

# Grain boundary segregation of copper, tin and antimony in C–Mn steels at 900°C

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The segregation of copper, tin and antimony to austenite grain boundaries at 900°C has been investigated in C–Mn steels using a scanning Auger microprobe (SAM). The specimens for microanalysis were prepared in a manner such that the prior austenite grain boundaries could be exposed by fracturing at room temperature in the UHV chamber of the SAM unit. Initial bulk concentrations ranged between 600 and 2600 ppm Cu, 50 and 360 ppm Sn and 8 and 35 ppm Sb. Significant enrichment of copper, tin and antimony was detected along the austenite grain boundaries. The grain boundary concentration of copper and tin was found to vary depending upon the initial bulk concentration while the average concentration of antimony at the grain boundaries was found to be approximately 1 at % for all of the heats studied. For heats in which a significant level of copper segregation was detected, a relationship of at % Cu = at % (Sn + Sb) at the austenite grain boundaries was observed. Deformation at 900°C prior to fracture in UHV was found to be necessary to promote segregation. Samples that were annealed at 900°C but not hot worked did not exhibit evidence of copper, tin or antimony segregation. These results have been interpreted in terms of the effects of deformation on segregation kinetics, and were correlated with hot ductility measurements made at 900°C.

## 1. Introduction

The present research was undertaken as part of a programme to study the hot ductility of high-strength low-alloy (HSLA) and C–Mn steels within the temperature range 800 to 1200°C. One of the purposes of this programme was to determine the effects of residual levels of impurity elements such as arsenic, tin, antimony and phosphorus. These elements were suspected as having a potentially detrimental effect since they have been shown to cause various types of embrittlement in carbon and low alloy steels [1].

The effects of residual impurity elements on hot ductility in carbon and low alloy steels have not been widely investigated. Harris and Barnard [2] found that hot cracking due to VN precipitation in a 1% Cr–1% Mo–0.3% V alloy steel increased in severity when copper, tin, antimony, and arsenic were present. However, no direct evidence of segregation was detected and no

definite link between segregation and hot ductility was established.

The possibility that segregation of tramp elements may lead to a loss of ductility during hot working of C–Mn steels would seem reasonable based on the effects that these elements have in causing high temperature brittleness in austenitic steels [3]. However, in order to show that a loss in ductility is directly attributable to the action of residual elements it is necessary to demonstrate that segregation is associated with the fracture process. This means that it must be possible to detect grain boundary segregation within the austenitic temperature range in the C–Mn steels used in this study. Early investigations into the mechanisms of temperature embrittlement suggested that segregation of impurities occurred during austenitization prior to quenching [4]. However, subsequent studies found no segregation of Sn or Sb along austenite grain boundaries and

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TABLE I Chemical compositions of C–Mn steels used in this study

Heat	Composition (wt %)														
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Nb	As	Sb	Sn	Al	N
A	0.17	1.40	0.009	0.001	0.232	0.059	0.031	0.111	0.019	0.027	0.0120	0.0008	0.005	0.012	0.0159
B	0.12	1.43	0.011	0.005	0.166	0.178	0.075	0.108	0.018	0.029	0.0107	0.0021	0.031	0.062	0.0109
D	0.19	1.32	0.009	0.019	0.218	0.263	0.203	0.160	0.061	–	0.0096	0.0035	0.036	0.036	0.0096
E1	0.18	0.97	0.008	0.028	0.192	0.186	0.138	0.073	0.029	–	0.0064	0.0037	0.006	0.014	0.0061
E2	0.18	1.03	0.007	0.028	0.197	0.195	0.140	0.100	0.034	–	0.0056	0.0028	0.054	0.014	0.0058

it was concluded that these elements do not segregate in austenite [5, 6]. This does not necessarily mean that segregation is impossible. It may simply be that the thermodynamic conditions for segregation are marginally favourable so that very little segregation will take place. However, a significant increase in segregation kinetics such as that provided by plastic deformation may be able to overcome the low driving force and therefore promote segregation of these impurities.

The purpose of this investigation was to determine if segregation of impurity elements such as copper, tin and antimony could be detected along the austenite grain boundaries and if this segregation has any influence on hot ductility behaviour at 900°C.

## 2. Experimental procedure

The compositions of the heats used in this study are given in Table I. Heat A is low in residual impurities while Heats B and D have much higher concentrations. These three heats are from commercial production and were chosen based upon the bulk concentrations of tin and antimony. The two experimental heats, E1 and E2, were melted with low and high tin respectively in order to verify the effect of tin on hot ductility observed in the commercial heats.

In studying hot ductility of these heats, knowledge of the critical temperatures,  $Ac_1$ ,  $Ac_3$ ,  $Ar_1$  and  $Ar_3$  is needed. These temperatures were determined by dilatometry at a heating rate of 275°C h<sup>-1</sup> and a cooling rate of 110°C h<sup>-1</sup>.

