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Detection of the α-γ Iron Phase Transformation by Differential Thermal Conductivity Analysis

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A method of phase change detection in solids involving differential thermal conductivity analysis is described. This method is applied to the α-γ transformation of iron at various pressures up to 100 000 atm. This transformation temperature was found to drop continuously with increasing pressure down to 605°C at 100 000 atm.

A DIFFERENTIAL method of detecting phase changes in solids, involving measurement of the thermal conductivity changes accompanying the transformation, has been worked out recently. The method is entitled differential thermal conductivity analysis (DTCA), in contrast to differential thermal analysis (DTA), which involves changes in latent heat during a transformation.[1] This DTCA method has been used under super-pressure conditions, up to 100 000 atm, to determine the effect of pressure on the temperature at which the α-γ transformation in iron occurs. The method was planned especially for those systems where electrical conductivity measurements could not be used for detection, as in ceramic materials; this aspect is now being pursued with initial success with silica, boron oxide, and selenium; a report will be forthcoming in the future.

The DTCA method as first employed consisted in placing a temperature gradient across two parallel pieces of material: iron, whose transformation was to be investigated, and nickel, used as a reference material. The apparatus is illustrated schematically in Fig. 1. The temperature gradient in each of the pieces of metal would be linear and identical provided that each piece was homogeneous in itself, as shown in curve 1. If the iron transformed partly to a second phase of a different thermal conductivity than the initial phase, the temperature gradient through the iron would become nonlinear, as in curves 2 or 3. This departure from linearity was found to be easily detectable by placing two thermocouples, one at the mid-point of each piece of metal, bucking one thermocouple against the other, and thus measuring the difference in temperature ΔT. The sign of the ΔT would be positive or negative depending upon whether the new phase forming had a higher or a lower thermal conductivity, respectively, than the first phase.

The complete cell design, shown in Fig. 2, includes the following: insulating alumina disks above and below the iron and nickel strips; next, metal (nickel) disks above and below, to equalize the end temperatures of the metal strips; a lava insulator between the two metal strips; stacks of alumina pills at the cool end and lava pills at the hot end, these causing the temperature gradient in the metal strips by virtue of their (lava and alumina) differences in thermal conductivities; an alumina bushing surrounding the just-described center core; a second alumina bushing surrounding the first, between which was inserted four nickel strip heaters; an outer lava bushing enclosing the whole. This cell was placed in a super-pressure belt apparatus along with suitable gasketing material, described elsewhere.[2]

The ΔT signal was obtained across two platinum wires,

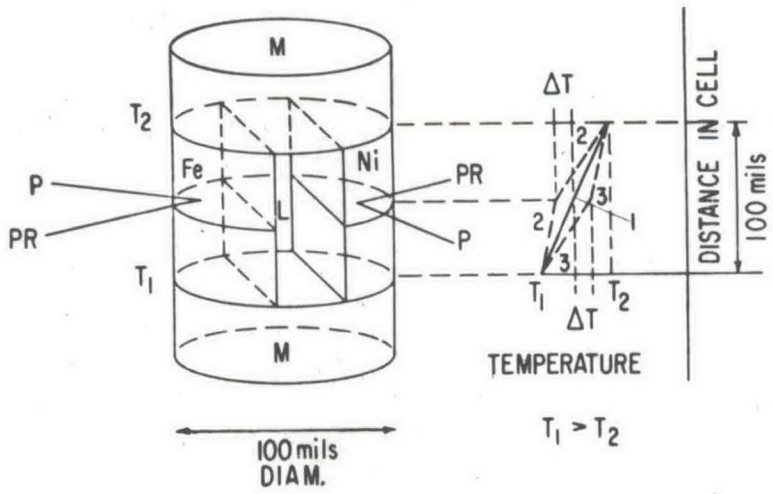

FIG. 1. Core design of DTCA cell. Thermocouples: P = platinum, PR = platinum −10% rhodium. ΔT, Read from the two P leads, with the two PR leads tied together. T, Read from "Fe" pair of P–PR leads. M = Metal pills for temperature equalization.

[1] J. Reilly and W. N. Rae, *Physico-Chemical Methods* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1953), p. 221.
[2] H. Tracy Hall, Rev. Sci. Instr. 31, 125 (1960).

