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Determination of thermal effects accompanying the austempering of copper–nickel ductile iron

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ABSTRACT

Using especially designed and constructed isothermal calorimeter, the austempering of Cu–Ni ductile iron was carried out at temperatures of T_{pi} = 270, 350, 390 and 430 °C, simultaneously with the measurement of accompanying thermal effects. The values of enthalpy changes ΔH show the correct and expected trend, varying from 45 J/g at T_{pi} = 430 °C to 70 J/g at T_{pi} = 270 °C.

The changes of enthalpy were observed to increase with decreasing temperature of the isothermal transformation during austempering. The results of the present work did not allow revealing the influence of alloying elements, i.e. Cu and Ni, on the heat of isothermal transformation.

The discrepancies between the results of the actual measurements and the results quoted in other papers were discussed in terms of DSC measurements.

1. Introduction

The structure and the resulting mechanical properties of austempered ductile iron depend on the mechanism and kinetics of phase transformations proceeding successively during quenching followed by isothermal transformation:

1. $\gamma(C_o) \rightarrow \alpha + \gamma_s$ (C) (ausferrite forming).
2. Stability of structure $\alpha + \gamma_s$ (C) (processing window).
3. γ_s(C) $\rightarrow \alpha + Fe_3C$ (or ε carbide) (carbides precipitation).

At the end of the 1st stage, ausferrite with maximum amount of fine acicular ferrite α and reacted stable carbon-saturated austenite γ_s (C) is forming. The beginning of the 3rd stage corresponds to the start of carbides precipitation from austenite and decomposition of ausferritic matrix. The heat treatment processing window (2nd step) is an optimum stage for ausferrite stabilization.

The temperature of isothermal transformation affects its kinetics and the cast iron microstructure; with decreasing temperature the ferrite plates become smaller, giving rise to increased strength and hardness.

The complex isothermal transformation generates energy changes and can be investigated by means of a calorimetric method, which enables quantitative analysis of the mechanism and kinetics of phase transformations.

There are several papers devoted to measurements of the thermal effects of ausferrite formation, mainly based on the Derivative Thermal Analysis method [1–3] applied to determine the transformation kinetics and heat treatment parameters.

From the thermodynamic point of view, phase transition resulting in ausferrite formation consists of the three elementary reactions giving at ~500 °C the total thermal effect of $\Delta H = -8.2$ kJ/mol [4]. These are the following reactions:

- exothermic: $Fe_\gamma \rightarrow Fe_\alpha$ in pure iron ($\Delta H = -6.9$ kJ/mol);
- exothermic: precipitation of carbon from austenite ($\Delta H = -3.5$ kJ/mol);
- endothermic: formation of cementite ($\Delta H = +2.2$ kJ/mol).

Depending on the transformation temperature and high-carbon austenite volume fraction, the enthalpy values of 20–40 J/g were calculated. This evaluation does not take into account the contributions of the energy of the austenite/ferrite interface formation and stress energy.

The new isothermal ADI calorimeter based on DTA (Differential Thermal Analysis) principle and operating in an isothermal "drop in" mode described in details in [5] enables manufacturing ADI in laboratory scale with simultaneous recording of the thermal effects of phase transformations proceeding during austempering. The calibration of the device equipped with a K type thermocouple-pile sensor guarantees the required measurement sensitivity and uncertainty at a level of 5%.

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Table 1
Chemical composition of the base ductile iron in wt%.

Alloy	C	Si	Mn	Mg	Cu	Ni
A0	3.70	2.30	0.10	0.080	0.55	–
A1	3.50	2.55	0.08	0.065	0.50	0.97
A2	3.50	2.57	0.08	0.085	0.50	1.43
B0	3.80	2.30	0.18	0.080	0.93	–
B1	3.50	2.70	0.20	0.075	0.93	0.90
B2	3.70	2.50	0.08	0.090	0.90	1.37

2. Preparation of materials

The melts of base ductile iron without molybdenum were performed and two groups of alloys with different Cu (designated A,B) and Ni (designated 0,1,2) contents were prepared. Table 1 shows chemical composition of the investigated materials. The typical as-cast ductile iron microstructure is shown in Fig. 1a and b.

Determined by a dilatometric method, the values of A_{c3} temperature were found to be in the range of 870–880 °C, and so the austenitizing temperature of $T_a = 900$ °C and the time of austenitizing $t_a = 60$ min were accepted for all the alloys under investigation.

