

EFFECTS OF NICKEL AND ANTIMONY ON TEMPER EMBRITTLEMENT
IN ALLOY STEELS

J. Q. Clayton* and J. F. Knott**

INTRODUCTION

Previous studies suggest that alloy content is an important factor in determining the susceptibility of Ni-Cr-Sb steels to temper embrittlement. This was first demonstrated by Low et al [1] who showed that the removal of either Ni or Cr dramatically reduced the transition temperature shift produced by step-cooling through the temper embrittlement range. The observation that both Ni and Sb segregated to grain boundaries in Ni-Cr-Sb steels led to the proposal of an enrichment of the interfaces by a Sb-Ni chemical interaction [2]. Such alloy and impurity interfacial concentrations (Sb-Ni, Sb-Mn, P-Ni, etc.) have subsequently been shown to be stable [3 - 5] and are thus in accordance with equilibrium (Gibbsian) segregation. These general observations are consistent with a recent thermodynamic analysis of solute interactions at an interface [6]. In this paper the nature of the Sb-Ni interaction is further examined by employing controlled variations of the Ni and Sb content in the steel. Previous studies have been largely concerned with embrittlement at high bulk Sb concentrations, and to extend the range, emphasis in the investigation is placed on lower Sb concentrations, more closely approaching the values found in commercial alloy steels.

EXPERIMENTAL PROCEDURES

The chemical compositions of the alloys are given in Table 1, and will be referred to by their nominal Ni and Sb contents. The materials were prepared by melting electrolytic iron together with high-purity alloying elements. The 15kg ingots were forged, hot-rolled, then cold-swaged to give specimen blanks 10 mm diam. x 100 mm long. The blanks were austenitized for 2h at 1373 K (5% brine quench), tempered at 923 K for either 3h or 30h, then sealed in evacuated silica capsules and aged at 793 K for times up to 3000h. Transition temperature specimens (6.25 mm diam. x 100 mm long, notched every 20 mm to a depth of 1.0 mm) were then machined from the blanks. The specimens were tested in bending in a thermostatically controlled chamber. Load-displacement curves were recorded at a crosshead rate of 0.03 mm s⁻¹ (3h temper) or 0.08 mm s⁻¹ (30h temper) and an area under the curve equivalent to 4J energy was used to define the transition temperature. This energy corresponded to fracture appearances which were (transgranular or intergranular) cleavage in all cases.

Grain boundary compositions were determined by Auger electron spectroscopy (AES) in a Physical Electronics system. The AES specimens, machined from the bend specimens, were fractured at about 175 K under a vacuum less than 1×10^{-10} torr. The system was operated with a beam current of 50 μ A, a

* Aeronautical Research Laboratories, Melbourne, Australia

** Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, England

beam size of 0.5 mm, and a modulation voltage of 6V. Typically 8 - 10 different areas of each fracture were analyzed; the measured peaks were normalized with respect to the Fe₇₀₃ peak, then weighted to obtain values corresponding to 100% intergranular fracture (the proportion of intergranular fracture was determined by subsequent SEM examination). The weighting procedure for trace elements (Sb, P and S) is simply to multiply the measured peak-height ratio by the reciprocal intergranular fraction, but for more concentrated solutes (e.g., Ni) the contribution to the signal from the transgranular proportion of the fracture is subtracted first [5].

RESULTS

Mechanical Tests

The changes in transition temperature with ageing time for the two steels containing 5 Ni + Sb are shown in Figure 1. In the materials tempered for 5h there is an initial rapid rise in transition temperature followed by a slow decrease corresponding to the decrease in hardness. The transition temperatures for 200 ppm Sb are clearly greater than those for 100 ppm Sb. Tempering for 30h produces a constant transition temperature between 300h and 1000h, followed by a decrease, again associated with the hardness change. The effect of Sb content, observed for the 3h temper, is almost absent with the longer tempering treatment. In these steels, ageing for over 5h produced brittle fractures that were predominantly intergranular cleavage.

Ageing curves for the two 0.5 Ni + Sb steels and the 2.5 Ni steel are shown in Figure 2. The effect of the Sb additions is very slight; the curves are, within experimental error, identical to that of the Sb-free curve, which was included to check any effects that might result from the segregation of impurities other than Sb (P, S, Sn and As). In these three materials the low energy fractures were entirely transgranular cleavage.