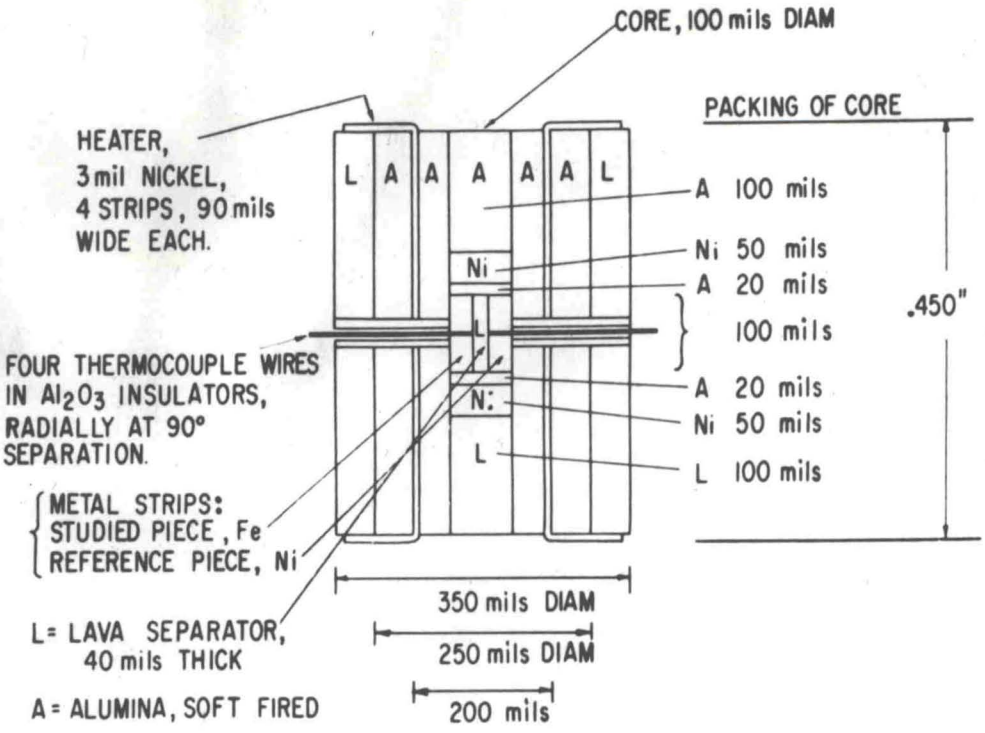

FIG. 2. Complete DTCA cell design.

one from each of the thermocouples, while the two companion Pt-10% Rh wires from the thermocouples were tied together outside the cell. The ΔT signal was amplified by a Beckman model 14 dc amplifier, and recorded on an L&N Speedomax recorder. Types of traces of the ΔT with time are given in Fig. 3. The ideal trace (curve 1) would be a straight vertical line when no transformation is taking place, with a deflection to one side, out and back, during a transformation. In practically all the cases, this ideal curve was only approached but never fully attained, the actual curves resembling 2, 3, or 4. In these actual cases, a spurious temperature gradient existed between the two metal strips, which gradient increased with the absolute temperature, giving the curve a slope to one side. Superimposed upon this slow change of ΔT with temperature was still another type of behavior, arising because of the transformation, which gave to the curve a decided shift instead of coming to a maximum and returning to the base line (curve 4). The cause of this behavior is probably related to the lack of ideality in the heat flow pattern around the metal samples. An explanation may utilize the following reasoning: The thermocouple junction for each metal strip was actually at the outer edge of each strip, at the boundary between the alumina bushing and the metal. If a large heat flux existed across this boundary from the heater to the metal strip, a change in the thermal conductivity accompanying a phase change would cause a decided change in the temperature at this point; this follows from reasoning similar to that used in the basic principle of the DTCA cell. The decided change in temperature would be reflected directly in a shift of the recorded ΔT. A perfectly insulated set of metal strips would not suffer from this fault, but of course this is impossible when pressure transmission requires intimately packed solids around the sample. However, the condition of zero heat flux can be approached by varying the amount of heat being produced at different points along the heater. This is a rationalization of the fact that more perfect maxima ΔT curves were obtained with cells containing nickel heaters than with Nichrome heaters. Nickel would tend to produce a hot spot, Nichrome would produce more even heat. What is apparently required is a hot spot at the hottest part of the cell, which would be at the metal disk on the hot side, along with a temperature gradient of equal magnitude in the core and the alumina bushing. At points near the hot spot the heat generated must be sufficient only to compensate for the heat flow along the bushing. More heat