Hot ductility was determined from elongation and reduction of area of tension tests performed at 900°C. All hot tension testing was done in a vacuum of approximately 13 mPa. The test pieces were initially heated to 1200°C using a resistance furnace and held for 1 h after which they were cooled at 900°C and held for 0.5 h prior to being tested. The tensile specimens were strained at a constant crosshead speed of 1.25 mm min<sup>-1</sup> using

an Instron universal testing machine. The tensile specimens were buttonhead type with a diameter of 4 mm and a gauge length of 25 mm.

Grain boundary segregation was detected by Auger electron spectroscopy. Two methods of specimen preparation were utilized for Auger analysis. The first method consisted of vacuum encapsulating suitable samples and solution treating at 1200°C for 1 h followed by furnace cooling to 900°C and holding for 0.5 h then quenching. The purpose of this heat treatment was to duplicate the conditions that existed at the start of the hot tension tests. The heat treated samples were charged with hydrogen for 12 h using a solution of M/2 H<sub>2</sub>SO<sub>4</sub> with 0.25 g l<sup>-1</sup> NaAsO<sub>2</sub> at a current density of 15 mA cm<sup>-2</sup>. Hydrogen charging was necessary in order to induce intergranular fracture. Without hydrogen charging, transgranular microvoid coalescence was the predominant fracture mode. Breaking the specimens at –196°C would result in brittle cleavage fracture. The second set of specimens was prepared from hot tensiles that had been elongated 10% at 900°C in vacuum after first being solution treated *in situ* at 1200°C. These specimens were fast cooled in an argon stream after hot deformation. Auger impact specimens were machined before heat treatment for the undeformed pieces and after straining for the deformed pieces. The Auger impact specimens were 3.6 mm in diameter and 25.4 mm long. A notch approximately 0.2 mm wide and 0.5 mm deep (minor diameter 2.6 mm) was cut a distance of 6.4 mm from one end.

The Auger analysis was performed in a Physical Electronics 550 scanning Auger microprobe (SAM). All samples were fractured by impact at room temperature in the UHV chamber. The fracture surfaces were examined by observing the secondary electron image so that a suitable area for analysis could be selected. The instrument was operated at 5 kV with a beam current of approximately 4 × 10<sup>-7</sup> A, sensitivity 2× and a modulation of

3 V. All analyses were done in the spot mode with a beam size of about 3  $\mu\text{m}$ . After removing the broken pieces from the UHV chamber, the fracture surfaces were examined in the SEM so that high resolution images of the fracture features could be obtained.

Grain boundary compositions were determined using the method given in [7]. All peaks were normalized to the 703 eV Fe peak. At least nine point analyses were taken on the samples from Heats B and D, however only three were obtained from Heat A due to the relatively low incidence of intergranular fracture. No attempt was made to determine compositional profiles due to the lack of a suitable sputtering source. Also the inherent uncertainty associated with trying to remove atom layers uniformly from a surface that exhibits a high degree of topography, results in some ambiguity in any profile determined by sputtering.

Microanalysis using a Philips 400T AEM was performed on foil samples from Heat B in order to determine if segregation detected by Auger electron spectroscopy (AES) could be verified by a method that was not sensitive to fracture mode. Foils were made from samples that were solution treated at 1200° C, cooled to 900° C and quenched. Additional samples were prepared from a tensile specimen that had been solution treated at 1200° C and strained 10% at 900° C and quenched. Foil preparation consisted of wafering a slice approximately 0.3 mm thick then punching 3 mm diameter discs. These discs were ground on 400 and 600 grit paper to approximately 0.05 mm. Next the foils were perforated using a twin-jet electropolishing unit and a solution of 2% perchloric acid in 50% 2-butoxyethanol, 50% methanol at a temperature of -20° C and 90 V. Microanalysis of grain boundaries was carried out in the STEM mode using a probe diameter of 5 nm. Quantitative analysis was made using the peak intensity ratio technique with  $k$  factors for  $K$  lines from the data of Wood *et al.* [8]. The  $k$  factor for the tin  $L$  line was determined by measurements made on a standard of 94.6% Fe, 5.4% Sn.