Fracture Surface Analysis

The AES results for the 5 Ni + Sb steels are shown in Figures 3 and 4. Except for Cr, all values are weighted peak-height ratios (the top scale shows the proportions of intergranular fracture produced in the AES specimens). The peak-height ratios refer to: Sb - 454eV, Ni - 849eV, P - 120eV, Cr - 489eV and S - 150eV. With the exception of carbon these were the only elements detected at the grain boundaries (oxygen was also present on the spectra, but the peak-height increased with time, indicating adsorption from the system). Two sets of data points were obtained by taking mean values for the first and second 4 - 5 areas analyzed.

Depth profiles, obtained by controlled sputtering with argon ions, indicated that Ni, Sb and P were segregated at the grain boundaries, but with Ni showing a more gradual profile than either Sb or P. Sulphur decreased slowly with prolonged sputtering and an even slower change in the Cr peak was observed, suggesting that these elements were present, partly or wholly, as grain boundary precipitates. Profiles taken after 20h and 1000h showed that ageing beyond 20h did not produce any major change in the depth distribution of the segregants.

DISCUSSION

The AES results show that over the range of ageing times little variation occurs in the peak-height ratios of the impurities Sb and P. These peak-height ratios represent equilibrium concentrations achieved within 100h or even 20h at 793K. This is confirmed by the mechanical tests which show that the transition temperature rises steeply (at constant hardness) during the first 100h, but then gradually falls with increasing ageing time. The decrease in transition temperature observed after 100h occurs at constant grain boundary composition and is associated with decreasing hardness.

The peak-height ratios in Figures 3 and 4 were converted to concentrations by means of calibration curves obtained with homogeneous alloys [5, 7]. From estimates of the appropriate Auger attenuation lengths, the constants derived from the curves are [8, 9]:

$$\begin{aligned} P \text{ (monolayer coverage)} &= 0.0069.k.A_p \\ Sb \text{ (monolayer coverage)} &= 0.033.k.A_p \\ Ni \text{ (monolayer coverage)} &= 0.069.k.(A_p - 0.9A_p(X_c)) \end{aligned}$$

where A_p is the normalized and weighted Auger peak-height ratio and $A_p(X_c)$ is the bulk (transgranular or deep-sputtered) value. k allows for the division of the segregant by fracture and for the strong segregants, P and Sb, $k = 2$, but for Ni, which generally showed a deeper segregation profile, k is taken as 1.5 for this investigation. Because the Ni peaks are at high energies there is a large contribution to the Ni signal from the bulk; this effect together with the apparently deeper profile make Ni segregation difficult to quantify by AES. It may be observed from Figures 3 and 4 that Ni appears to show a slight decrease with ageing times up to 300h and this could be a non-equilibrium effect associated with carbide rejection [10]. Because of this uncertainty only the 300h and 1000h Ni peaks are taken as equilibrium values to calculate grain boundary coverage. For P and Sb, coverages have been taken from the 100h, 300h and 1000h results to give:

	5 Ni + 100 Sb		5 Ni + 200 Sb	
	Mean A_p	Monolayers	Mean A_p	Monolayers
Ni	7.45 ± 0.2	0.40 ± 0.02	9.36 ± 0.2	0.58 ± 0.02
P	9.08 ± 1	0.13 ± 0.02	10.17 ± 1	0.14 ± 0.02
Sb	1.29 ± 0.2	0.085 ± 0.013	1.84 ± 0.2	0.121 ± 0.013

(Errors refer only to the standard deviation in Figures 2 and 3, and do not include Auger calibration errors).

For the Sb-Ni-Fe system, the effect of bulk Sb concentration on segregation may be estimated from the theory of Guttman [6, 11]. In his derivation, Guttman has considered the case where the segregants obey the limited-site assumptions of McLean [12] and the isotherms are written in the form:

$$N_i^s = N_i^b \exp(-\Delta G_i/RT) \left[1 + \sum_{j=1}^{n-1} N_j^b (\exp(-\Delta G_j/RT) - 1) \right]^{-1} \quad (1)$$

where N_i^s = boundary concentration, N_i^b = bulk concentration, ΔG = free energy change, for solutes $i = 1, 2, \dots$