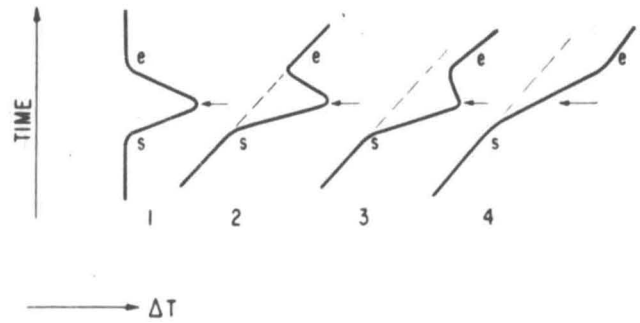

FIG. 3. Typical ΔT curves on recorder charts. s=Start of transformation, e=end of transformation, →=transformation half completed.

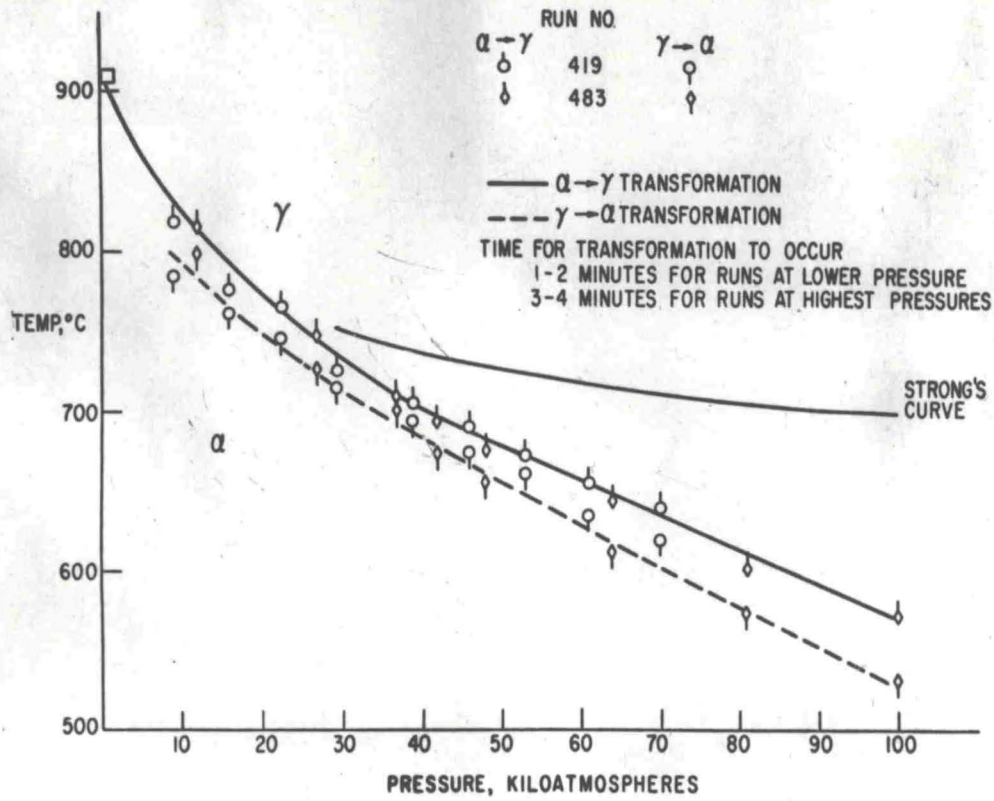

FIG. 4. Effect of pressure on α-γ transformation in iron. Pressure calibration is based on the transitions for Bi and Ba, which were assumed to occur at 24 800 and 77 400 atm, respectively. See footnote reference 2.

production would tend to flow into the core, producing this undesirable heat flux. The even heat produced by the Nichrome heater would seem to produce too much heat at cooler portions of the cell and thus would cause the undesirable shift of ΔT at the transformation.

