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# INFLUENCE OF PHOSPHORUS AND SULPHUR SEGREGATION ON STRESS RELIEF CRACKING

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## Abstract

Three commercial weldable fine grained structural steels and four experimental melts with lowered contents of trace elements were subjected to a welding simulation treatment followed by stress relaxation (SR) tests. After testing times of up to 8 hours the samples were removed from the testing rig, broken in the fracture stage of an Auger instrument, and the fracture surface was examined in situ for segregation of elements. SEM investigations of the fracture surfaces and light microscope served to characterize fracture mode and microstructure.

The microfractural appearance of the grain boundaries exposed by the impact loading in the Auger instrument and of the ones separated by SR-testing was significantly different. While the fracture surfaces originating from SR-testing were flat, the samples subsequently broken in the Auger instrument showed a dimpled structure.

It could be shown that cracks always started at MnS - precipitates, and that the intergranular crack propagation was enhanced by the segregation of phosphorus. The segregation of elementary sulphur was initiated by the stress field of the cracks already formed and, contrary to the phosphorus enrichment, could be prevented by lowering the S-content in the melt. The other trace elements seemed to play no part in the stress relief cracking of the steels investigated.

## Introduction

Stress-relief-annealing of welded joints in fine grained structural steels can cause a form of embrittlement known as stress-relief cracking. Microstructurally, this phenomenon is characterized by an intergranular crack path in the coarse grained heat affected zone (HAZ).

There are different theories concerning the mechanisms of this particular type of embrittlement (3, 5). The segregation of tramp elements to the grain boundaries (1, 2), the precipitation of MnS at the grain boundaries (3), as well as the precipitation of carbides or nitrides within the grains and the resulting impediment of relaxation (5), all these theories endeavour to explain the cause. It was the objective of this research, to investigate whether the segregation of the elements phosphorus and sulphur to the grain boundaries could be the cause of this embrittlement.

## Materials and Methods

### Test procedure

The investigations were carried out on three commercial steels with the German designations STE 690 (grade No. 1.8921) in the following indicated as steel I, 20 MnMoNi 55 (grade No. 1.618o) indicated as steel II, and 15 NiCuMoNb (grade No. 1.6368) indicated as steel III. The chemical composition of these steels is shown in Fig. 1.

| Steel | Element [Wt %] | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Cr | Mo | Ni | V | Cu | Nb | As | Sb | Sn |
| I | 0,20 | 0,24 | 0,99 | 0,013 | 0,012 | 0,51 | 0,22 | 0,06 | 0,06 | 0,05 | 0,001 | 0,002 | 0,001 | 0,004 |
| II | 0,18 | 0,28 | 1,20 | 0,005 | 0,009 | 0,06 | 0,52 | 0,67 | 0,005 | 0,06 | 0,002 | 0,007 | 0,002 | 0,004 |
| III | 0,19 | 0,38 | 1,13 | 0,015 | 0,006 | 0,28 | 0,41 | 1,18 | <0,01 | 0,68 | 0,041 | 0,006 | <0,002 | 0,006 |

Fig. 1.  Chemical composition of the commercial steels.

In addition, four variants of each commercial grade were made as laboratory melts differing in their sulphur, phosphorus and trace element contents, Fig. 2.

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**Steel I**

| commercial [wt-%] | melt A [wt-%] | melt B [wt-%] | melt C [wt-%] | melt D [wt-%] |
|---|---|---|---|---|
| P  0,013 | 0,004 | <0,002 | <0,002 | 0,017 |
| S  0,012 | <0,002 | 0,013 | 0,011 | 0,003 |
| As 0,002 | 0,005 | 0,005 | 0,003 | 0,003 |
| Sb 0,001 | <0,002 | <0,002 | <0,002 | <0,002 |
| Sn 0,004 | 0,002 | 0,002 | 0,006 | 0,005 |

**Steel II**

| commercial [wt-%] | melt A [wt-%] | melt B [wt-%] | melt C [wt-%] | melt D [wt-%] |
|---|---|---|---|---|
| P  0,005 | <0,002 | <0,002 | <0,002 | 0,005 |
| S  0,009 | <0,001 | 0,006 | 0,005 | <0,001 |
| As 0,007 | 0,003 | 0,010 | 0,010 | 0,005 |
| Sb 0,002 | 0,002 | <0,002 | 0,002 | 0,003 |
| Sn 0,004 | 0,002 | 0,002 | 0,005 | 0,002 |

**Steel III**

| commercial [wt-%] | melt A [wt-%] | melt B [wt-%] | melt C [wt-%] | melt D [wt-%] |
|---|---|---|---|---|
| P  0,015 | 0,006 | 0,005 | 0,006 | 0,022 |
| S  0,006 | <0,003 | 0,004 | 0,004 | <0,003 |
| As 0,006 | 0,010 | 0,011 | 0,002 | 0,002 |
| Sb <0,002 | <0,002 | <0,002 | <0,002 | <0,002 |
| Sn 0,006 | 0,009 | 0,008 | 0,007 | 0,007 |

Fig. 2. Variants of the chemical analysis.

melt A - lowest possible contents of S, P, Sb, As, Sn

melt B - lowest possible contents of P, Sb, As, Sn

melt C - lowest possible contents of P

melt D - lowest possible contents of S.

