Technical Note

Heat Evolved and Volume Change in the Alpha-Sigma Transformation in Cr-Fe Alloys

by Howard Martens and Pol Duwez

EXPERIMENTS were performed on a Cr-Fe alloy containing 44.7 pct Cr in order to determine the heat evolved during the transformation of the α solid solution into the σ phase, and the change in volume accompanying the transformation. Since previous measurements on the rate of formation of α from σ indicated that the reaction was quite fast as soon as the equilibrium temperature of 820°C was exceeded by some 50°, standard thermal analysis experiments were performed on heating specimens of σ at the rate of approximately 40°C per sec. A definite thermal arrest was observed at 870°C, Fig. 1. This result indicates that the reverse reaction of α into σ is exothermic.

From the heating curve of Fig. 1, taking 15°C per sec as the heating rate in the neighborhood of the transformation, 2.4 sec as the time for transformation, and assuming that the specific heat of the alloy at 850°C is an average between iron and chromium, namely 9.5 cal per mol per °C, the latent heat of transformation is approximately 342 cal per mol. The order of magnitude of this latent heat was also obtained by comparing the heating curve of Fig. 1 with a similar curve obtained with pure iron under identical experimental conditions. It was found that the length of the thermal arrest for σ was about 1.8 times as long as that for iron. Since the latent heat of the α to γ iron transformation is 203 cal per mol[1, 2] the latent heat of σ to α would be 365 cal per mol, which is in relatively good agreement with the value determined from the heating curve.

For the determination of volume change, thermal expansion curves were recorded using a specimen containing 44.7 pct Cr and completely transformed

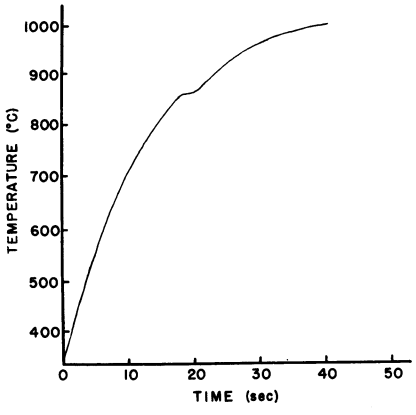

Fig. 1—Heating curve is charted for a 44.7 pct Cr, 55.3 pct Fe alloy transformed to 100 pct σ before heating.

to σ by previous treatment. The curves were recorded at a rate of heating of about 4°C per min and at approximately 840°C a sharp increase in length of about 0.08 pct took place, Fig. 2. It is therefore established that the specific volume of σ near the transformation temperature is about 0.24 pct smaller than that of α, and consequently, when the σ phase forms in an α matrix, it would tend to shrink away from the matrix. Since the σ phase is known to be extremely brittle, these results offer an explanation for the microscopic cracks often observed in the σ phase under the microscope.

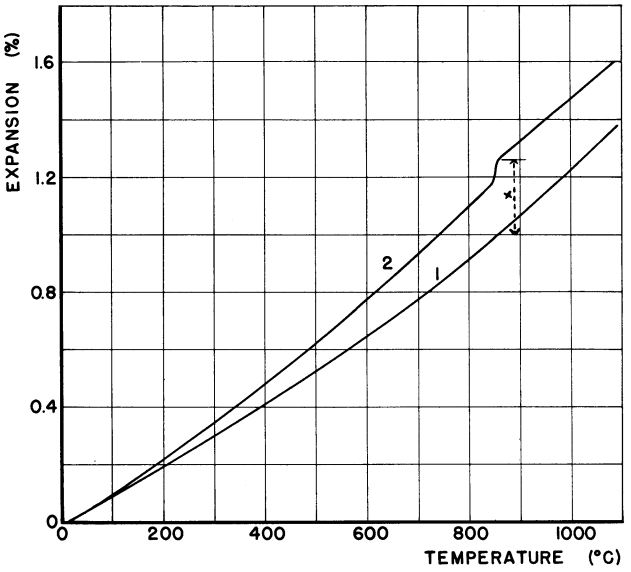

Fig. 2—Thermal expansion of a 44.7 pct Cr, 55.3 pct Fe alloy is charted. Line 1 shows 100 pct α solid solution at start; line 2, 100 pct σ at start.

The results of this study are in qualitative agreement with previously published data on stainless steel 19-9DL[3] and on a Cr-Fe alloy containing 45 pct Cr.[4] The increase in density due to the transformation from α to σ given in ref. 4 is 0.90 pct. These measurements, however, were made at room temperature, whereas the presently reported 0.24 pct is the change at the temperature at which the transformation takes place during heating. In the graph of Fig. 2, the percentage change in length that would be observed at room temperature is given by the length X, which is about 0.27 pct. This would correspond to 0.81 pct in volume change.

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References

[1] H. Klinkhardt: Measurements of True Specific Heats at High Temperatures. *Annalen der Physik* (1927) 84, pp. 167-200.
[2] H. Esser and W. Bunghardt: Influence of the Method of Determination on the Measured Heat Content of Iron. *Archiv für das Eisenhüttenwesen* (1934) 8, pp. 37-38.
[3] J. J. Gilman, P. K. Koh, and O. Zmeskal. Delta Ferrite Formation and its Influence on the Formation of Sigma in a Wrought Heat Resisting Steel. *Trans.* ASM (1949) 41, pp. 1371-1388.
[4] J. M. Thomas: Discussion of ref. 3. *Trans.* ASM (1949) 41, pp. 1390-1392.

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