EXPERIMENTAL RESULTS—THE α-γ TRANSFORMATION OF IRON

The DTCA method was first tested on this transformation, and the results are shown in Fig. 4. The $\alpha \rightarrow \gamma$ transformation was observed with rising temperature, while the $\gamma \rightarrow \alpha$ transformation was observed at lower temperatures and with falling temperature. The temperatures for the forward and reverse transformations differed by as much as 40°C, with a trend toward a minimum of 10–15°C at around 40 000 atm. This subject will be pursued further when better data are available. It is apparent that the DTCA method is applicable to studies of this type, which involve thermodynamic equilibria as well as kinetics of transformation.

The transformation temperature drops regularly with increasing pressure in contrast to that reported earlier by Strong.[3] While this latter work indicated a drop of the transformation temperature to about 700°C at 90 000 atm, the present work indicates that the temperature is around 590°C. The reason for this discrepancy may lie in the failure of Strong's method of detection of phase change, which was by electrical resistivity measurement, to give as sharp an indication of the phase transition as does differential thermal conductivity. Also, Strong's interpretation of the break in the resistivity versus temperature curve as being the start of the change might have caused an error, the break actually corresponding to the end of the transformation which was occurring at the cool ends of the cell.

The transformation temperature is subject to a correction because of temperature gradients which occur along the thermocouple wires while in the pressure field.[4] The platinum 10% rhodium-platinum thermocouple may read 30° low at 600°C and 100 000 atm. Since one might expect this correction to be linear with respect to both temperature and pressure, the entire curve of Fig. 4 would then be shifted upward slightly. At 100 000 atm, the corrected transformation temperature would then be 605°C.

This DTCA method affords an intimate view of temperature gradients within the cell. A typical ΔT curve, as in Fig. 3, would have recorded, at various points along it, the absolute temperature. These temperatures, obtained by means of a potentiometer using one of the two thermocouples, are for the mid-point of one of the metal strip samples. The temperature at the maximum (or inflection) corresponds to the transformation temperature (see arrow, Fig. 3). The initial deflection from linearity s corresponds

[3] H. M. Strong, J. Geophys. Research **64**, 653 (1959).

[4] F. P. Bundy, Sagamore High Pressure Conference, Lake George, New York, June, 1960.

to the point when the transformation is starting, at the hottest point when the temperature is rising. The temperature at this hottest point must be the transformation temperature, which is observed at the maximum a little later in the curve. The observed temperature at s from the centered thermocouple is lower than the transformation temperature and from these two values we know precisely the temperature gradient within the cell. Similar reasoning can be employed to determine the gradient to point e at the end of the transformation.

The temperature gradients from s to e within the cells for the runs 419 and 483 were calculated to be in the range 23–40°, and 37–70°C, respectively. The gradients varied irregularly with pressure, probably because of the changes in thermal conductivity of the various cell components and changes in the heater characteristics with pressure.

Data on the absolute thermal conductivities of α and γ iron were lacking when this work was done. However, such data are now about to be published by Cody, Abeles, and Beers.[5] This work indicates a 7% decrease in the thermal conductivity from approximately 0.305 to 0.283 joules/cm°C through the $\alpha \rightarrow \gamma$ transformation.

One may calculate from the DTCA method the relative values of the thermal conductivities of α to γ iron at the transformation temperature. When the peak ΔT is reached on the Speedomax curve, half the length of the iron would be transformed. On assuming ideal heat flow, the quantity K (=thermal conductivity) multiplied by the temperature gradient for each iron half-segment would be equal to each other. If T_{gr} is the temperature gradient (s-e) across the entire iron sample, the gradient across each part, α and γ, becomes $[(T_{gr}/2)-\Delta T]$ and $[(T_{gr}/2)+\Delta T]$, respectively. Hence,

$$K_\alpha\left(\frac{T_{gr}}{2}-\Delta T\right)=K_\gamma\left(\frac{T_{gr}}{2}+\Delta T\right).$$

Then,

$$\frac{K_\alpha}{K_\gamma}=1+\frac{4\Delta T}{T_{gr}-2\Delta T}.$$

At 9000 atm, the ratio of the thermal conductivities were calculated to be 1.21, 1.10, and 1.13, which corresponds to about a 15% decrease for $\alpha \rightarrow \gamma$. This may indicate the crude nature of the calculation, which may be refined by further work.

ACKNOWLEDGMENTS

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[5] G. C. Cody, B. Abeles, and D. S. Beers, to be published in Acta Met. (Received February 8, 1960).