### 3. Results

Dilatometrical measurements on transformation temperatures for Heats A, B and D are summarized in Table II. These values were determined with a heating rate of 275° C h<sup>-1</sup> and a cooling rate of 110° C h<sup>-1</sup>. However, the rate of cooling during the hot tension tests is approximately 400° C h<sup>-1</sup>

TABLE II Data of critical temperatures\*

Heat	Critical temperature (° C)			
	$Ac_1$	$Ar_1$	$Ac_3$	$Ar_3$
A	714	631	905	851
B	716	624	864	805
D	723	624	897	847

\*Heating rate 275° C h<sup>-1</sup>, cooling rate 110° C h<sup>-1</sup>.

from the solution treatment temperature of 1200° C to an 800° C test temperature. This cooling rate is well in excess of the rate used to determine  $Ar_3$ . Therefore the actual  $Ar_3$  temperature during the tension testing cycle will be depressed somewhat from the values reported in the table. This is an important point since the start of the ferrite transformation may have a significant effect on ductility. For Heats A, B and D, samples that were solution treated, cooled to 800° C and held for ½ h, then quenched, no ferrite was detected in the microstructure.

Data of tensile elongation and reduction of area for Heats A, B and D are presented in Table III. As can be seen, the ductility of Heat A, which had the lowest residual content, is significantly better than Heats B and D.

Examination of the Auger spectra from grain boundary facets of the annealed and quenched samples of the three heats failed to reveal any enrichment of impurity elements other than sulphur. A typical spectrum from a grain boundary region in Heat B is shown in Fig. 1. The high resolution micrographs in Fig. 2 show that the fractures in these specimens were predominantly intergranular. The failure to detect any grain boundary segregation in these samples is consistent with previous studies that utilized similar austenitization and quenching treatments.

While no segregation was detected in the annealed and quenched samples, the Auger spectra from intergranular regions of the hot work samples of Heats B and D showed a consistent pattern of copper, tin and antimony segregation. No copper segregation was detected in Heat A, however, there