3. Calorimetric measurements in isothermal conditions

The samples prepared for measurements in isothermal calorimeter [5] had fixed dimensions of $\Phi 3.5$ mm × 3 mm. Calorimetric measurements were carried out according to the adopted procedure of ADI manufacture. The ductile iron samples were austenitized at 900 °C for 60 min in an austenitization furnace followed by drop into a transient cooling chamber to quickly reach the temperature of austempering (T_{pi}). Adjacent to the chamber, a water cooler and an inert gas cooler enabled quick cooling down of the sample. Finally, using simple manipulator, the sample was dropped into the calorimeter crucible placed inside the calorimeter sensor.

Table 2
Optimum parameters of ductile iron heat treatment in isothermal calorimeter.

T_{pi} (°C)	T_{pi} (min)	τ_o (s)	q (K/s)
270	120	27	23.3
350	90	20	27.5
390	45	17	30.0
430	30	15	31.3

At a constant austempering temperature, the holding time τ of the sample in a transient chamber depends only on the sample temperature T_s and as such has been established experimentally (Table 2). Minimalization of specific thermal effects ($C_p\Delta T$), arising as a result of temperature difference $|T_s - T_{pi}|$ which should approach zero, was the criterion for optimum cooling time choice $\tau = \tau_o$. This simplified approach was successful because the samples of an identical geometry and similar thermal properties were heat treated in the calorimeter characterized by stable and reproductible conditions. Additionally, two measurements were taken for each alloy at different but very close cooling rates q to produce two different thermal effects: endothermic if $\tau > \tau_o$ ($T_s < T_{pi}$) and exothermic if $\tau < \tau_o$ ($T_s > T_{pi}$).

The data from [1] and the metallographic examinations prove that the applied cooling rates have been sufficient to produce the correct ADI structures (Fig. 2a and b).

Figs. 3 and 4 show calorimetric curves (upper part of diagram) for optimum conditions of isothermal transformation (processing window). Depending on the sign of the expression $|T_{pi} - T_s|$, either endothermic (heating of "colder" sample up in the calorimeter crucible) or exothermic (cooling of "warmer" sample in the calorimeter crucible) effects occur.

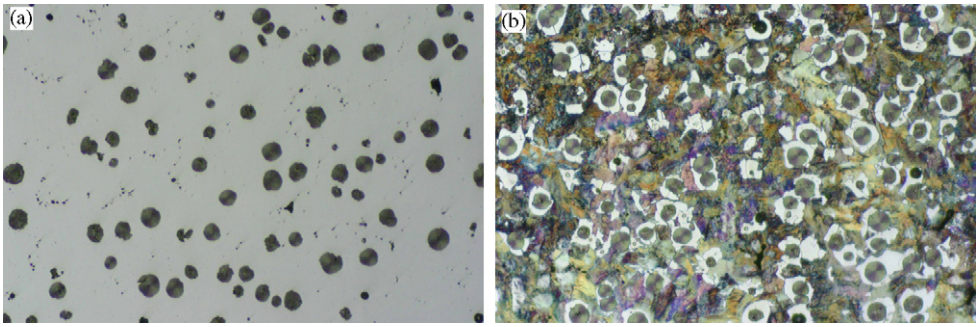

Fig. 1. Microstructure of alloy A0; magnification 100×, (a) metallographic cross-section after polishing; (b) metallographic cross-section after etching.

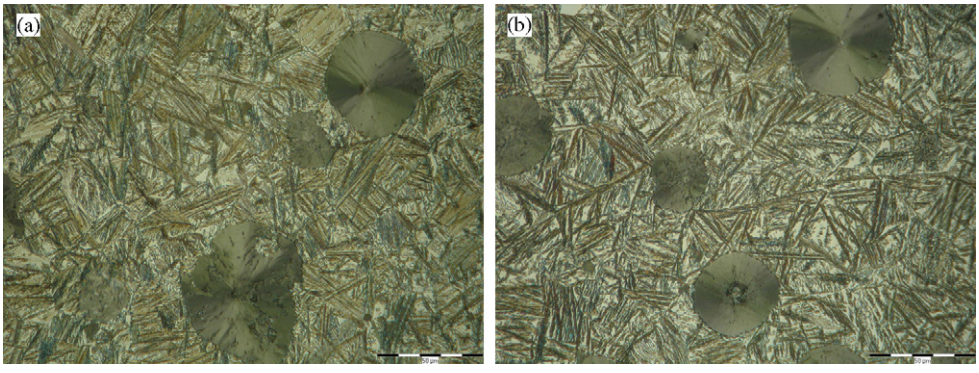

Fig. 2. Microstructure of alloys after heat treatment at 350 °C for 60 min in isothermal calorimeter; magnification 500×, metallographic cross-section etched with HNO_3 (a) alloy A0; (b) alloy A2.