In order to produce the coarse grained structure of the HAZ, all test materials were subjected to a welding simulation treatment with a peak temperature of 1300 °C and a holding time of 5 seconds at this temperature. The cooling time $t_{8/5}$ was 10 s. The samples were machined from the steels overheated in this way and the testing length was well within the welding simulation zone. These samples were then subjected to stress relaxation (SR) tests using the following testing parameters:

| | |
|---|---|
| sample diameter | 10 mm |
| testing length | 25 mm |
| heating rate | 30 °C/min |
| holding time before loading | 60 min |
| testing temperature | 610 °C |
| starting strain | 0.2 to 0.5 % |

The testing times were 2, 4, 6 and 8 h, and, in order to investigate the time dependence of the precipitation or segregation behaviour in these materials, in selected cases over 24 h. At the end of the tests the samples were unloaded and cooled to room temperature in the furnace.

All SR tested samples were subjected to Auger electron spectroscopy (AES) investigations using PHI 550 and 595 instruments. For this purpose specimens were prepared with a notch in the coarse grained zone for fracturing "in situ" in the Auger instrument. Fracturing was done at room temperature at a pressure of less than $6 \cdot 10^{-8}$ Pa with the notch serving to initiate the crack. The pressure was low enough for the fracture surfaces to remain uncontaminated for a time duration sufficient for the AES-investigations to be carried out.

Analysis started about 5 min after fracture and, at the longest, lasted 1.5 h during which time 8 to 10 AE-spectra could be measured. This time was too short for any changes of the peak heights of carbon and oxygen to be produced by the residual gas.

For the majority of investigations a lateral beam diameter of 20 μm and a beam current of 0.4 to 0.6 μA were used. The extent of coverage of the segregating tramp elements mentioned below was calculated using a procedure by Seah (4), and assuming that the segregated elements were distributed equally between both fracture surfaces.

The degree of damage during SR testing was investigated on the samples fractured in the Auger instrument by light and scanning electron microscopy (SEM). Metallographic sections normal to the fracture surface were prepared and etched with 2 % $HNO_3$ in alcohol to reveal the microstructure. The SEM (Cam Scan 4) investigations were carried out to determine the fracture modes on the exposed surfaces.

## Results

### Degree of damage in the samples

Fig. 3 ilustrates the stress-relief-behaviour of the commercial steels at 610°C by showing the decrease of the highest possible stress not causing any failure within 8 hours, with the testing time. Steel I could only be loaded with an initial stress of 60 % of the 0.2 % yield strength at 610 °C, while materials II and III reached the time required with an initial stress of 80 % of the yield strength at this temperature. It is noteworthy, that the stress-relief-capacity of these two steels is substantially higher than that of steel I. This phenommenon can be traced back to the different precipitation behaviour of these grades. With steel I the precipitation of vanadium nitride within the grains during stress-relief-annealing leads to this reduced relaxation capacity.

The investigations of the cracking suffered during SR-testing revealed that all samples tested at 610 °C showed signs of the beginnings of grain boundary separations even after testing times as short as 1 h. Fig. 4 illustrates this observation.

Fig. 5 reveals clearly that formation of voids started at particles precipitated on the grain boundaries, the sizes of which were mostly

substantially smaller than 1 µm and therefore not clearly identifiable by EDX analysis. With increasing testing times the grain boundaries became completely separated, with the edges of the crack appearing smooth even at highest magnifications (Fig. 6).
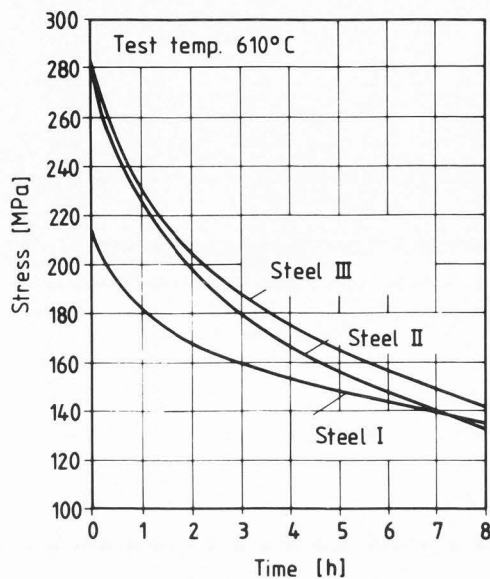


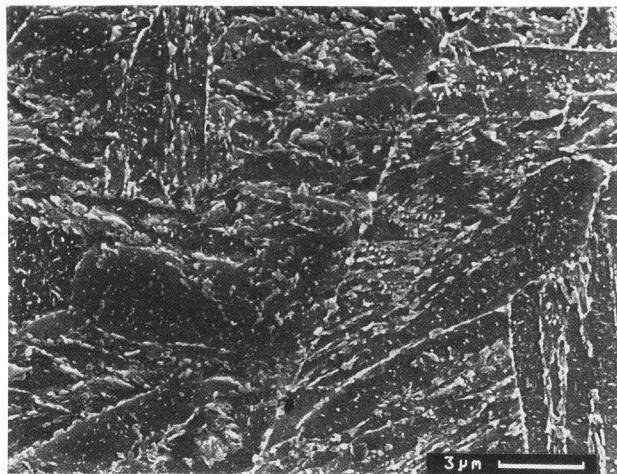Fig. 3. Stress-relief behaviour of the commercial steels.



