Differential Scanning Calorimetry and Microscopy Study of Transformations in Ductile Cast Irons: Part II. Continuous Cooling

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The study of the cooling processes of ductile cast irons using the differential scanning calorimetry technique in the temperature range of 20–950°C shows three thermal effects. They are due to three transformations: the restoration of magnetic properties ($T_{Cc}$), austenite-pearlite transformation ($T_{Pc}$), and austenite to ferrite plus graphite transformation ($T_{Fc}$). The data allow studying the kinetics of the transformations at different testing conditions, cast iron composition and as-cast microstructure. During cooling the temperature sequence at which the transformations occur is $T_{Fc}>T_{Pc}>T_{Cc}$. The increase in cooling rate changes the intensity and temperatures of the different transformations in different ways. This results in the overlapping of the thermal effects.

KEY WORDS: differential scanning calorimetry; microscopy; ductile cast iron; heat treatment; microstructure; kinetics; phase transformations; magnetic properties.

1. Introduction

This second part of the two-part paper on differential scanning calorimetry and microscopy study of ductile cast irons is concerned with phase transformations during continuous cooling at constant rates. In the practice of casting and heat treatment of ductile irons, the final stage is always unavoidably cooling. Therefore it is important to characterise and understand the microstructural development during this process. The background of the types of materials investigated and previous research is given in part 1 of this paper.

2. Experimental Procedure

The composition and the production process of the two alloys studied, alloys 1 and 2 are given in the companion paper, part 1, and the references therein.

The cooling experiments were all conducted on samples after the heating experiments discussed in Ref. 1), at constant cooling rates using the differential scanning calorimeter. Therefore, the specimen preparation and the calorimetry procedures are identical to those described in part 1, where the three types of time-temperature cycle are detailed. In addition, a fourth type of time-temperature cycle was used for cooling experiments. The samples were heated at a constant rate of 20°C/min to 900°C, held at this temperature for 20 min, and then cooled to room temperature at various constant cooling rates ranging from 1 to 50°C/min.

It should be noted that because of the different types of cycle, the samples under cooling had different thermal history prior to cooling. The heating process will be mentioned below when presenting cooling results so that the effect of different history can be demonstrated.

Microstructural analysis was carried out using procedures described in part 1 of the paper. The microhardness measurement procedure is included in the Experimental Procedure of part 1. These will not be repeated here.

3. Results and Discussion

3.1. DSC Measurements and Phase Transformation Kinetics

Figures 1–4 show the DSC cooling curves of the two alloys at different cooling rates after being heated to 900°C at 20°C/min and held at this temperature for 20 min. Three phase transformations are apparent: the austenite decomposition to ferrite and graphite, the Curie transformation, and the austenite decomposition to pearlite. Alloy 1, which has a ferrite metal base in the as-cast condition, shows no sign of the third transformation, from austenite to ferrite and graphite phases, at low cooling rates. This indicates that there is enough time for the complete redistribution of carbon in the austenite to ferrite and graphite transformation, as shown by the large peak in the DSC curves in Fig. 1. The presence of a significant number of graphite inclusions helps for this process. The diffusion of carbon in the austenite and the grain boundary diffusion control the process. The carbon

* In this paper, austenite = A = γFe, ferrite = F = αFe.
Fig. 1. Results from DSC runs for alloy 1 employing 1°C/min (a) and 5°C/min (b) cooling rates. The samples were heated to 900°C at 20°C/min and held at this temperature for 20 min before cooling. Note: W/g = 10^3 W/kg; “exo” indicates that downward peaks are exothermic and upward peaks are endothermic.

Fig. 2. Results from DSC runs for alloy 1 employing 10°C/min (a), and 20 and 40°C/min (b) cooling rates. The samples were heated to 900°C at 20°C/min and held at this temperature for 20 min before cooling.
does not diffuse in the ferrite; in practice, at these cooling conditions there is no carbon in the ferrite. When in some parts of the austenite there is enough quantity of carbon and the temperature of the transformation is below the equilibrium temperature in the metastable system, the austenite transforms to pearlite. At higher cooling rates, there is not enough time for the complete austenite decomposition to ferrite and graphite, and the remaining austenite decomposes to pearlite, as shown in Fig. 2.

In the case of alloy 2, which has a ferrite plus pearlite metal base in the initial as-cast condition, the austenite to pearlite transformation is always present, even at very slow cooling rates (Figs. 3 and 4). However, the trend of increasing amount of pearlite phase in the final microstructure with increasing cooling rates is the same as in alloy 1.

Experiments were conducted to examine the effect of varying heating rates. Some samples were heated to 900°C using varying heating rates, isothermally held at this temperature for 20 min before cooling.

