Alpha-Gamma Transformations in Iron Alloys--Calibration of Pressure by Duplex Differential Thermal Conductivity Analysis

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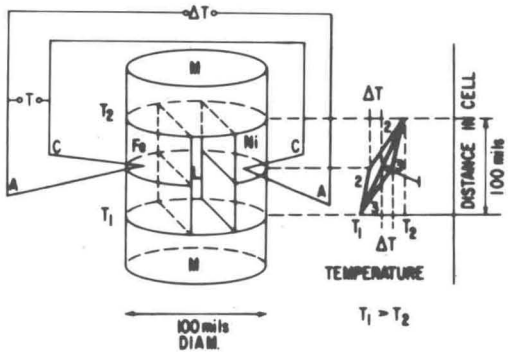

THERMOCOUPLES: C = CHROMEL A = ALUMEL
ΔT READ FROM THE TWO A LEADS, WITH THE TWO C LEADS TIED TOGETHER.
T READ FROM "Fe" PAIR OF C-A LEADS.
M = METAL PILLS FOR TEMPERATURE EQUALIZATION.
L = LAVA SEPARATOR

Fig. 1 Differential thermal-conductivity cell with temperature gradient

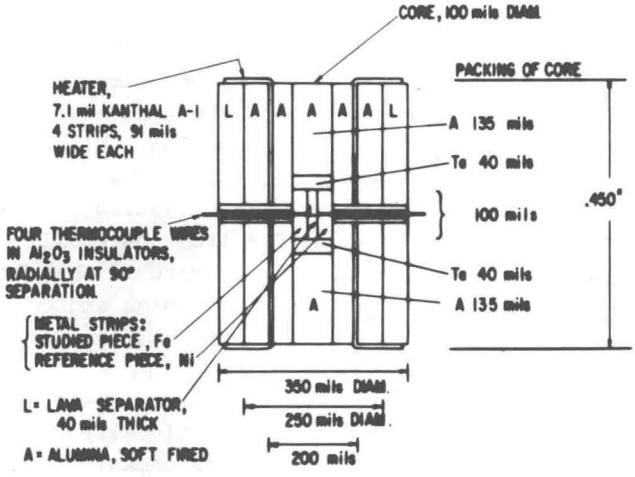

Fig. 2 Differential thermal-conductivity cell. Plan as used in superpressure apparatus

The effect of pressure on the α-γ transformation temperature in iron and iron binary alloys was studied in order to seek the general trends in the pressure-temperature curves as well as to observe possibly abnormal effects in these curves. The availability of the "belt" apparatus (1)[1] permits work up to 90 kb and upwards of 1000 C for long sustained times. The invention of differential thermal-conductivity analysis (DTCA) (2) permits one to observe phase changes in materials with slowly changing temperatures in a medium which is far from being considered as insulating. In contrast, the more common differential thermal analysis (DTA) requires much higher rates of temperature change through the transformation when in a superpressure cell, since the latent heat of the transformation is so quickly lost to the highly conducting surroundings.

The development of improved techniques with external pressure and temperature control permits one to detect phase changes with a very high precision, and the point is now reached where this precision is masked by the systematic errors of both pressure and temperature calibration.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Belt Apparatus

These superpressure studies were carried out in the "belt" apparatus, developed at the General Electric Research Laboratory (1). This apparatus was installed in a 300-ton Elmes 3-column hydraulic press. Refinements in control of the hydraulic oil pressure were accomplished by the use of a sensitive pressure controller (Bristol, vane-type, Series 500) and a low-volume pump (Minipump by Milton Roy Company, Philadelphia, Pa.) for delivering small, controlled amounts of oil to the hydraulic system. These two devices permitted control over the hydraulic oil pressure to $\pm$ 5 psi; this corresponds to $\pm$ 0.15 kb pressure within the superpressure cell. It should be noted that this constancy in cell pressure is not realized over long periods of time, since the gasket does not remain perfectly uniform.