TABLE III Hot ductility at 900° C

Heat	% E1	% RA
A	34.0	46.8
B	22.1	28.2
D	29.3	33.2
E1	45.7	91.8
E2	20.9	32.0

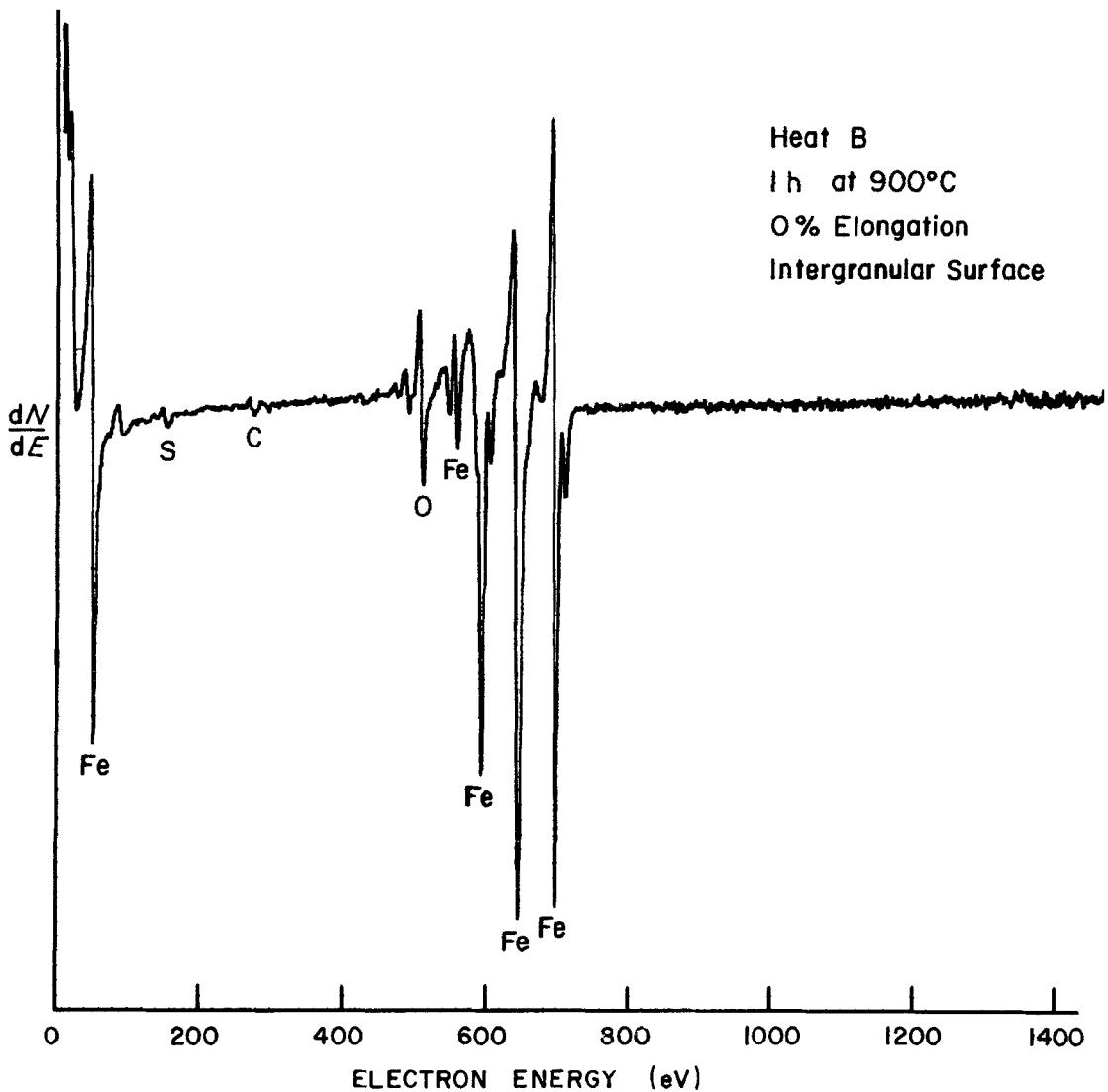


Figure 1 Auger spectrum from a grain boundary region of an undeformed sample of Heat B. The sample was heat-treated and subsequently embrittled by hydrogen charge. Segregation of Cu, Sn and Sb is not detectable.

was a slight enrichment of tin noted. The concentration of antimony on the grain boundaries was approximately the same in all three heats regardless of the bulk antimony content. Tin levels seemed to depend on the bulk concentration and were highest in Heat B while in Heat A the average grain boundary tin level was only 0.45 at%. A typical Auger spectrum from a grain boundary

region of a hot worked sample of Heat B is shown in Fig. 3 and the average grain boundary compositions are given in Table IV. Comparing the results in Tables III and IV it can be seen that ductility at 900°C agrees well with the overall levels of copper, tin and antimony which segregated to the austenite grain boundaries.

Failure during hot tension testing occurred

TABLE IV Grain boundary compositions

Heat	Cu		Sn		Sb		S		N		Cu/(Sn + Sb)
	at %	wt %	at %	wt %	at %	wt %	at %	wt %	at %	wt %	
A	—	—	0.45	1.05	1.12	2.72	9.89	6.23	6.58	1.81	—
B	3.65	4.27	3.09	6.75	1.09	2.44	5.55	2.95	4.17	1.09	0.87
D	3.60	4.12	2.30	5.15	1.15	2.67	5.73	3.32	4.95	1.19	1.04