Fig. 4. Beginning of grain boundary separation. (Steel II) Rel. Test 610 °C/2 h.

This mechanism of crack formation was the same in all steels investigated; the crack plane was mostly normal to the loading direction. Transverse micrographs of samples not broken in the SR test revealed a number of cracks in the coarse grained zone of steels II and III which could not be observed in samples of steel I, tested, however, at lower loading stress/yield strength ratio. At the same loading stress/yield strength ratio

the samples of steel I failed after short testing times. Obviously, the crack propagation rate is so high in this case, that a small number of crack nuclei is sufficient to cause failure of the sample.

The degree of damage caused by SR-testing was also investigated on the AES-samples of the trial melts. Again, the intergranular separation started at inhomogeneities on the grain boundaries, and after longer testing times wide open grain boundary separations could be observed.
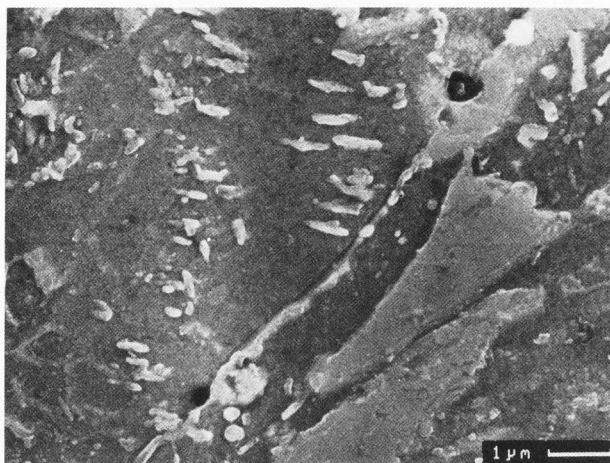


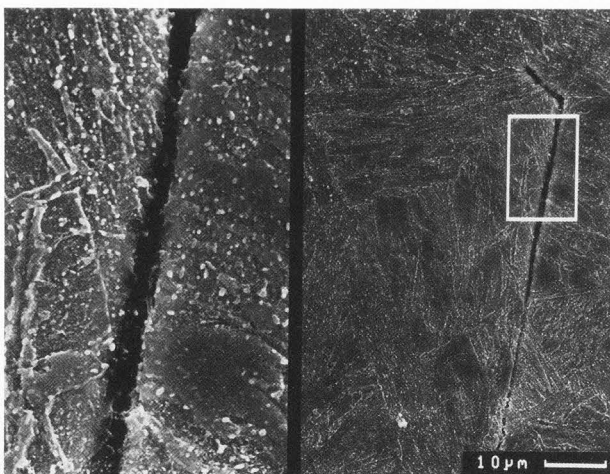Fig. 5. Grain boundary separation at an inclusion. (Steel II) Rel. Test 610 °C/2 h.



Fig. 6. Smooth intergranular crack. (Steel III) Rel. Test 610 °C/2 h.

### AES and fracture surface investigations

Steel I. The crack path of the samples broken in the Auger instrument was mainly intergranular. A noticeable phosphorus enrichment on the intergranular fracture surfaces was analysed after testing times of less than 8 h. The typical Auger-spectrum of such a surface is shown in Fig.7. It could be proved by depth profiling that the phos-

phorus was present on the grain boundaries in monolayer enrichment. Fig. 8 illustrates the good correlation between the intergranular fracture surface and the phosphorus map.

Segregation of sulphur could not be detected by integral AES-investigations of the exposed intergranular surfaces. Point analysis with lateral resolution less than 2 μm, however, revealed a pronounced dimple structure on those surfaces, and very small precipitations within those dimples, which could be identified as MnS particles (Fig. 9). Samples tested for 24 h at 610 °C before AES-analysis showed a noticeable increase in sulphur segregation (Fig. 10).



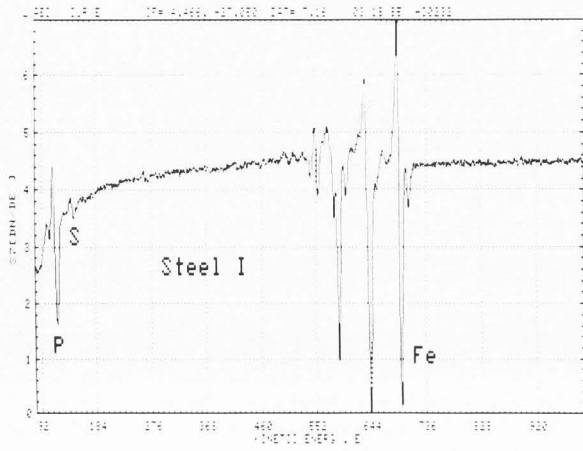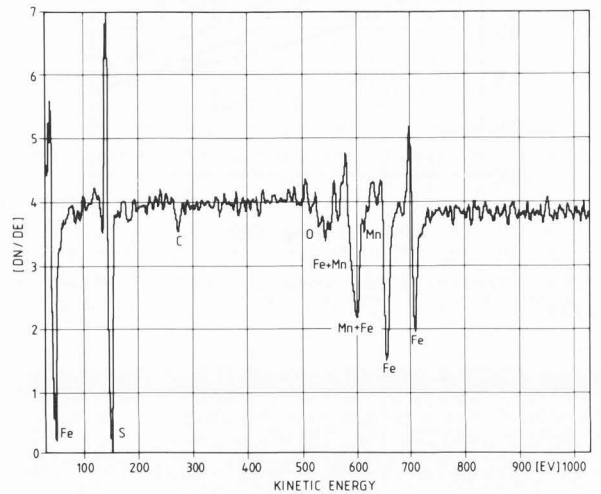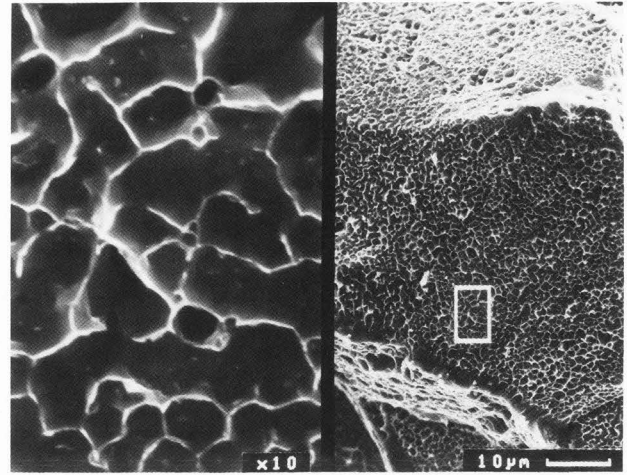Fig. 7. Typical AES-Spectrum of Steel I.



