MEASURED TRANSPORT PROPERTIES OF STEEL ALONG THE FERROMAGNETIC TO PARAMAGNETIC TRANSITION (CURIE POINT)

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Abstract

A review of published steel thermal diffusivity and conductivity investigations in the vicinity of the Curie point is given. Respective data are supplemented by own measurements of various iron based alloys. The results show strong composition effects on the Curie temperature, distinct composition dependent specific heat and thermal diffusivity peaks (positive and negative respectively) and resulting thermal conductivities with clear minima around the Curie temperature. Own results are compared with literature data and main influences are discussed.

Keywords: Iron alloy, steel, thermal conductivity, thermal diffusivity, Curie point

1. Introduction

Steel is one of the most important construction materials in high-temperature technologies for heat transfer, melting, annealing, burning, testing. Material selection is commonly governed by mechanical strength, corrosion and further characteristics which typically depend on temperature and/or temperature distribution. Modern machine design, lay-out of thermal processes, control of materials production and further engineering tasks ask for increasingly exact prediction methods. Regularly numerical tools are applied needing improved and detailed information about thermophysical properties like specific heat, thermal conductivity and diffusivity, among others.

2. Overview of Previous Investigations

The thermal conductivity as the most important property for machine and process design can be obtained in 3 different ways: (a) measured directly requiring temperature differences in the order of some Kelvin; (b) evaluated from measured thermal diffusivity and specific heat following $\lambda = a \rho c_p$; (c) evaluated from measured electrical resistivity following the Wiedemann-Franz-Lorenz law. The thermal diffusivity regularly shows a sharp minimum at the Curie point when plotted vs. temperature caused by a related sharp maximum of the specific heat. The thermal conductivity is mostly not characterized by such singularities. For pure iron and dilute alloys a monotonic decrease of the thermal conductivity is found, mostly passing through a weak minimum close to the Curie point with a subsequent increase. In cases of high contents of alloying components the behaviour is modified showing an increase of the thermal conductivity with or without a local minimum at the Curie temperature.

2.1 Pure Iron

Purity is crucial for such experiments and their intercomparisons, however, concentration of non-iron components is typically in the order of several 100 ppm in the respective investigations found in literature. The widely accepted Curie point temperature of pure iron is $T_{Curie} = 1043 K$ as confirmed in some of the investigations but not in all.

The thermal conductivity of pure iron close to the Curie point was first studied by Powell [1] and he found a continuous decrease without significant changes which may be due to the applied direct method requiring large temperature differences. Cody et al. [2] presented measured thermal diffusivity results with a destinct minimum (at $T_{Curie} = 1043 K$) and evaluated thermal conductivities with a clear, maybe stepwise, decrease of the thermal conductivity followed by an increase. Similar results are reported by Bäcklund [3] who used electrical resistivity measurements together with a modified Wiedemann-Franz-Lorenz law to evaluate thermal conductivities. He thorougly analysed the results in the light of the electronic and lattice contributions, and for the Curie point region he found a weak minimum of the first one but a significant downward step of the latter. Shanks et al. [5] obtained a sharp minimum of measured diffusivities at $T_{Cwie} = 1038 K$ ($a_{Cwie} = 0.03 cm^2 s^{-1}$) and a weak minimum of conductivity fairly above the Curie point. Lanchbury and Saunders [6] evaluated electrical conductivity measurements and obtained decreasing thermal conductivities with a local minimum at the Curie temperature followed by a weak local maximum. Taylor and Fowler [7] measured thermal diffusivities of various iron samples below and above the Curie point $(T_{Curie} = 1041 K)$ with the typical negative peak.

2.2 Iron Alloys

There is a limited number of measurements regarding iron alloys partly with systematic variations of selected components like cobalt [7, 12], chromium [7, 9, 10, 13], aluminium [14] and others [7]. In some of the experiments alloys of practical interest are handled [8, 11]. One of the most careful investigations comes from Taylor and Fowler [7] who measured thermal diffusivities of various iron alloys with selected single elements with the following observations: (a) the Curie point temperature is found to be increased for the Co and V alloys,

decreased for Mn and Si with no effects in cases of Ni, Cr and Mo contents; (b) Curie point thermal diffusivities seem to be uneffected being constantly somewhat above $a_{Curie} = 0.03 \ cm^2 s^{-1}$; (c) below T_{Curie} a strong decrease of the diffusivity is found for Si and Cr contents, and also for Mn, however to a smaller extend, while Co, Ni, V and Mo bring only weak effects; (d) above T_{Curie} some effects on the diffusivity are found which, however, diminish when the comparision is done at some constant "distance" $T - T_{Curie}$ above the Curie temperature. Strongest effects are concluded for silicon showing the largest difference to iron regarding the electronic configuration, having the halfth of the atomic mass and the strongest decrease of the lattice parameter (by 0.11%).