McLean segregation applied where the maximum coverage is limited to unity (one monolayer or less) and in a ductile solution the summation term above effectively allows for the decrease in free sites as the total segregation of solutes approaches the saturation level. Apart from the assumptions of the thermodynamic theory, equation (1) cannot provide a complete description of metalloid segregation because coverages are known to exceed one monolayer. This has been shown for the Sn-Fe system, where a coverage of about 3 monolayers has been observed [13], and as will be shown below, Sb segregation in Ni-Cr steels may reach a similar value. Ideally, a description of segregation in systems of the Sb-Ni-Fe type would require a multilayer isotherm, perhaps resembling the BET analogue of the Sn-Fe system [14], but which also embodies the thermodynamic theory of Guttman. The multilayer isotherm of the Sn-Fe system, which is the only system where multilayer segregation has been analyzed, is approximated at low coverages, by both the McLean isotherm and by:

$$N_i^s = N_i^b \exp(-\Delta G_i/RT) \quad (2)$$

For the purposes of this simplified analysis we will assume that the true isotherms of the Sb-Ni-Fe system are given by equation (2). This isotherm is reasonably accurate up to about 0.5 monolayers which is sufficient to cover the important range over which the Ni-Sb grain boundary interaction is expected to develop. In equation (2) the Sb and Ni segregation levels are taken to be independent as far as site availability is concerned, but it should be noted that there is no reason to assume *a priori* that Sb and Ni will compete for sites (for example, S and Sn do not compete for grain boundary sites [14], and at a free surface Ni and Sb do not compete for sites [15]).

Taking Sb, Ni and Fe as components 1, 2 and 3, the approximate segregation equations are:

$$N_1^s = N_1^b \exp[-(\Delta G_{13}^0 + \alpha' \cdot N_2^s)/RT] \quad (3)$$

$$N_2^s = N_2^b \exp[-(\Delta G_{23}^0 + \alpha' \cdot N_1^s)/RT] \quad (4)$$

where α' represents the Sb-Ni interaction coefficient. The problem in applying these equations is that measured values of ΔG_{13}^0 and ΔG_{23}^0 are not available and it is necessary to resort to estimated values. The measured value of ΔG for Sn in Fe at 793K is -44 kJ mol^{-1} [16] and because of the similarity between Sn and Sb atoms it is reasoned that ΔG_{13}^0 will be close to this value. Free surface studies of Ni segregation [15], associated with this research, show that ΔG_{23}^0 , at a free surface, is about $-14.7 \text{ kJ mol}^{-1}$ and for this approximate analysis ΔG_{23}^0 at grain boundary is taken as half the free surface value. Setting the Ni in solution at 4At% and using the interaction coefficient α' as the only adjustable parameter, the graphical solutions obtained for $\beta_{\text{Sb}}(N_1^s/N_1^b)$, and β_{Ni} at 793K are shown in Figures 5 and 6. The experimental points at high Sb concentrations are drawn from the literature [5, 17] and the fit shown corresponds to $\alpha' = -15 \text{ kJ mol}^{-1} \text{ m}^{-1}$.

In a quaternary system with Ni + Cr + Sb, the interactions of Cr with Sb and Ni should also be considered. However, it has been shown that the Sb-Ni interaction is stronger than that of Sb-Cr [4] and the effect of Cr in enhancing segregation seems to result largely from the strong Cr-Ni interaction [18]. Thus in the preceding equations the effect of Cr may be considered as entering through ΔG_{23}^0 .

This approximate analysis allows a prediction to be made only up to the solute range where the interaction terms become large and the Sb coverage begins to increase rapidly. However, it is interesting to compare the predictions of equations (3) and (4) with experimental data at other temperatures. If we take the same values of ΔG_{23}^0 and α' and correct ΔG_{13}^0 for entropy changes (based on the Sn-Fe system, where the entropy term is about $44 \text{ J mol}^{-1} \text{ K}^{-1}$) the results shown in Figure 7 are obtained for temperatures in the range 673 - 833K. Unfortunately, apart from 793K, there are no experimental points for comparison at low bulk Sb concentrations, where the isotherms are expected to be more accurate, but the changes in the positions of the curves clearly agree with the known experimental data for Ni-Cr steels. It should be noted that similar results can be obtained using the McLean isotherm as a low-coverage approximation and in this case the fit to the data requires an interaction coefficient of about $-24 \text{ kJ mol}^{-1} \text{ m}^{-1}$.