Fig. 8. Map of the fracture surface (Steel I).





Fig. 9. High resolution AE-Spectrum of a particle found in a void. (Steel I)
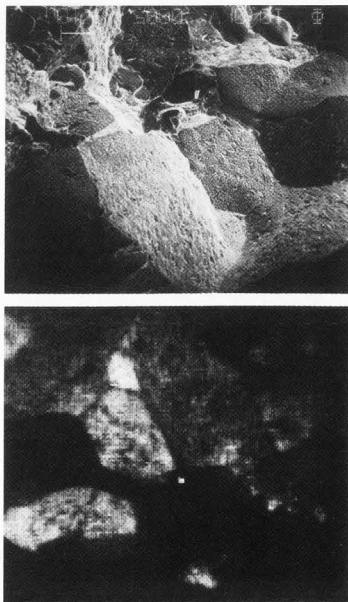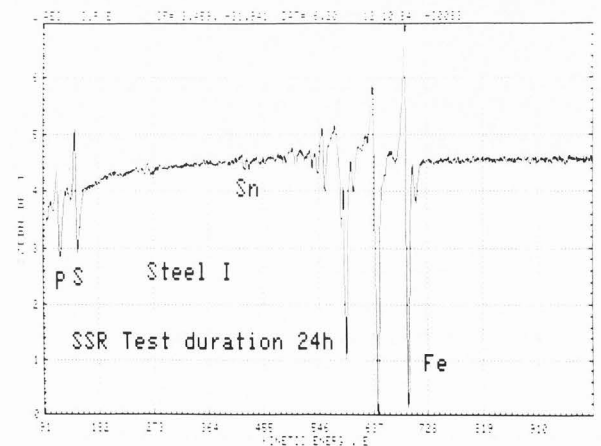


Fig. 10. AE-Spectrum of Steel I.

Steel II.   The majority of samples tested
exhibited intergranular crack paths after being
fractured in the Auger instrument. An estimation
from the secondary electron image yielded inter-
granular area fractions of 20 % at times of less
than 4 h before failure in the SR test to almost
100% at times of more than 8 h. The grain bound-
ary surfaces were predominantly smooth, with
only isolated areas dimpled, again containing
fine MnS precipitates.

An AE-spectrum of a smooth intergranular
fracture surface typical for this steel is shown
in Fig. 11. Phosphorus and sulphur segregations
could be identified on all intergranular areas
of this nature. The phosphorus coverage was on
the average about 35 % and the sulphur coverage
between 15 and 30 % of a monolayer. Manganese
was always found together with sulphur, and
notably in higher concentrations than in the
original analysis of the melt. However, the
depth profiles indicated that sulphur obviously
occurs on the grain boundaries in segregated form,
also. The stringent correlation between tramp ele-
ments and intergranular fracture areas can again
be proved by distribution scans of the elements.
Fig. 12 clearly indicates that the sulphur distri-
bution reflects the intergranular areas of the
fracture surfaces. The partly high oxygen enrich-
ment at the edge of the sample is probably due to
the fact that some grain boundary areas were sepa-
rated sufficiently to provide a connection path
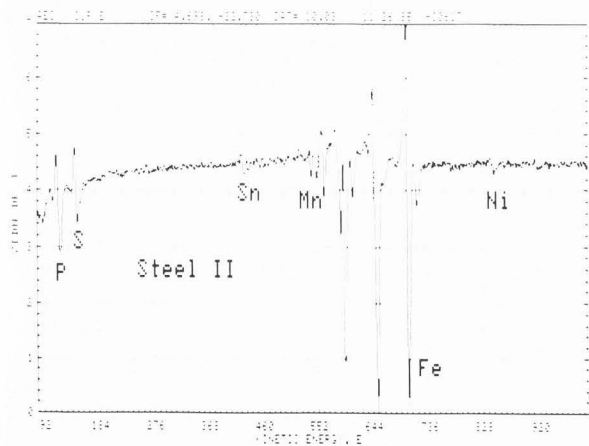to the atmosphere.