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Fig. 3. Results from DSC runs for alloy 2 employing 1°C/min (a) and 5°C/min (b) cooling rates. The samples were heated to 900°C at 20°C/min and held at this temperature for 20 min before cooling.

Fig. 4. Result from DSC runs for alloy 2 employing 20°C/min and 40°C/min cooling rates. The samples were heated to 900°C at 20°C/min and held at this temperature for 20 min before cooling.
perature for 20 min, and then cooled down with a rate equal to the heating rate used. In each figure of Figs. 5(a) and 5(b), Figs. 6(a) and 6(b), DSC curves with a same cooling rate but with different heating rates are compared. The results have demonstrated that the different heating regimes have no or relatively small effect on the subsequent cooling. The effect, if any, is within the error range of the equipment. This indicates that, especially after 20-min isothermal holding at 900°C, equilibrium has been achieved for all practical purposes, before cooling. Further experiments were carried out where the samples were heated to 900°C and cooled without holding at this temperature. It was found that the behaviour at cooling was identical for the same cooling rates to the samples with 20-min holding.
This means that the heat treatment history does not affect the kinetics of the phase transformation at cooling.

Figure 7 shows the continuous-cooling-transformation (CCT) diagrams constructed using the DSC cooling curves collected over different cooling rates. There is a certain degree of estimation because the start and the end of the peaks are not always clearly defined, especially with the presence of significant peak overlapping. It should also be mentioned that the thermal effect that is due to the magnetic properties restoration appears as a separate peak only at relatively low cooling rates. At the higher cooling rates this effect is “hidden” in the peak due to the formation of the ferrite phase that is the phase with magnetic properties.

3.2. Microstructural Investigations

Figure 8 shows the as-cast, initial microstructures of the two alloys imaged using an optical microscope without and with etching (from different but adjacent areas of the alloy casts). It can be seen that etching brings out the base metal microstructure, which is of prime interest in the present study. In particular, the pearlite structure is clearly seen in alloy 2, which accounted for approximately 15% of the base metal material. The micrographs that follow all used etched metallographic samples.

In agreement with the DSC observation and data interpretation given in the previous section, increasing quantities of pearlite were observed with increasing cooling rate (Figs. 9(c) and 9(f), Figs. 1 and 2). It is also noted that little change can be observed in the graphite phase, indicating that perhaps there is only a small fraction of this phase involved in the transformations, during both heating and cooling. This is reasonable even for Fig. 9(f) where massive amount of pearlite formed after fast cooling, because the pearlite only contains a small proportion of the carbon in the system compared to graphite that is of course 100% carbon. Figure 10 shows similar results, this time using differing heating rates as against the one heating rate of
Fig. 9. Microstructures of alloy 1 after cooling with different rates from 900°C (heating 20°C/min and holding 20 min).

Fig. 10. Microstructures of alloy 1 after heating and cooling with identical rates: heating temperature 900°C, holding 20 min.
Fig. 11. Microstructures of alloy 2 after cooling with different rates from 900 °C (heating 20 °C/min and holding 20 min).

Fig. 12. Microstructures of alloy 2 after heating and cooling with identical rates (heating temperature 900 °C, holding 20 min).
20°C/min used for samples in Fig. 9. As discussed in the previous section, the effect of heating rate is negligible in the DSC cooling curves, and comparison between Figs. 9 and 10 mirrors that in Fig. 5. It should be mentioned that further experiments were conducted with samples cooled from 900°C without the 20-min holding. The microstructure appears identical with and without 20-min holding, for the same cooling rates.

Parallel metallographic studies were carried out for alloy 2, where there is higher amount of pearlite in the as-cast base microstructure (Figs. 11 and 12). The graphite particles in alloy 2 are large and therefore much less dense than in alloy 1 (Fig. 8). So the distance between the graphite particles is larger in alloy 2. The higher pearlite quantity in alloy 2 is a result of large diffusion distance in this alloy.

It is reasonable that in all cases, pearlite after cooling is concentrated more in areas away from the graphite particles. There is a low carbon region around the graphite after the austenite to ferrite and graphite transformation because the carbon from these nearest areas can diffuse to and join the graphite. The zones around the graphite are depleted of carbon. For the zones that are away from the graphite, especially in alloy 2, there is not enough time for the carbon to redistribute and to join the graphite inclusions. In addition, the local silicon content also influences the carbon redistribution. The above influences are confirmed by the data from the microhardness measurements. For both ferrite and pearlite the microhardness results for each phase are in very wide ranges (see next section). The situation is essentially akin to the distribution of the secondary precipitation in nickel-base superalloys, where there is narrow zone around the primary γ’ containing no secondary precipitates.2

