1.09
		2.6–2.7wt.% Si		
Jimbo & Cramb ^[5]	Sessile drop	3.91wt.% C	1,247–1,553	-0.536
Mills ^[4]	Calculation	3.74wt.% C	1,190–1,500	-0.5
		1.89wt.% Si		
Saunders et al ^[6]	Simulation	2.5wt.% C	1,412–1,603	-0.9009
		4.27wt.% C	1,203–1,603	-0.83
Present work	Dilatometer	C400	1,147–1,276	-0.2121
		C375	1,167–1,278	-0.2187
		350	1,197–1,304	-0.2136 ^a
			1,192–1,241	-0.5081 ^b (Type II)
		C325	1,238–1,370	-0.2152 ^b
			1,229–1,363	-0.4237 ^b (Type II)
		C300	1,252–1,365	-0.2215
		C275	1,283–1,380	-0.2164
		C250	1,319–1,410	-0.2197
		C225	1,336–1,435	-0.2211
Thermo-Calc	Calculation	C400	1,170–1,260	-0.5350
		C375	1,171–1,260	-0.5470
		C350	1,200–1,290	-0.5429
		C325	1,240–1,330	-0.5501
		C300	1,260–1,350	-0.5540
		C275	1,290–1,380	-0.5559
		C250	1,320–1,410	-0.5662
		C225	1,340–1,430	-0.5695

Note: The values are from measurement data, together with calculated data from Thermo-Calc and literature data. Temperature data is based on the values logged at the experiment, which in this case will be lower than the temperature in the sample, due to position of the thermocouple. (a) Two sets of data; (b) One set of data. Data from Lucas, Ash & Saeger, Benedicks and Saunders: slope calculated from data given in paper.

Table 6: Slopes of density curves in the austenitic range: data from measurement and calculations with Thermo-calc

References	Methods	Alloys	Temperature interval (°C)	Slope ($\frac{dp}{dT}$) ($\text{kg}\cdot\text{m}^{-3}\cdot^\circ\text{C}$)
Present investigation	Dilatometer	C050	923–1,266	-0.4769
		C080	930–1,254	-0.4728
		C100	956–1,203	-0.4641
		C125	978–1,217	-0.4719
		C150	1096–1,152	-0.6167
Thermo-Calc	Calculation	C050	790–1,318	-0.4811
		C080	908–1,253	-0.4658
		C100	985–1,250	-0.4667
		C125	976–1,230	-0.4660
		C150	1,040–1,197	-0.4618

cases been made with Fe-C alloys, thus not containing silicon at all, or in very small amounts. The experimental data for Fe-C-Si alloys are the works of Kusakawa et al.^[3] and Ash & Saeger^[21]. Both these investigations have been performed with the pycnometric measurement method. This method does, however, not enable monitoring of the expansion and contraction behaviour with temperature but measures the density one temperature at a time. The method is considered reliable as long as the volume of the vessel at the investigated temperature is truly known.

In the current experiments, it was clear that two types of dilatation curves could be distinguished. The Type-I curve (so called because it turned out to be the more common of the two) displayed no clear inflection point at the presumed liquidus temperature, thus making it difficult to discern when the solidification process actually began. The Type-II curve, on the other hand, showed a clear inflexion point at liquidus temperature, and, in some cases, also at other temperatures (assumed to be caused by the release of gaseous elements).

One of the problems with dilatometer measurements, when the sample is remelted, is that the material will undergo a certain change. The microstructure of the solidified sample will not be the same as in the initial material. Another problem is the encasing of the sample. Release of gas will in many cases interfere with the measurements, as it has nowhere to go in the container but to occupy space that the molten metal should occupy. Moreover, conditions for nucleation and solidification differ between the aluminum oxide container and an ordinary sand mould. Favorable nucleation sites in the cylinder will be the double-curved surface that arises between cylinder wall and piston of the container. In the experiment, the focus has been set on the melt for the molten samples, thereby avoiding some of the negative aspects of remelting.

Regarding the samples for measurement in the austenitic range, isotropy was assumed. However, there was no way to monitor if that assumption was true. It may well be that the dilatation in radial direction is greater, or smaller, than in axial direction.

Evaluation of the first set of samples tested in the austenitic range revealed large areas of shrinkage porosity in many of them, they had therefore to be repeated with new samples taken from quick-cups. However, the two alloys with the highest carbon content (C175 and C200) were found to display little data or none at all in the austenitic range, they had therefore to be excluded from this study. The remaining samples of alloys, C050–C150, were either found to be free of pores or contain what could be normally expected. However, another factor that probably has influenced the measurements, especially in alloy C150, is the presence of graphite nodules.

In the measurements and the following calculations, it has been assumed that the pressure is constant. There is, however, no way to know if that is true. It may well be that the pressure conditions in the samples tested in the liquid range is responsible for the occurrence of two types of curves. To find any truth in this claim, further investigations will be necessary.

Measurements in a dilatometer of this kind, where the thermocouple is placed adjacent to the outer wall of the sample container, means that the logged temperature will not be the same as the sample temperature. On heating, the sample will therefore be cooler than what the measurement data will tell, and on cooling, it will be warmer.

As the silicon content was kept at the same level for all of the alloys, it is hard to say anything about its influence on the density. This will also have to be the subject of further investigations.

5 Conclusions

(1) A complex experimental and interpretation procedure was applied to calculate the density variation of the liquid and austenite phase in lamellar cast iron. The complexity of the interpretation procedure is caused by the incorporation of gaseous porosities in the liquid and the presence of shrinkage porosity in the austenitic matrix when the volume change was measured. Use of elements such as aluminum contributes to deoxidate the liquid and reduces the tendency for gas porosity formation in the solidifying sample. The shrinkage porosity forms generally in the low carbon-containing samples and is reduced by producing the samples under rapid solidifying conditions.

(2) The thermal expansion coefficient, which is the primary result of the applied experimental measurement, was compared with the calculated thermal expansion coefficient by the Thermo-Calc software. The measured and calculated data for the liquid phase expansion were in the same range, while a slight difference was observed between the measured and calculated thermal expansion coefficient of the austenite phase. The observed differences are interpreted as being dependent

on the general assumption of material isotropy in both the liquid and austenite phase. While the observed unidirectional length deformation in the dilatometer is nearly isotropic in the case of the liquid phase measurement, the length deformation registered only in axial direction for the austenite sample is anisotropic. In the case of the calculated data in Thermo-Calc a perfect isotropy is considered.

(3) The slope of the density variation as a function of temperature for the various alloys and the density data in the close vicinity of the liquidus and solidus line are calculated data derived from the primary measurement of the unidirectional length deformation. Literature data are available only for the density slope over the solidus temperature and the density data at the solidus temperature for comparison. The literature and the interpreted measurement data are found to be in the same range. The calculated data based on the experimental measurement in the austenite phase and in the vicinity of the solidus line can be considered as novel data since no literature data are found.

(4) The major benefit of the obtained data is considered to be the wide range of used carbon content for unextensively used industrial cast iron alloy investigated and interpreted under similar experimental conditions.

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