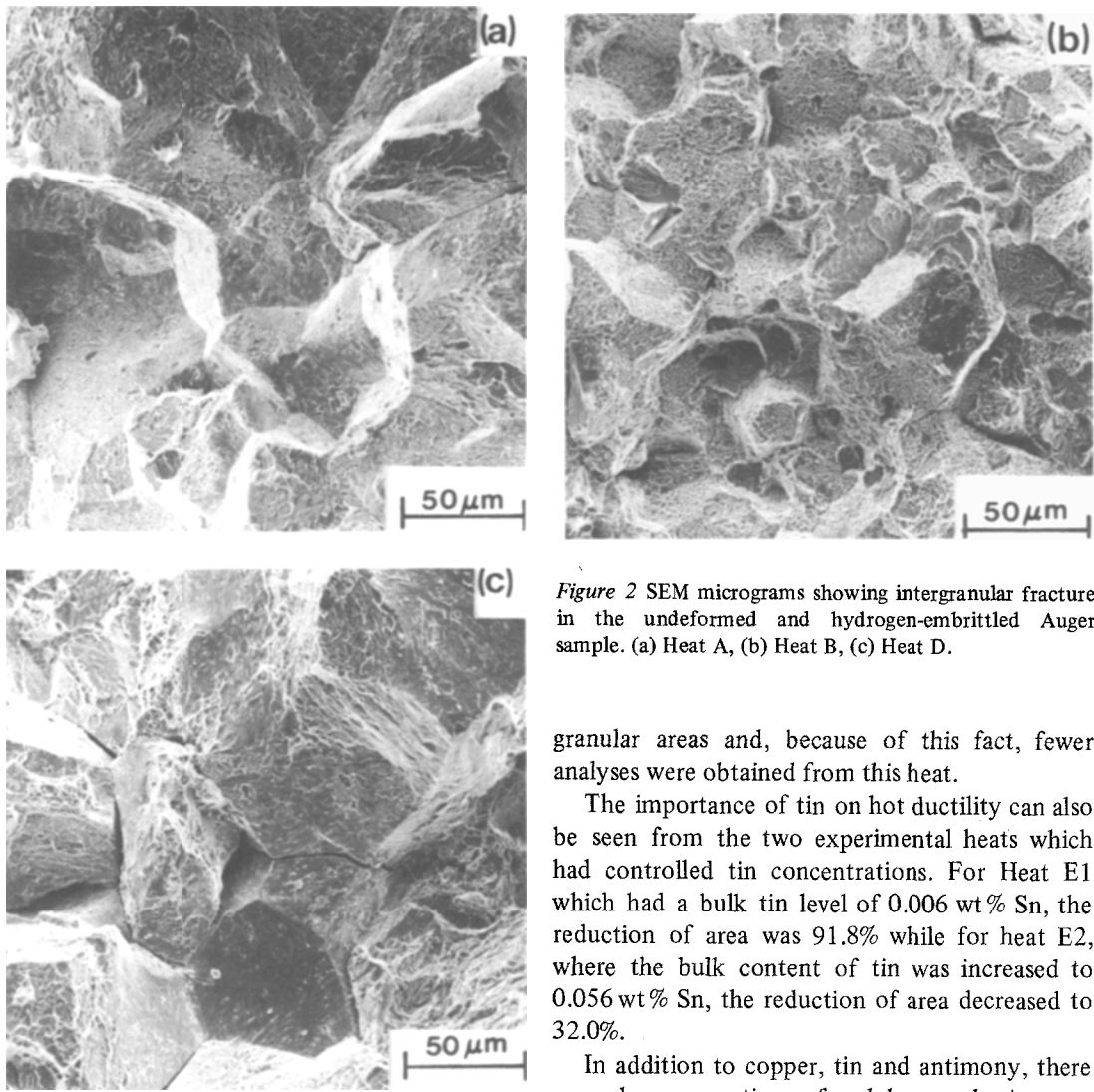


Figure 2 SEM micrograms showing intergranular fracture in the undeformed and hydrogen-embrittled Auger sample. (a) Heat A, (b) Heat B, (c) Heat D.

through the formation and growth of cavities along the austenite grain boundaries as shown in Fig. 4. The high resolution SEM micrographs of the fracture surfaces from the hot worked Auger specimens in Fig. 5 also show that failure occurred through intergranular microvoid coalescence. Pre-straining the Auger specimens served to initiate the intergranular cavities, and impact in the AES served to complete the fracture along the weakened grain boundaries. The primary particles that nucleated the intergranular microvoids were identified as aluminium and niobium rich grain boundary precipitates [9]. No MnS precipitates were found by the methods used to extract and identify these particles. The fracture surface from the sample of Heat A had relatively few inter-

granular areas and, because of this fact, fewer analyses were obtained from this heat.

The importance of tin on hot ductility can also be seen from the two experimental heats which had controlled tin concentrations. For Heat E1 which had a bulk tin level of 0.006 wt% Sn, the reduction of area was 91.8% while for heat E2, where the bulk content of tin was increased to 0.056 wt% Sn, the reduction of area decreased to 32.0%.

In addition to copper, tin and antimony, there was also segregation of sulphur and nitrogen. However, there was no correlation between the concentration of sulphur or nitrogen at the grain boundaries and loss of ductility. Heat A had the highest levels of sulphur and nitrogen enrichment and also the highest ductility.

In an attempt to verify the observed segregation by a method which did not require producing an intergranular fracture, STEM microanalysis was performed on the prior austenite grain boundaries of foil specimens. Several methods of sample preparation were utilized in trying to duplicate the high temperature segregation at room temperature. No segregation was detected in foils made from material that had been annealed at 900°C and quenched. No segregation was detected along any boundary in samples slow cooled from 900°C. The only method that gave any indication of segregation was for samples strained at 900°C and