3.3. Hardness Measurements in Relation to Phase Constitution

The difference in pearlite volume fractions in the two alloys after cooling with varying rates, as shown in Figs. 9–12, is quantified using image analysis techniques. The results are shown in Figs. 13 and 14, for alloys 1 and 2, respectively, where \( V_h \) and \( V_c \) refer to the heating and cooling rates, respectively. In addition, the Vickers microhardness of the two different phases are measured using a Mitutoyo HM-124 machine, with a load of 50 g. The results are also shown in Figs. 13 and 14, for the two alloys. Due to the large variation in the hardness measurements within one phase, quite definitely outside the equipment errors, it is hard to discern the variation of the hardness as functions of cooling rate. It is conceivable, however, for the microhardness to vary according to the size and sub-structure within one phase. There is also the contribution from the limited thickness of the phase grain(s) under the indenter. It is clear, nevertheless, that pearlite is consistently harder than ferrite.

3.4. Comparison between the Results from Heating and Cooling

In this work it was found that for both heating and cooling there are three thermal effects noted as \( T_C \), \( T_F \) and \( T_P \). These effects are related to three phase transformations, namely:

- \( T_C \) – magnetic transformation,
- \( T_F \) – phase transformation related to the Fe–C–Si system,
- \( T_P \) – phase transformation related to the Fe–Fe₃C–Si system.

At continuous heating the sequence of these thermal effects is \( T_C \), \( T_F \), \( T_P \) (see part 1). Increasing the heating rate results in larger shifts of the \( T_F \) and \( T_P \) towards higher temperatures as compared to the shift of \( T_C \). Consequently, the thermal effects of the phase transformations are well separated and the overlap is insignificant. At cooling, the ideal sequence is \( T_F \), \( T_P \), \( T_C \). This is the reverse sequence.

* The second subscript refers to heating ("h") and cooling ("c").
of the transformations upon heating (see part 1 of this paper series), and the correct sequence of transformations according to equilibrium temperatures of them. These are elaborated in the Discussion section of part 1. The thermal effects are clear and separated only at relatively low cooling rates. Increasing the cooling rate results in significant changes of the character and the appearance of the thermal effects. This is because \(T_{Fe}\) and \(T_{Fe}\) do not appear as separate peaks and they are shifted significantly towards lower temperatures. As a result, they reach and even fall below the \(T_{C}\) temperature. Besides, for the \(T_{C}\) effect to appear, it is necessary to have the phase with the magnetic properties, i.e. the ferrite, to appear first. As a result the thermal effects from all transformations in practice are summed up and only one peak appears in the curves.

**Figures 15 and 16** are constructed to illustrate the differences in the transformations on heating and cooling. Some of the peak values for \(T_{F}\) and \(T_{C}\) are used to design these figures. It is clear from the figures that the increase of the heating and cooling rates does not influence much the peak corresponding to \(T_{C}\). For \(T_{F}\) there is a large temperature interval between the temperatures characterising this transformation at heating and cooling. It is clear that the temperature interval in which \(T_{F}\) varies is larger for cooling and smaller for heating. This means that at heating the transformation completes in conditions of relatively small degrees of overheating, above the equilibrium temperature of this transformation. At cooling the transformation takes place at higher degrees of undercooling and even at temperatures lower that the equilibrium temperature for the Fe-Fe₃C-Si system. Hence, some or all of the retained austenite at that stage can transform to pearlite.

### 4. Conclusions

1. The study of cooling in ductile cast irons by the differential scanning calorimetry technique in the temperature range of 900 to 20°C shows three thermal effects. They are due to the following three transformations:
   - (i) austenite \(\rightarrow\) ferrite and graphite, \(T_{Fe}\)
   - (ii) the restoration of magnetic properties (Curie point), \(T_{C}\)
   - (iii) austenite to pearlite, \(T_{Pc}\)

2. The calorimetry data from the three thermal effects allow studying the kinetics of the corresponding transformations at different time-temperature testing conditions, for different cast iron chemical compositions and initial microstructures.

3. During cooling, the temperature sequence at which the transformations occur manifests itself as \(T_{Fe}>T_{C}>T_{Pc}\). Though theoretically, the sequence may be \(T_{Fe}>T_{Pc}>T_{C}\), the different undercooling of pearlite and Curie transformations has changed the sequence to what is observed. Increasing cooling rate changes the intensity and temperatures of the different transformations to different extents. This results in overlapping of the thermal effects.

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### REFERENCES

1. R. Ivanova, W. Sha and S. Malinov: *ISIJ Int.*, 44 (2004), 886.
2. K. M. Delargy and G. D. W. Smith: *Metall. Trans. A*, 14A (1983), 1771.