3. Experiments

Own experiments have been carried out by measuring thermal diffusivity (Laser flash instrument LFA 427, Netzsch) and specific heat (Multi-Detector High-Temperature Calorimeter, Setaram) and subsequent evaluation of the thermal conductivity ($\lambda = a \rho c_p$). A wide temperature range is covered from room temperature up to values far above the Curie point. Various industrial alloys have been investigated (see table 1, all contents given in %):

| Alloy | Si | Mn | Al | С | Р | Cr | Σ |
|-------|------|------|------|--------|--------|------|------|
| #0 | 0.14 | 0.33 | 0.09 | 0.01 | 0.07 | 0.04 | 0.75 |
| #1 | 1.61 | 0.21 | 0.11 | 0.03 | 0.05 | 0.04 | 2.09 |
| #2 | 1.60 | 1.53 | 0.05 | 0.09 | 0.02 | 0.05 | 3.37 |
| #3 | 2.50 | 0.23 | 0.38 | 0.01 | 0.02 | 0.03 | 3.21 |
| #4 | 2.95 | 0.10 | 0.47 | 0.02 | 0.02 | 0.03 | 3.62 |
| #5 | 3.23 | 0.09 | 1.05 | < 0.01 | < 0.01 | 0.02 | 4.42 |

Table 1: Composition of the samples

where Ni<0.03, Cu<0.02 and Mo, Nb, S, Ti, V<0.01 in all cases

Additional experiments with highly pure iron have been carried out for reference. These measurements have also been used for calibration of the temperature sensors in the measuring instruments which brought the Curie point temperature read from the thermal diffusivity minimum and the specific heat maximum somewhat above the standard Curie point ($T_{Curie} = 1043 K$). All measured temperatures have respectively been been corrected.

Thermal diffusivity measurements have been carried out both, with increasing and with decreasing temperatures and the temperatur steps in the vicinity of the Curie point have chosen very small for getting the Curie point in the best possible accuracy. This was the precondition for the subsequent evaluation of thermal conductivity.

4. Results and Discussion

4.1 Thermal Diffusivity

The Taylor/Fowler [7] experiments brought a strong Silicon effect (2.18 % Si) on the thermal diffusivity of respective iron alloys decreasing both the thermal diffusivity in the ferromagnetic range and the Curie point temperature when compared with pure iron. These data are ploted together with our own results for the Silicon series in Fig. 1 where the findings of Taylor/Fowler are clearly confirmed. Starting at $T < T_{Curie}$ the diffusivity is found to decrease monotonically from 0 % up to 3.23 % Si content. There is one exception for the alloys 1 and 2, both of them with around 1.6 % Si, where the latter one is shifted to smaller diffusivities due to the increased Mn content. For $T > T_{Curie}$ the curves are much closer to each other generally showing the same order with the Mn rich alloy 2 above the other ones.



Fig. 1: Thermal diffusivity of various steel alloys close to the Curie point

4.2 Thermal Conductivity

Fig. 2 shows a thermal conductivity plot for selected results from the Silicon series (alloys 1, 3, 4) which is expected to yield strongest effects. Two additional series are supplemented namely alloy 0 with a similar composition but much smaller Si content than the others (see table 1) and one series measured with highly pure iron.

All own measurement series agree in the following within the given temperature range: the thermal conductivity decreases almost linearly at temperatures far below the Curie point, i.e. in the range: $T < (T_{Curie} - 10K)$; the same trend seems to be continued above the Curie point for

 $T > (T_{Curie} + 20K)$; a sharp negative peak is found directly at the Curie point, i.e. in the range $(T_{Curie} - 10K) < T < (T_{Curie} + 20K)$, where the thermal conductivity is remarkably reduced to a figure for the conductivity which seems to be widely independent of the purity $\lambda \approx 22 \div 24 Wm^{-1}K^{-1}$. This observation is in a certain agreement with the "universal" Curie-point thermal diffusivity $a_{Curie} \approx 0.031 \div 0.035 \ cm^2 s^{-1}$ observed many scientists.



Fig. 2: Thermal conductivity of various steel alloys close to the Curie point

Typical differences between the various curves can also be observed: in the range $T < (T_{Curie} - 10K)$, the thermal conductivity shows the well known decrease with a rising level of impurities; the Curie point temperature decreases in parallel to that; in the range $T > (T_{Curie} + 20K)$ the impurity effect on the thermal conductivity is similar as below the Curie point with, however, a reduced intensity.

There are 2 additional conductivity series taken from the literature: Cody's [2] data show good agreement with our own ones but unfortunatelly the temperature steps in the "Curie range" are too large for any conclusion; Lanchbury's [6] results obviously confirm Cody's and our own pure-iron data far below and far above the Curie point. But remember, those thermal conductivities have been evaluated from electric resistivity measurements by the Wiedemann-Franz-Lorenz law which is not in the state to consider lattice resistances. And following Bäcklund [3], the lattice resistance is expected to force a downward step of the thermal conductivity at the Curie point.

5. Conclusions

Thermal diffusivity and thermal conductivity of iron alloys with various Si contents have been measured, and both properties are found to exhibit sharp negative peaks at the Curie point temperature. This behaviour is unusual and new with respect to the conductivity and it has been discussed in the light of previous studies from the literature.

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