Effects of Residual Impurities, Carbide Precipitation, and Carbide Stabilization on the Toughness of Alloy Steels

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INTRODUCTION: The problem of impurity-induced embrittlement of alloy steels (typified by temper embrittlement) has lately received renewed attention,(1, 2) primarily because of actual and potential failures of large structures such as turbine rotors and pressure vessels. The phenomenon is now known to involve the build-up of specific residual impurities at grain boundaries,(3, 4) although the precise mechanisms leading to this build-up and the bases for the dominating role of alloying elements(5, 6) are not yet understood. Recent work in our laboratory has indicated the existence of hitherto unsuspected embrittling elements (Te, Bi, Se, and Ge),(6) has demonstrated a non-equilibrium type of impurity build-up caused by carbide precipitation which operates even in (doped) Fe-C alloys without additional alloying elements,(7) and has shown that Sb-induced temper embrittlement may be greatly reduced by the addition of titanium,(8) which fixes C and N (among other possible effects).

NATURE OF EMBRITTLING ELEMENTS: Consideration of the positions of the known embrittling elements Sb, Sn, P, and As in the periodic table prompted examination of the behavior of some neighboring elements. Based on the degrees of embrittlement observed in step-cooling and isothermal ageing experiments,(6) we are now in a position to make the approximate and tentative comparisons as shown in Table I. Much additional work must be done on this and other alloy systems, however, before we can consider such data reliable enough to use for specifications of commercial alloys.

It has been found(6, 9, 10) that addition of 0.1 to 1% Mn produces pronounced temper embrittlement of otherwise undoped vacuum melted Ni-Cr steel, and on this basis it has been concluded that Mn is an embrittling element. This must be considered anomalous,

TABLE I

IVB	VB	VIB
C not embrittling	N apparently not embrittling	O strongly embrittling not reversible
Si weakly embrittling at 2000 ppm	P strongly embrittling	S embrittles iron but precipitated by Cr and Mn
Ge weakly embrittling at < 100 ppm	As weakly embrittling at 600 ppm	Se weakly embrittling at < 100 ppm
Sn strongly embrittling	Sb very strongly embrittling	Te very strongly embrittling
Pb ?	Bi probably like Sb, Te	Po ?

since Mn bears no resemblance to the elements in Table I. An Auger electron spectroscopy (AES) study by Stein et al(10) failed to detect Mn segregation in a 3340 steel doped with 0.9% Mn, and a similar result was found by Schulz and McMahon(6) in a 3340 steel with 0.7% Mn. However, a recent AES study(11) on an Fe-12% Ni-6% Mn alloy has demonstrated that Mn does indeed segregate in an embrittled steel, as shown in Fig. 1. Note that Ni and P are also found on the intergranualr fracture surface. This alloy contained a residual 40 ppm P, and it is significant that the other Mn-doped alloys studied previously(6, 9, 10) contain similar or greater amounts of P. Hence, the role of Mn is still uncertain. Is it inherently embrittling or does it promote embrittlement by P, or even some other element, such as O? Operationally, we must continue to treat it as an embrittling element, since there is yet no hope of reducing residual elements in commercial steels below the levels found in vacuum melted laboratory alloys.

EMBRITTLEMENT INDUCED BY CARBIDE PRECIPITATION: A recently completed study(7) of doped Fe-0.04% C alloys containing no additional alloying elements has shown that precipitation of carbides during cooling leads to a nonequilibrium build-up of the dopants Sb, As, Sn and P in the carbide-ferrite interfaces (Fig. 2a). This lowers their cohesive strength to the extent that they split apart when stressed in tension at low temperatures. The embrittlement can be removed by prolonged heating in the temperature range 350 to 550°C where segregation of these elements normally occurs in alloy steels. The embrittlement can be removed very quickly by heating above 600°C, because of partial dissolution of the carbide, (Fig. 2b), but it re-occurs on a finer scale when carbides precipitate during aging at a lower temperature (Fig. 2c). The elements Sb, Sn, and As cause embrittlement of carbide-ferrite interfaces in all cases studied; however, P is effective only if carbides are formed at temperatures below about 500°C. According to diffusion calculations made in a Zener-type analysis of carbide growth,(7) this can be understood in terms of the greater diffusivity of P in Fe, which enables the non-equilibrium build-up to disperse at higher temperatures. Preliminary results on the effects of Ni, Cr, and Mn additions have indicated that Ni stabilizes the build-up of Sb (i.e., equilibrium segregation is presumably superimposed upon the carbide-rejection effect) and Cr and Mn stabilize the build-up of P. How important this mechanism is in the embrittlement of alloy steels is yet to be determined.