The effect of Ni content at low Sb concentrations is difficult to assess. The solutions shown in Figure 7 suggest that Ni content may exert only a modest effect for bulk Sb concentrations below 200 ppm. The AES measured value of ΔG_{Sb} (793K) for the 5Ni steels is -48 kJ mol^{-1} which is very close to the value of -44 kJ mol^{-1} for Sn in pure Fe. On this basis the effect of Ni appears to be small, but due to the lack of thermodynamic data the precise components of Sb segregation resulting from the Sb-Fe and Sb-Ni interactions are unknown. The clear variation in transition temperature with Sb content and the lack of measurable embrittlement in the 2.5Ni and 0.5Ni + 200Sb steels suggest that the effect of Ni could be somewhat greater than the adopted values for the thermodynamic constants would predict. In the 5Ni steels Ni will interact with Sb and to a lesser extent with P (as shown elsewhere [4], the Sb-Ni interaction is stronger than P - Ni), but the total effect is really one of P + Sb interacting with Ni. The P coverages are appreciable and the observed transition temperature shifts may be partly associated with P segregation (which is presumably higher than in the 0.5 Ni steels).

A combined plot of the known equilibrium coverages for P and Sb segregation is shown in Figure 8. There are important differences in the effect of impurity concentration. Due to the strong Sb-Ni interaction and multilayer segregation, the Sb coverage builds up exponentially with bulk concentration. In contrast P appears to show site saturation at about one monolayer which indicates the firm restraint imposed by McLean segregation (experiments are in progress to verify this limit). Thus the behaviour of P in this respect seems to resemble that of S in Fe (where site saturation occurs at about 0.5 monolayers [14]).

CONCLUSIONS

The main points of this investigation are: (1) The susceptibility of Ni-Cr-Sb steels to temper embrittlement varies with Ni content. After tempering for 3h at 923K, 0.5Ni steels containing up to 200 ppm Sb show almost no susceptibility to embrittlement at 793K. Under the same conditions

5Ni steels show about 100K rise in transition temperature. (2) Equilibrium grain boundary segregation of Sb, P and Ni was observed in the 5Ni steels. At the 200 ppm Sb level equilibrium concentrations are achieved for ageing times ≥ 100 at 793K. (3) Limited results suggest that bulk impurity content may be an important variable in systems where alloy/metalloid impurity interactions occur. In the case of Sb a large increase in the enrichment factor may occur at high bulk concentrations. Because of the approximately linear dependence of the transition temperature on the grain boundary concentration (references [2] and [5], for example), high bulk concentrations may be proportionately much more embrittling than lower concentrations. (4) The effect of Sb content on segregation seems to be in qualitative agreement with the Guttman analysis, but more comprehensive thermodynamic data will be required if the effects of Ni and Sb on segregation are to be determined in detail.

ACKNOWLEDGEMENTS

The authors wish to thank Professor R. W. K. Honeycombe for making research facilities available. Thanks are also extended to Professor C. J. McMahon for helpful discussions. Auger analyses were performed at the University of Pennsylvania during a visit by J.Q.C., and in this respect Professor C. J. McMahon and Dr. H. C. Feng are thanked for their cooperation. Research support (for J.Q.C.) by the U. S. Army, European Research Office, London, (Contract No. DAJA 37-74-C-1309) is gratefully acknowledged.

REFERENCES

1. LOW, J. R., STEIN, D. F., TURKALO, A. M. and LAFORCE, R. P., Trans. TMS-AIME, 242, 1968, 14.
2. LOW, J. R. and SMITH, C. L., Met. Trans., 5, 1974, 279.
3. GUTTMANN, M., KRAHE, P. R., ABEL, F., AMSEL, G., BRUNEAUX, M. and COHEN, C., Met. Trans., 5, 1974, 167.
4. MULFORD, R. A., Ph. D. Thesis, Univ. of Pennsylvania, November, 1974.
5. OHLANI, H., FENG, H. C., McMAHON, C. J., Jr. and MULFORD, R. A., Met. Trans., 7A, 1976, 87.
6. GUTTMANN, M., Surface Sci., 53, 1975, 213.
7. SUZUKI, H. G., M. Sc. Thesis, Univ. of Pennsylvania, 1974.
8. SEAH, M. P., Surface Sci., 40, 1973, 595.
9. POWELL, C. J., Surface Sci., 44, 1974, 29.
10. McMAHON, C. J., Jr., FURUBAYASHI, E., OTANI, H. and FENG, H. C., Acta Met., 24, 1976, 695.
11. GUTTMANN, M., Ph. D. Thesis, Univ. of Paris, 1974.
12. McLEAN, D., Grain Boundaries in Metals, London, Oxford University Press, 1957.
13. SEAH, M. P., Surface Sci., 53, 1975, 168.
14. SEAH, M. P. and HONDROS, E. D., Proc. R. Soc. London, A335, 1973, 191.
15. CLAYTON, J. Q., Ph. D. Thesis, University of Cambridge, 1976.
16. SEAH, M. P. and LEA, C., Phil. Mag., 31, 1975, 627.
17. MULFORD, R. A., McMAHON, C. J., Jr., POPE, D. P. and FENG, H. C., Met. Trans., to be published.
18. GUTTMANN, M., Metal Sci., to be published.