Fig. 11.   Typical AE-Spectrum of Steel II.



Fig. 12.   S- and O-Map of the fracture surface.
(Steel II)

Steel III.   After SR testing at 610 °C for
4 h and longer the samples broke "in situ" with
intergranular areas between 40 and almost 100 %.
After shorter testing times the samples exhibited
a completely transgranular fracture appearance.

An AE-spectrum of a smooth intergranular
fracture surface typical for this material is
shown in Fig. 13. Apart from the segregation of
phosphorus and sulphur, pronounced increase in
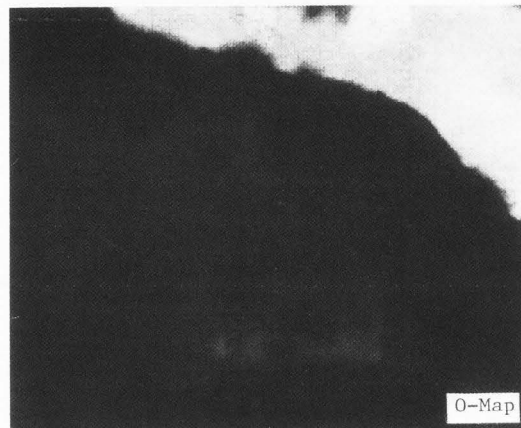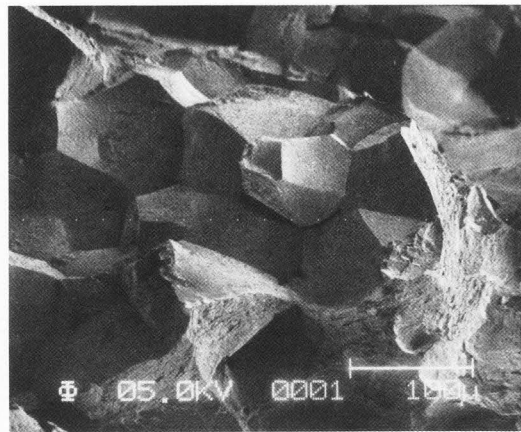copper and nickel concentration could be detected
on the grain boundaries. For the phosphorus en-
richment an average of 30 %, and for the sulphur
enrichment an average of 20 % of a monolayer
could be calculated.

The AE-spectrum of a dimpled fracture sur-
face was distinguished from a smooth surface
again only by the lower sulphur concentration. In
this case also, the dimples contained MnS preci-
pitates.

## Experimental melts

The experimental melts of Steel I showed large intergranular fracture areas and a dimpled pattern quite similar to the original steel (Fig. 14). However, the segregation behaviour of the melts showed noticeable differences: only small phosphorus enrichment on the intergranular surfaces could be observed on samples of melts A and B (Figs. 15a, b). The AE-spectra of melt C showed distinct sulphur segregation together with manganese, which were even detectable by integral measurement with a lateral beam diameter of 20 µm, therefore likely to be MnS precipitations (Fig. 15c). The Auger-spectra of melt D were distinguishable from the other melts by considerably higher phosphorus enrichment (Fig. 15d).

The experimental melts of the steels II and III also broke at least partly in an intergranular mode when fractured "in situ", the appearance of the fracture surface of these melts, though, was quite different from each other. The melts A, B and C were characterized by a pronounced dimpled
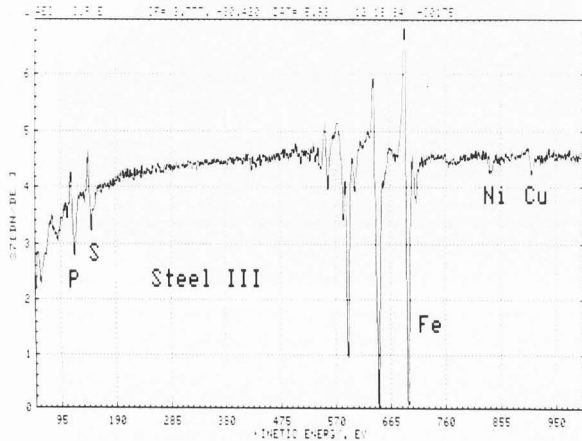


Fig. 13. Typical AE-Spectrum of Steel III.
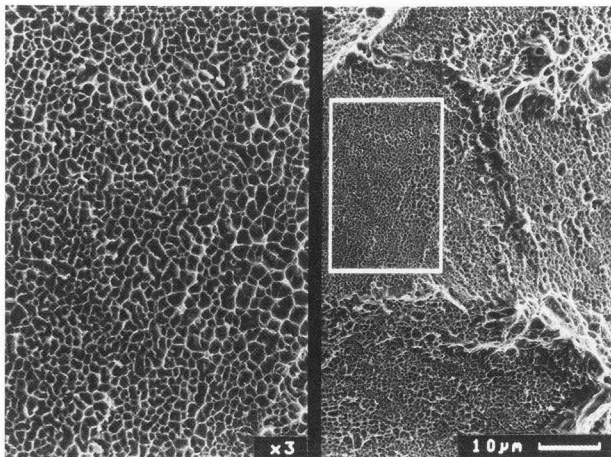


