Comment on "Structural characterization of rapidly solidified white cast iron powders"

In a recent paper by Eiselstein *et al.* [1], the presence of martensite in rapidly solidified white cast iron powder particles, whose calculated martensitic start temperatures, M_s, were substantially below ambient temperatures, was attributed to the occurrence of plastic deformation above the M_s temperature. This deformation was surmised as being the result either of the thermal strains experienced by the powder, or of the mechanical strains arising from particle collisions during rapid solidification and cooling. There are two factors, however, which indicate that it is not necessary to invoke an argument based on plastic deformation of the austenite to explain the presence of martensite plates in the microstructure.

First, the M_s temperatures of the alloys were calculated from published regression equations which relate M_s to chemical composition for low and high alloy steels. The most reliable regression equations [2] are those of Steven and Haynes [3] and of Andrews [4], given respectively, as:

$$M_s(^\circ\mathrm{C}) = 561 - 474\,\mathrm{C} - 33\,\mathrm{Mn} - 17\,\mathrm{Cr} - 17\,\mathrm{Ni} - 21\,\mathrm{Mo} + 10\,\mathrm{Co} - 7.5\,\mathrm{Si} \quad (1)$$

$$M_s(^\circ\mathrm{C}) = 539 - 423\,\mathrm{C} - 30.4\,\mathrm{Mn} - 12.1\,\mathrm{Cr} - 17.7\,\mathrm{Ni} - 7.5\,\mathrm{Mo} + 10\,\mathrm{Co} - 7.5\,\mathrm{Si} \quad (2)$$

where alloy composition is in wt%. The coefficients for cobalt and silicon are those proposed in [2]. In both of these equations it can be seen that carbon exerts an influence per wt% addition at least an order of magnitude stronger than that of any of the other alloying elements. However, both equations were derived from M_s measurements of steels over a limited composition range. In particular, the maximum carbon contents for which the equations were derived were 0.55 and 0.60 wt% respectively.

In order to calculate M_s temperatures for their white cast irons, Eiselstein *et al.* [1] first calculated the amount of carbon in solution in the retained austenite from lattice parameter measurements and the linear regression equation of Dyson and Holmes [5], which relates austenite lattice parameter to the carbon, nickel and chromium contents. By this technique a dissolved carbon content of 1.67 wt% C was determined for a 2.4 wt% C powder and 1.43 wt% C for a 3.0 wt% C, 1.5 wt% Cr powder. These values for carbon in solution were then inserted into Equation 2, along with the appropriate values for the other elements, to give calculated M_s temperatures of − 196 and − 102° C respectively. The carbon content of retained austenite in a 3.0 wt% C powder was not determined in the same way, but was assumed to be equal to the value measured for the 2.4 wt% C powder, and the M_s temperature for the 3.0 wt% C alloy was calculated to be − 183° C.

It is highly questionable whether regression Equation 2 can be used to calculate M_s temperatures for alloys with carbon contents greater than 0.60 wt% [6], particularly since the required extrapolation extends to a carbon concentration over 150% greater than the maximum value to which the equation strictly applies. Indeed, there is strong evidence that the relationship between M_s temperature and carbon content is not linear, and that increasing amounts of carbon in solution exert a gradually diminishing effect on M_s per wt% or at% C [7]. This observation is further supported by the splat quenching experiments of Ruhl and Cohen [8], in which the absence of martensite in alloys containing more than 1.9 wt% C was attributed to the M_s temperature falling below ambient at about this carbon level. It would appear, therefore, that the calculated values of M_s temperature are underestimates of the true values, and that, in fact, the M_s temperatures in all three alloys are probably greater than room temperature.

The second point relates to the necessity for advocating that the presence of martensite is the consequence of plastic deformation above the M_s temperature, when the influence of the high cooling rate may have shifted the M_s temperatures to values higher than those which would exist in the same alloys quenched by conventional processes. Although a common observation in studies of some rapidly-quenched ferrous alloys has been a depression of the M_s temperature as a result either of the small as-solidified austenite grain size [9, 10] or of the increase in the amount of austenite-stabilizing alloying elements remaining in solution [11], other studies have shown that the M_s temperature in carbon-containing ferrous alloys may increase with cooling rate [12, 13]. For example, measurements of M_s in a number of Fe–C and Fe–C–X alloys over a quench rate

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range from 2.75×10^3 to 2.48×10^4 K $\sec^{-1}$ have shown that M_s increases by about 100 K [13]. The shift in M_s has been accounted for on the basis of the segregation of carbon atoms to structural imperfections in the austenite during quenching. At relatively slow quench rates significant carbon segregation occurs prior to the austenite to martensite transformation, strengthening the austenite and thereby hindering the transformation. The effect of increasing the quench rate is to limit the time available for carbon segregation to the defect structure of the austenite. Therefore, the austenite is no longer as effectively strengthened by the segregate and the transformation to martensite may occur more readily, i.e. at a higher M_s temperature.

Eiselstein *et al.* [1] stated that "no martensite should be found in the as-received powders at room temperature" on the basis of calculations which showed that M_s temperatures were substantially below room temperature, and hence deduced that the martensite which was observed was nucleated by plastic deformation of the austenite above its M_s temperature. However, on the grounds that:

1. the calculated M_s temperatures are underestimates of the true values for retained austenites of the given carbon contents; and
2. the possibility that the M_s temperature is shifted to higher values at high cooling rates;

some martensite would be expected to exist at room temperature even in absence of prior plastic deformation of the austenite.

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