Table 1 Chemical Compositions of Alloys

C	Wt %		ppm			
	Ni	Cr	Sb	Mn	P	S
0.24	0.47	1.43	105	50	40	45
0.28	0.51	1.40	190	nd	50	nd
0.26	4.82	1.52	125	nd	60	nd
0.28	4.90	1.38	200	nd	50	nd
0.29	2.46	1.26	<10	nd	50	nd

nd = not determined

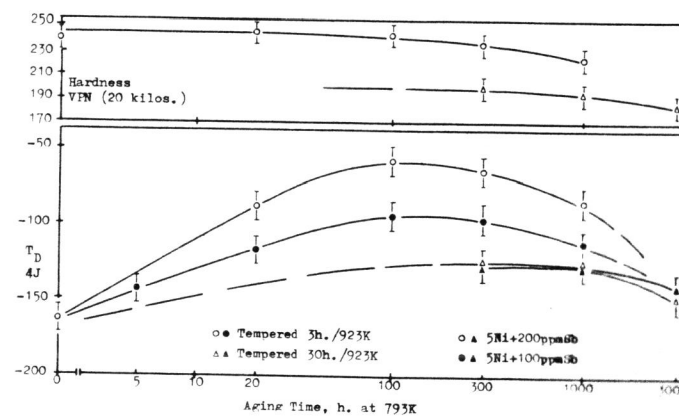


Figure 1 The Variation in Transition Temperature with Ageing Time for Steels Containing 5Ni + 1.4Cr + Sb

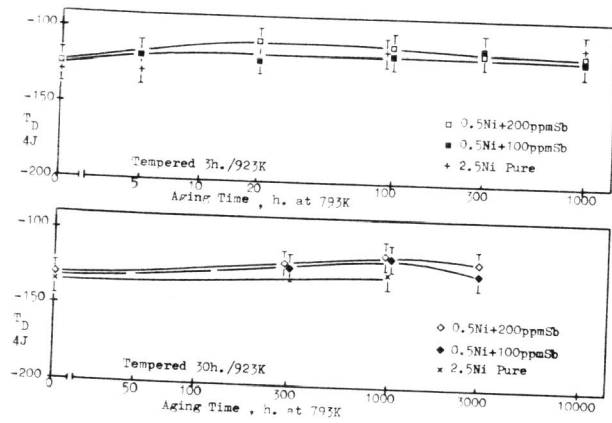


Figure 2 The Effect of Ageing Time on Transition Temperature for Steels Containing 0.5 Ni + 1.4Cr + Sb and 2.5Ni and 1.4Cr

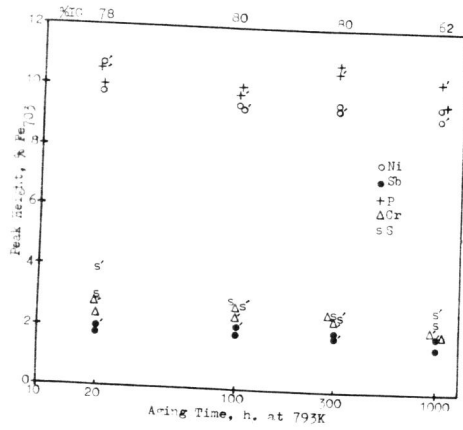


Figure 3 Normalized and Weighted Auger Peak-Heights as a Function of Ageing Time in 5Ni + 1.4Cr + 200Sb Steel