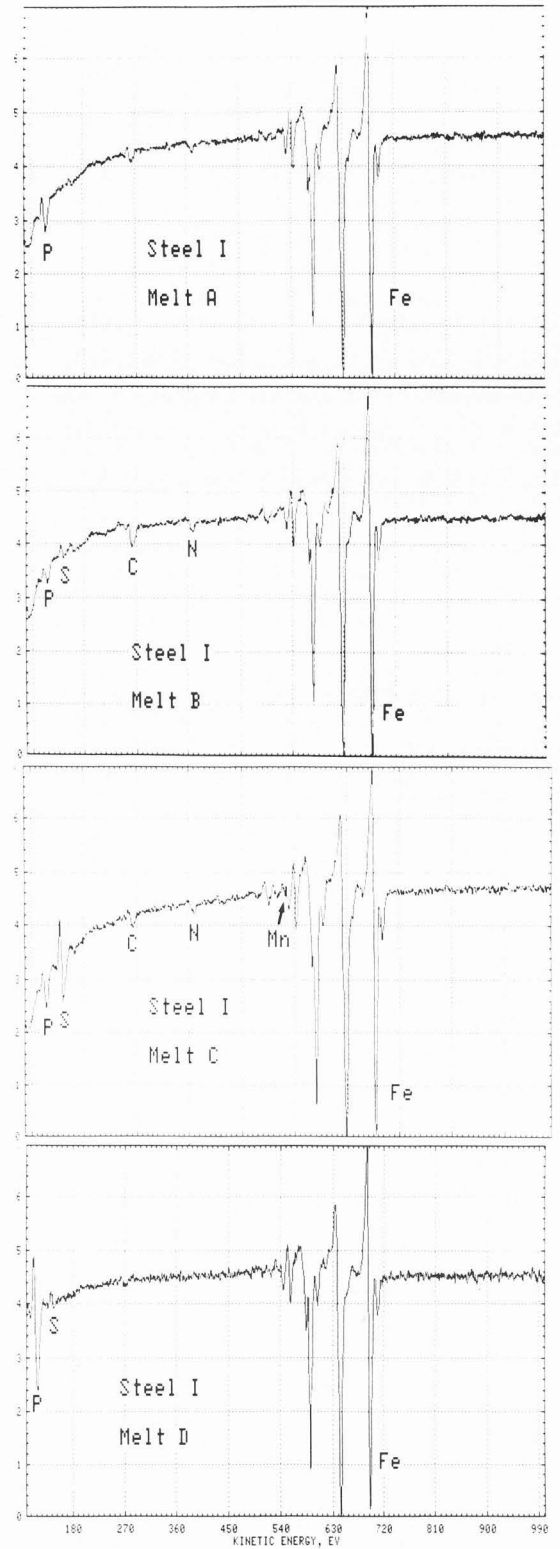Fig. 14. Fracture surface Melt A Steel I.