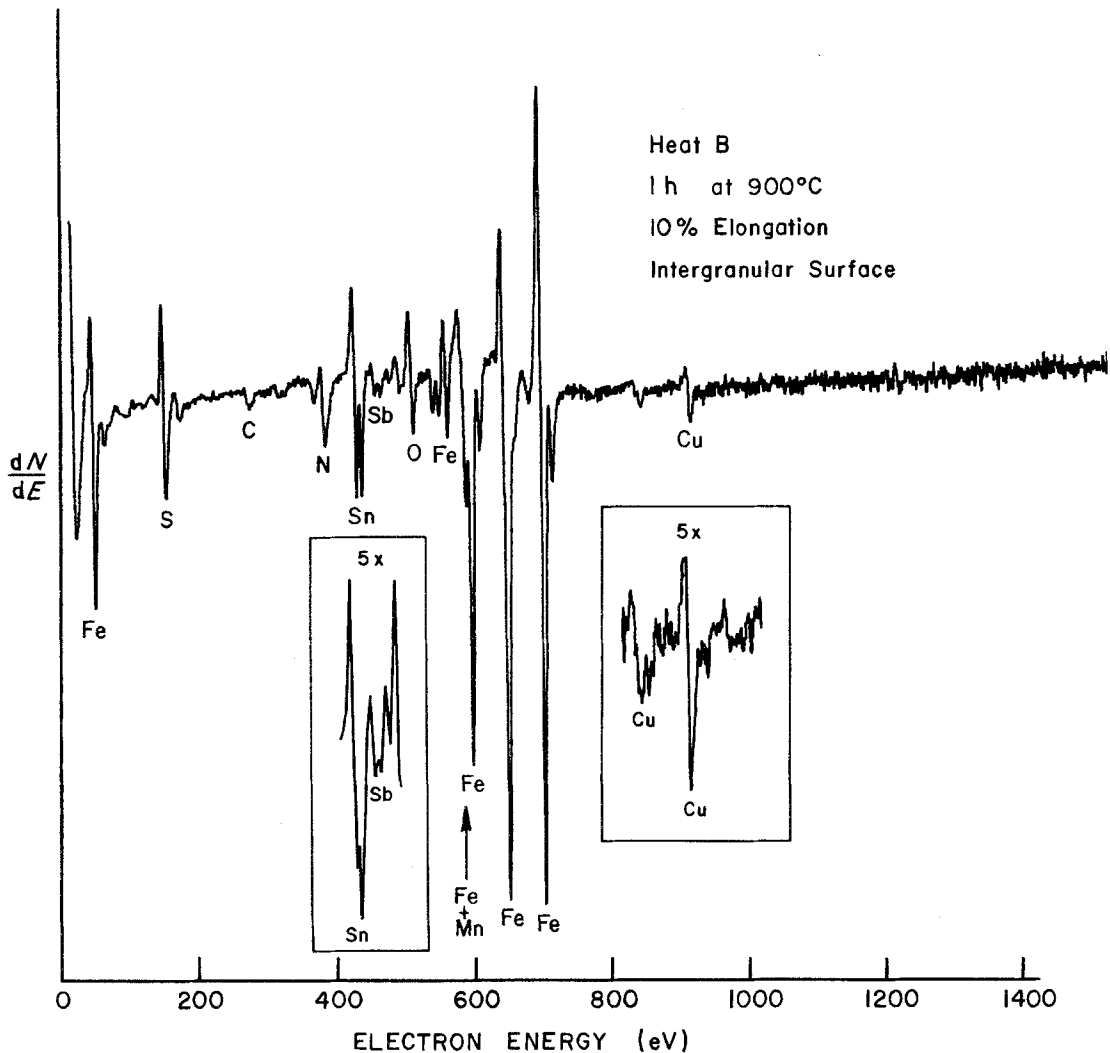


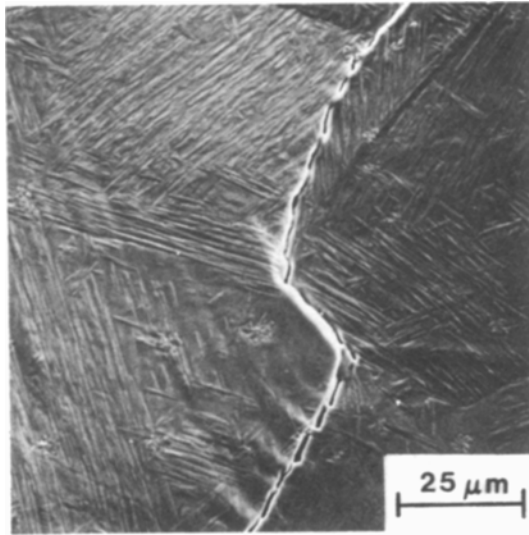
Figure 3 Auger spectrum from a grain boundary region of a hot-worked sample (10% strain at 900° C) of Heat B. The sample was heat-treated and hydrogen-embrittled. Segregation of Cu, Sn and Sb is visible.

quenched from the furnace. The average composition of tin on the prior austenite grain boundaries was 0.22 wt% Sn for ten boundaries from samples of Heat B. Using the procedure for estimating grain boundary composition outlined by Michael [10], 0.22 wt% Sn in the analysed volume corresponds to approximately 7 wt% Sn on the grain boundary assuming a foil thickness of 250 nm and using a 10 nm probe. This result agrees well with that based upon the Auger measurements. The problem with measuring monolayer segregation at this low level concentration of tin is that the tin *L* line used for the analysis does not produce a statistically significant peak in the spectrum since the peak to background is so low. However,

recent work by Doig and Flewitt [11] has demonstrated that monolayer segregation of tin can be detected with an AEM if suitable techniques are used.