The DTCA Technique

The DTCA technique (2) for observing phase

[1] Numbers in parentheses designate References at the end of the paper.

changes may be understood by considering the temperature gradients which may be imposed upon a sample of metal, Fig.1. A homogeneous iron sample would, in the ideal case, possess a linear gradient (curve 1). A nonhomogeneous sample, with the hotter half transformed to gamma iron would now possess a broken line gradient (curve 3). This results because the thermal conductivities of the two forms, alpha and gamma, are not identical. By subjecting this sample of iron and a second sample of a nontransformable material (e.g., nickel) to the same temperature gradient, one may compare the midpoint temperatures of these two materials. These two temperatures would be identical in all cases except during the time the iron sample was in the process of transforming from one phase to another. Thus, by raising (or lowering) the temperature of this pair of metals through the transformation temperature of iron, one may observe a difference in temperature ΔT which is first zero, then departs from zero and reaches a maximum when one half of the iron has transformed, and finally returns to zero when the transformation is completed.

For infinitesimally low rates of heating or cooling of single-component materials, the midpoint temperature when the difference temperature, ΔT, is a maximum corresponds to the true equilibrium temperature of the transformation. With heating and cooling rates that are too rapid to allow equilibrium to prevail, the midpoint temperature at maximum ΔT will differ from the equilibrium temperature; however, the average of the midpoint temperatures obtained from heating and cooling cycles may be expected to approach the equilibrium temperature.

The analysis of data from multi-component systems with two-phase regions is additionally complicated by the fact that the transformations may take place over a range of temperatures. In this case, it is expected that there will be an even greater hysteresis in the transformation temperature obtained by heating and cooling, and the average transformation temperature here has no clear physical significance. Nevertheless, a plot of average temperature versus pressure still provides a convenient method for searching for the existence of new phases, which would be revealed by discontinuous changes in slope of the P-T curve.

A Speedomax Model G X_1-X_2 recorder permits the continuous recording of the two separate DTCA variable; (a) temperature of the cell, and (b) difference temperature between the sample and the reference material. A Rubicon potentiometer is used to buck out a large portion of the voltage from the temperature thermocouple, while a Beckman Model 14 dc breaker amplifier is used to amplify the difference voltage from the ΔT thermocouples.

In order to minimize uncertainties in the pressure measurements, it was advantageous to use a modified (duplex) DTCA technique in which the nontransforming material was replaced by a material that, for a given pressure, undergoes a transformation at a known temperature slightly different from that of the material under investigation. The additional maximum in the ΔT trace generated by the transformation of the standard material provides a convenient "built-in" pressure calibration. The ΔT trace from such a cell shows either positive and negative ΔT maxima, or two positive ΔT maxima, or two negative ΔT maxima, depending on the relative senses of the thermal conductivity changes in the two transformations. Fig.3 shows a typical ΔT versus T trace obtained with a duplex cell. The first part of the present work, described under "Experimental Results," relates to the establishment of the pressure dependence of the α-γ transformation in pure iron by the simple DTCA technique. Once these data were available, pure iron could be used as the reference standard in the duplex method.

The Superpressure Cell

The superpressure cell used in most of these investigations follows the pattern of Fig.2. An outer lava sleeve encloses a pair of concentric alumina sleeves between which are encased the heaters. The heater strips shown in the drawing were constructed from Kanthal A-1, because of its constant temperature coefficient of resistance and because of its high safe operating temperature of around 1200 C. The development of a satisfactory temperature gradient along the length of the iron sample was accomplished either by the use of 15-mil-deep symmetrical notches in the strip heaters 340 mils from the top, or by shorting out the heater tabs at the top of the cell by means of a 5-mil copper disk.

The thermocouple used in this work was chromel-alumel. This couple gives a very high response, and according to Bundy (3) the pressure correction may amount to only several degrees. No attempt was made to apply a pressure correction.

The core of the superpressure cell is 100 mils dia, and contains in its center two partially cylindrical pieces of the metal under investigation and two like-sized pieces of the reference material. These are shown in perspective in Fig.1. Between the two pieces of each of the materials lies a thermocouple junction, and between the two pairs of metals is located a spacer, 40 mils thick, composed of either lava or alumina. Immediately above and below the metal pieces are tantalum