Fig. 15. AE-Spectra of Melts A-D Steel I

Melt A Steel II          Melt A Steel III

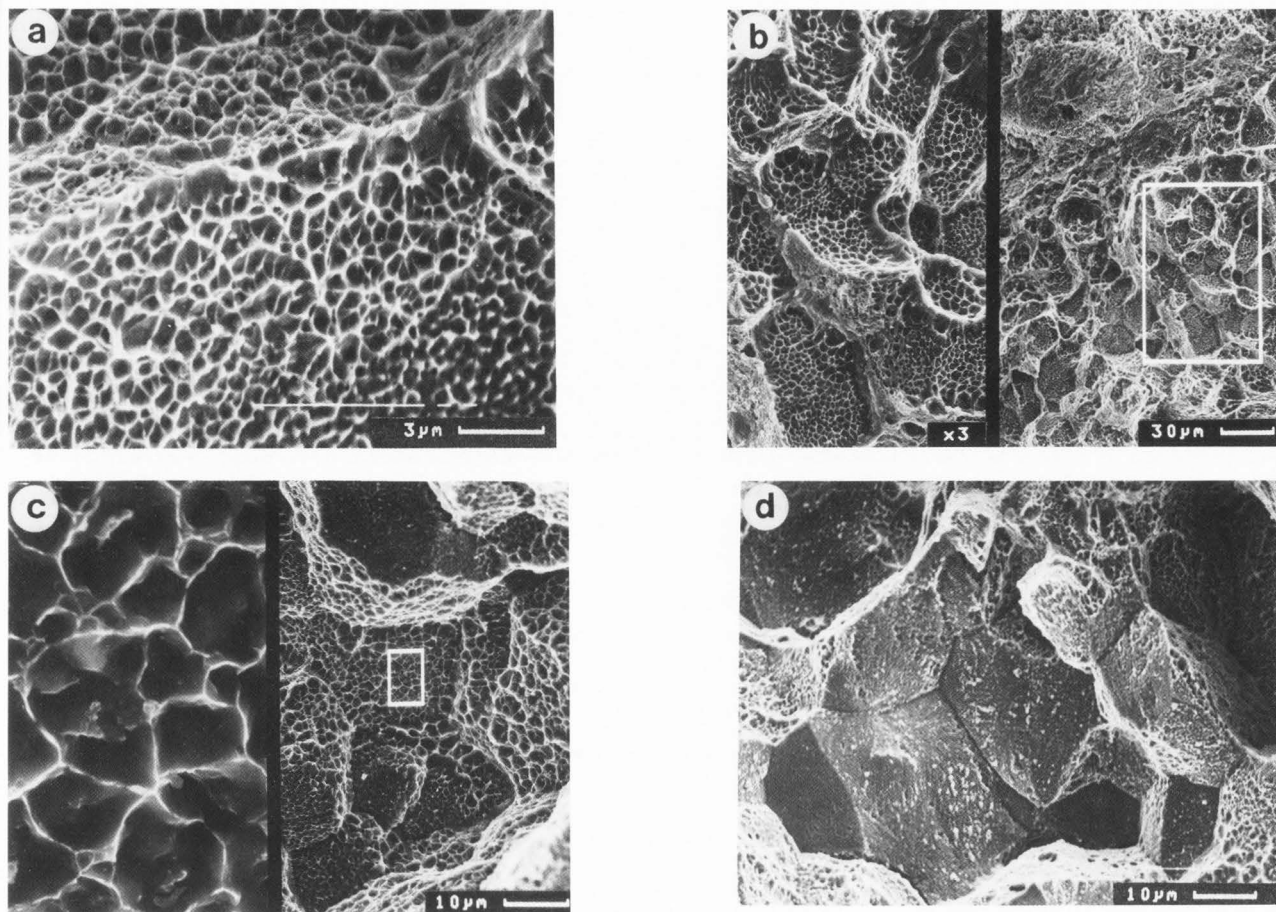Melt D Steel III         Melt D Steel II

Fig. 16. Typical fracture surface of the experimental melts of Steels II and III.

a) Melt A Steel II      b) Melt D Steel III

c) Melt A Steel III     d) Melt D Steel II

structure (Figs. 16 a–c), which was contrary to the original steels, while the fracture surface of the melts D was predominantly smooth (Fig. 16 d). The AE-spectra of melts A, B and C revealed only very small phosphorus and sulphur enrichment, in the case of the melts D of steels II and III the intergranular fracture surfaces were noticeably covered with phosphorus (Figs. 17 a–d).

## Discussion

It has been ascertained by metallography on the fractured samples, that the intergranular crack path in the original steels as well as in the melts is initiated at inhomogeneities in the grain boundaries. Under the influence of the stress applied the mostly void shaped separations widen to form a crack. During this process the original shape of the separations are obviously lost, because the grain boundary surfaces of the resulting separations are completely smooth. The light microscopic investigations of the sections, as well as the completely smooth fracture surfaces of the highly damaged heat resistant steels prove this fact.

EDX- and AES-investigations likewise revealed that the cracks originated from precipitates, mainly MnS. These particles could also be found within the dimples on the intergranular fracture surfaces. However, the area portion of these MnS precipitates is too small in most cases to be detected by integral Auger analysis. An estimate of the portion of MnS - precipitates in an area measured yields about 0.5 % of a monatomic covering compared with a detection sensitivity of about 1 %.

Smooth and dimpled intergranular fracture surfaces are distinguished in their respective AE-spectra mainly by the fact that sulphur segregations could be measured on the smooth fracture surfaces of the original steels even by integral measurements. It could also be proved by depth profiling that the sulphur measured is present on the smooth intergranular surfaces in segregated form. The melts D of the heat-resistant steels with lowered sulphur contents also reveal smooth intergranular fracture surfaces. But, because the sulphur content is completely taken up as MnS, segregation to the grain boundaries is not possible any more. These results support the theory by Hippsley et al. (2) that the stress-field of a
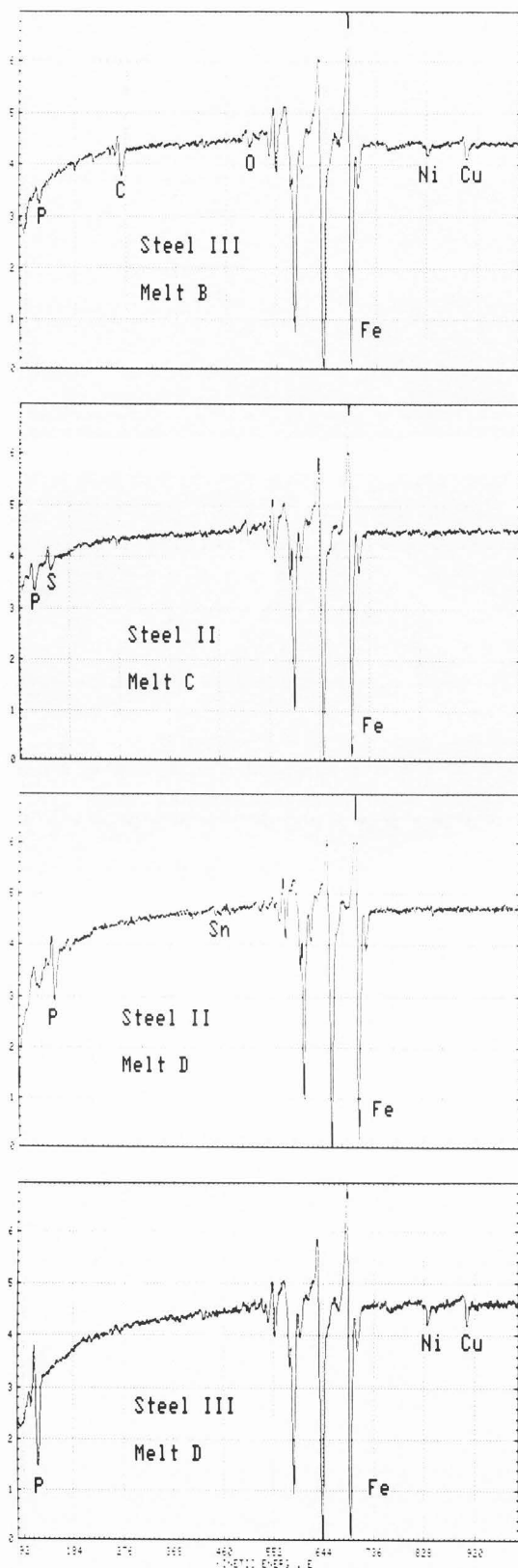
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Fig. 17. AE-Spectra of the experimental melt of Steels II and III.