### Discussion

All previous studies have found that elements such as tin and antimony do not segregate in austenite grain boundaries [5, 6]. These studies involved austenitizing and quenching specimens then suitably embrittling them to produce fractures along the prior austenite grain boundaries. These procedures were similar to the method used to prepare the annealed and quenched samples in this study. The present results confirm that



*Figure 4* Grain boundary cavities in Heat B revealed by thermal etching during tension testing in vacuum at 900° C. The sample was strained to maximum load then fast cooled in a stream of argon.

segregation does not occur during normal austenitization treatments. Segregation was only detected in samples that were deformed at 900° C. The copper, tin and antimony detected on the fracture surfaces of these heats could be the result of enrichment along either the austenite grain boundaries or the surfaces of the grain boundary cavities. The major contribution of segregation to the fracture process in these steels is through its effect on the nucleation and growth of intergranular cavities. The absence of segregation prior to hot deformation and the relatively short time available (< 120 sec) for appreciable diffusion of copper, tin and antimony during prestraining suggests that plastic deformation enhances the kinetics of the segregation process.

Two possible means by which plastic deformation can enhance segregation are dislocation transportation of the embrittling elements to the austenite grain boundaries [12–14] and strain enhanced diffusion along dislocation pipes [15–17]. Both processes rely on dislocation mechanisms; however, the effects of temperature and strain rate do not affect each process in a similar manner. Temperature and strain rate are important since they affect the dislocation substructure and dislocation density that develops as a result of plastic deformation. High temperatures and low strain rates result in a low dislocation density and a coarser substructure while lower temperatures

and higher strain rates produce a substructure with a finer subgrain size and high dislocation density.

Dislocation transport involves the formation of solute atmospheres around mobile dislocations. The atmospheres form as a result of the elastic accommodations afforded through the interaction of the strain fields around the dislocations and the solute atoms [18–21]. Based on considerations of elasticity, it would be expected that the largest substitutional atoms will interact most strongly with a dislocation. As a dislocation moves during deformation it cannot pass through a grain boundary and thus the solute atoms dragged by the dislocation will be deposited on the boundary. The solute atoms will remain attached to the boundary as long as the binding energy of the solute and the boundary is greater than between the solute and the dislocation. Although the transport model was originally proposed for the interstitial solutes [12–14], it should be applicable also for the substitutional solutes, especially at high temperatures where their mobility may be as high as that of the dislocations. This mechanism is supported by the results of the strain rate effect on hot ductility of the three commercial heats [9]. In all cases, the hot ductility decreased with decreasing strain rates, indicating that at lower rates the substitutional solutes were able to catch up with the glide dislocations and enhance grain boundary segregation.

Another possible effect of the increase in dislocation density due to deformation is that the diffusivities of the embrittling solutes could be enhanced through the introduction of short circuit paths such as subgrain boundaries. The mechanisms of this process were described by Cohen [17]. The basic feature of strain enhanced diffusivity is that any factor that produces an increase in the dislocation density will serve to increase the diffusivity of the solute compared to an undeformed sample. As Cohen [17] pointed out, strain enhanced effects should be in proportion to the amount of diffusion which takes place along dislocation pipes or dislocation subboundaries. This leads to the result that segregation should be enhanced at high strain rates and lower temperatures since these factors increase the dislocation density in the deformation substructure. However, from the results of the strain rate effect on hot ductility [9], it seems unlikely that the pipe diffusion mechanism would play a

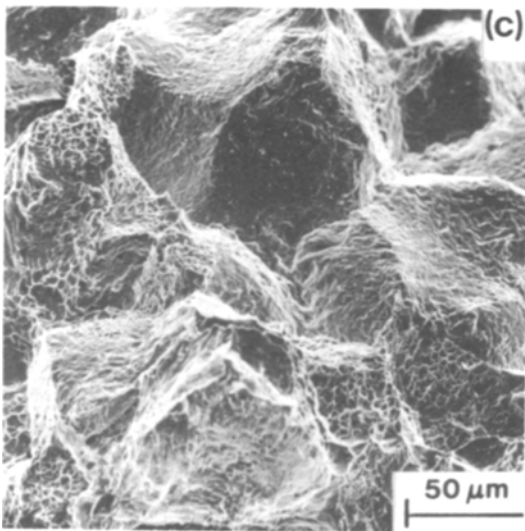
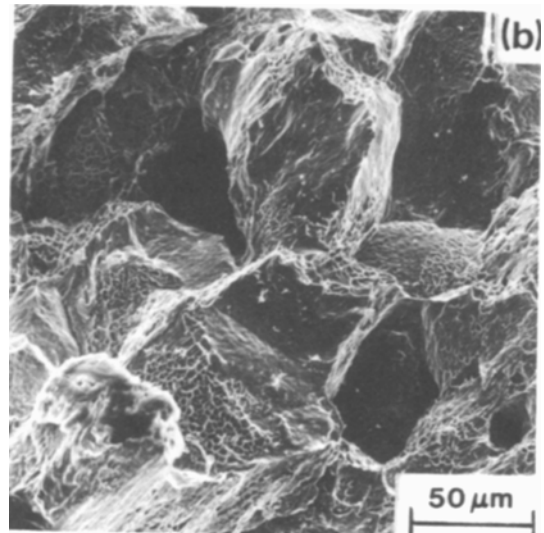
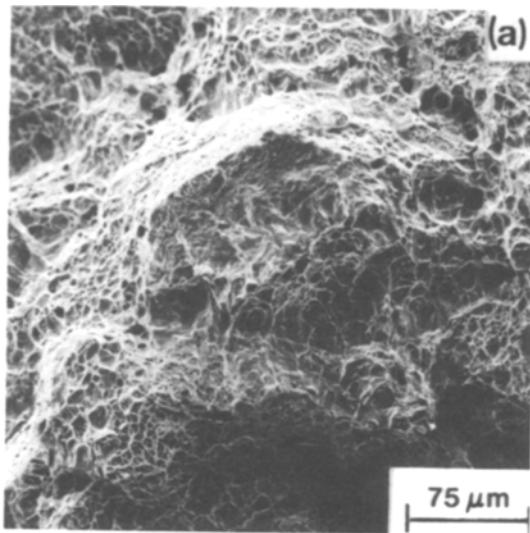