EFFECT OF A TITANIUM ADDITION: In an effort to separate the carbide-rejection effect from the inherent effects of embrittling elements, we have been studying Sb-doped Fe-Ni-Cr alloys to which no C has been added and others in which residual C is stabilized by the addition of 0.1% Ti. The compositions of these Fe-3.5% Ni-1.7% Cr alloys are as follows:

TABLE II

Alloy	C ppm (wt)	Sb ppm (wt)
Sb-1	~ 50	600
Sb-2	80	820
Sb-Ti	30	650

The Ti addition greatly reduces the isothermal embrittlement in both the quenched and tempered condition (Fig. 3) and in the fully recrystalled condition.(8) In Fig. 4 we show the increase in transition temperature (a) and the excess Ni and Sb on the fracture surface (b) in alloys quenched after each of the first five steps of step cooling. When the excess Ni and Sb is normalized in terms of the amount of intergranular fracture (c), it appears to increase in the Sb-2 alloy and decrease in the Sb-Ti in the successive steps (d). This can be rationalized in terms of the stabilization of carbides by Ti and the removal of the carbide-rejection mechanism. This would imply that the equilibrium segregation effect is relatively less important. However, there are other possible effects, such as the possible scavenging of Sb by Ti, on which we cannot comment at present.

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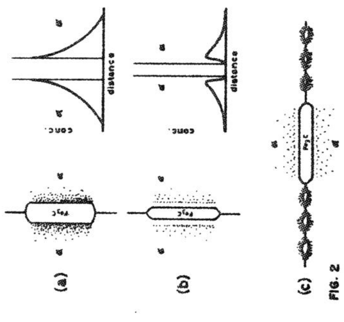

FIG. 2

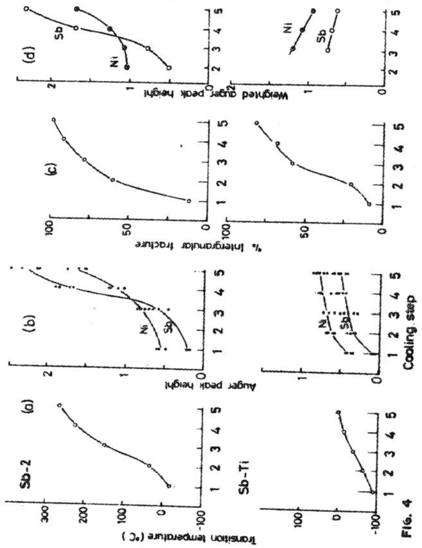

FIG. 4

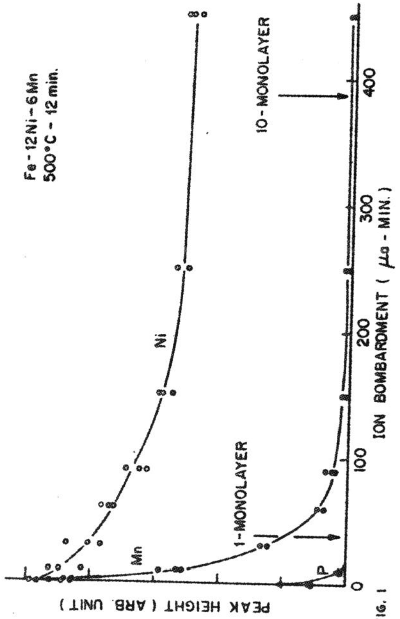

FIG. 1

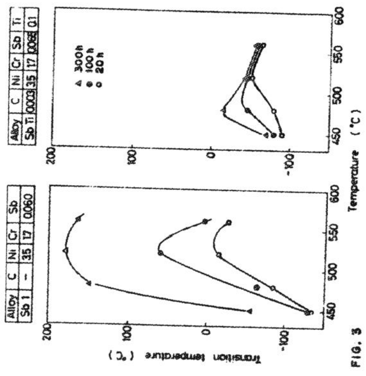

FIG. 3