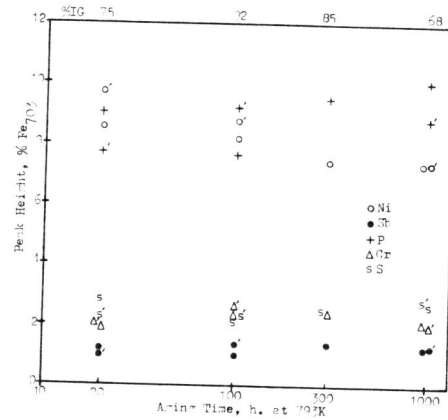


Figure 4 Similar to Figure 3, but for 5Ni + 1.4Cr + 100Sb Steel

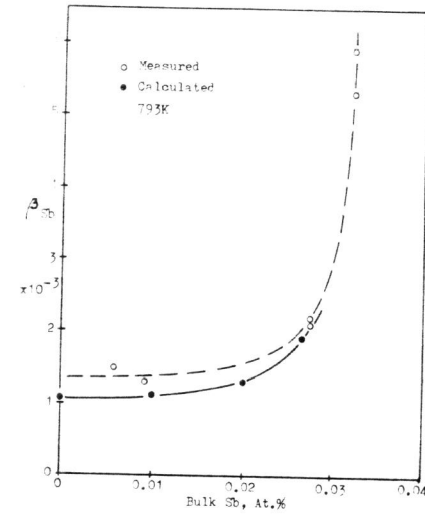


Figure 5 Enrichment Factors for Sb Segregation in Ni - Cr - Sb Alloys, Equilibrated at 793 K, as a Function of Bulk Sb Concentration. Measurements were Taken in Same Auger System and Results from the Present Work are Shown Together with Results from [5] and [17]

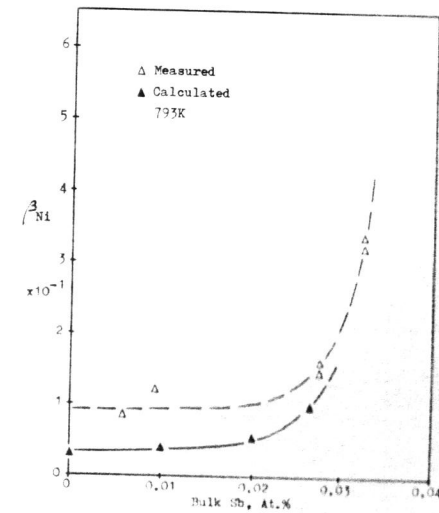


Figure 6 Similar to Figure 5, but for Ni Segregation

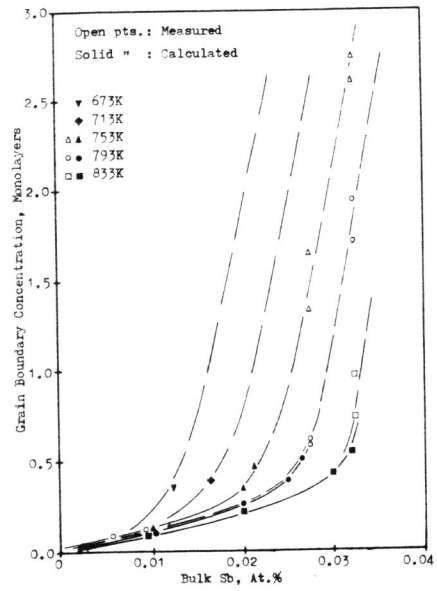


Figure 7 Segregation of Sb in Ni - Cr - Sb Steels, Calculated up to 0.5 Monolayers, Together with Experimental Data from the Present Work, [5] and [17]

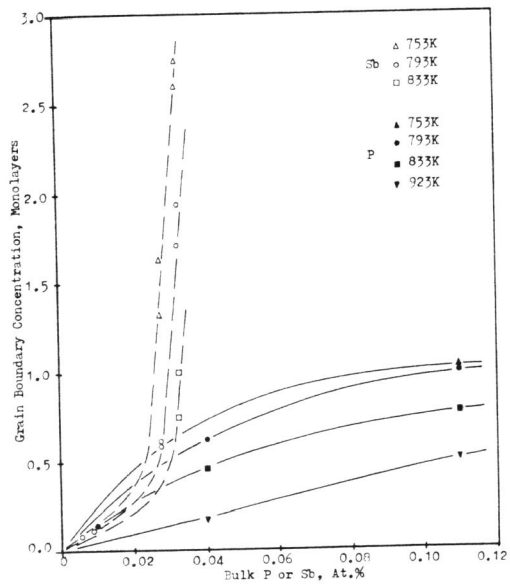


Figure 8 A Comparison of Sb and P Segregation Showing Experimental Results from Present Work, [4, 5] and [17]