Figure 5 SEM micrographs showing intergranular fracture in the hot-worked Auger sample (a) Heat A, (b) Heat B, (c) Heat D.

major role in the segregation process in the present case.

Tin and antimony are known to cause embrittlement in steels and it seems reasonable to suppose that segregation of these elements during hot working would have a deleterious effect on ductility. However, the effect of copper segregation and its role in hot cracking is somewhat more difficult to explain. While copper, tin and antimony have been found to be responsible for surface hot shortness [22, 23], copper has not been found to segregate at the bulk concentrations typical of the heats used in this study, particularly since it has a relatively high solubility in austenite. However there are several factors that may be important in copper segregation. In temper em-

brittlement, it has been determined that the presence of alloying elements that can cosegregate with the embrittling species greatly enhances both the amount of segregation and the severity of embrittlement. A model of cosegregation for grain boundary embrittlement was proposed by Guttman [24, 25]. It has also been shown that all the embrittler-cosegregants form stable compounds and that these compounds belong to a very limited group of crystal structures. The most common of these crystal structures is the Type B8 or NiAs structure. In the present case of copper segregation, possibly the role of copper is to act as a cosegregant. A check of the Cu–Sn phase diagram shows that  $\text{Cu}_6\text{Sn}_5$  has the NiAs structure. Assuming, as Guttman has proposed, that the formation of an embrittling compound is more detrimental than element segregation alone and that copper, tin and antimony form a compound similar to  $\text{Cu}_6\text{Sn}_5$ , then the interaction of these elements can be explained on the basis of the formation of an alloy embrittler couple between copper and tin plus antimony.

The low bulk concentration of copper in the heats used in this study would generally not be considered detrimental since copper by itself does not cause embrittlement at these concentration levels. However, the role of copper is not as an embrittling species but rather it enhances the segregation of tin and antimony. On an atomic



basis, copper and tin were found in this study to segregate in a ratio close to 1:1. On a weight basis this means that approximately twice as much copper over tin is needed to cosegregate. More copper would not increase embrittlement. If the bulk copper content is so low that copper segregation does not occur then the embrittling effect of tin is likely to be reduced due to the absence of a Cu-Sn/Sb compound formation in the austenite grain boundaries. This conclusion is supported by the Auger data from Heat A. There was no copper segregation and no embrittlement in this alloy. Low levels of tin and antimony were detected but at the concentrations present these elements did not cause embrittlement.

Although manganese and sulphur were found to segregate, it is not possible to ascribe any embrittlement to these elements based on a comparison of the Auger results. Heat A had the highest concentration of manganese and sulphur and yet was not embrittled. Sulphur is very surface active and will segregate in austenite so that in the absence of other species sulphur is likely to be found along the prior austenite grain boundaries. In fact, all the intergranular fracture surfaces for both the deformed and the hydrogen embrittled samples had some amount of sulphur segregation.

## 5. Conclusion

Segregation of copper, tin and antimony to austenite grain boundaries during high temperature deformation at 900°C will lead to a loss of ductility in C-Mn steels. Deformation is necessary in order to produce detectable levels of segregation. The deformation process aids the segregation kinetics through the increase in dislocation density. Dislocations provide a transport mechanism to assist the movement of copper, tin and antimony to the austenite grain boundaries. The action of copper in reducing ductility is through its interaction with tin and antimony. Copper most likely acts as a cosegregant thereby increasing the adverse effect of tin and antimony.

## Acknowledgement

The authors are grateful to their colleagues at the Research Department of Lukens Steel Company, in particular, Dr C. R. Roper Jr and Mr I. Mair for helpful discussions and Dr W. W. Scott Jr for

his continuing interest and encouragement. This research was supported by the Lukens Steel Company under a university education grant.

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Received 17 March  
and accepted 21 September 1983