crack is to able attract segregating sulphur atoms. Accordingly, the dimpled intergranular fracture surface indicates that the "in situ" fracturing open up mainly grain boundary areas not damaged in the SR test. The presence of smooth grain boundary surfaces is an indication of grain boundary areas separated during the SR testing. This separation originates from MnS-inclusions.

It has also been shown in this investigation that phosphorus becomes enriched on the grain boundaries of the original steels as well as melt D at an early stage during testing. This is independent of the microfractural appearance of the fracture surface. Melts A, B and C also show phosphorus segregations at the grain boundaries, although much less pronounced. One may conclude, that after crack initiation by the MnS precipitates the first stage of the progagation of the crack is controlled by phosphorus segregation in conjunction with the stress supplied. At alter stage segregation sulphur increases the grain boundary embrittlement, as described by Hippsley. In case of very fast crack propagation (i.e.,pronounced embrittlement) the time between crack initiation and fracture is too short for the segregating sulphur to reach the edges at the tip of the crack. The microfractural investigation then reveals a predominantly dimpled pattern, as is the case in steel I. A prerequisite for the fracture mechanisms described, however, is precipitation within the grains, which, during stress-relief-annealing, restricts the relaxation processes to the grain boundary.

### Acknowledgements

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### Discussion with Reviewers

V. Thien: Normally, a phosphorus segregation on grain boundaries leads to embrittlement; in your investigation, you come to an opposite judgement. How can this be explained?

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Authors:    Segregation of phosphorus undoubtedly
leads to embrittlement it is, however, not the
crack  initiating factor in this case. The first
crack forms at the MnS/steel interface and the
further crack propagation is then determined by
the P-segregation, while the segregation of sul-
phur is initiated by the interaction with the
crack already formed, as described by Hippsley
et al.

V. Thien:       Where are the other tramp elements
(like Sb, Sn, As), which are also known to enrich
on grain boundaries?
Authors:  No measurable segregation of these ele-
ments takes place during the short time of stress
relief annealing (generally $\leq$ 8 h). It was only
after longer annealing times ( > 20 h) that these
elements could be detected.

C.A. Hippsley:    Previous investigation of SRC in
low alloy steels has shown that the heating
period of PWHT is important in determining the
mechanism of fracture. Smooth brittle intergranu-
lar fracture tends to occur at lower temperatures
than the more ductile intergranular microvoid
coalescence mechanism. Do you consider, therefore,
that the rapid heating rate employed in your
tests gives adequate opportunity for the brittle
mechanism to be manifested in its characteristic
form, i.e., totally distinct from the microvoid
coalescence mechanism ? It is possible that the
voids, which you have interpreted as brittle-
crack nuclei, may rather be symptomatic of the
transition between fracture mechanisms ( see
Hippsley at al, Acta Metall., vol. 30, p 641-654,
1982).
Authors:  The heating rate of PWHT as well as the
parameters of welding simulation clearly had a
major influence on the results of this investiga-
tion. SEM investigations on transverse sections
revealed MnS-particles in the voids present at
the grain boundaries (Fig. 3). This observation
lead to the assumption that the voids were grain
boundary separations starting at these particles.

C.A. Hippsley:    In your discussion, you suggest
that the presence of smooth grain boundary sur-
faces in AES specimens is an indication of grain
boundary areas which have separated during SR
testing. If this is the case, these boundaries
will effectively have become free-surfaces while
still at elevated temperature, although shielded
from the atmosphere for the most part. This has
been shown to result in rapid segregation of ele-
ments such as sulphur and phosphorus to the opened
boundaries. In order to distinguish the effects
of stress-induced segregation from free- surface
segregation some measurement of the kinetics of
free-surface segregation is required. Is such
information available for these steels, and if so
has it been taken into account in your interpre-
tation of results (see your reference 2) ?
Authors:    An accelerated segregation to a sepa-
rated grain boundary can particularly be found
with sulphur, as described in (2). The conclusion
that the smooth grain boundary areas were sepa-
rated by the SR tests was gained by the following
technique:         The samples broken in the Auger

instrument were investigated with respect to
smooth and dimpled fracture areas. With steel I
the dimpled areas without S-segregation prevailed,
with steels II and III the smooth grain boundaries
with S-segregation. The transverse micrographs of
the Auger sample "ends" subsequently collected
showed many cracks in case of steels II and III,
but almost none with steel I. These cracks could
only have been formed in the SR tests, i.e., a
large number of relaxation cracks consistently
corresponded with smooth intergranular fracture
areas. The high sulphur coverage of these grain
boundary areas can therefore be attributed to an
accelerated sulphur segregation to the separated
grain boundary.