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Presented at the Cryogenic Engineering Conference,
St. Charles, IL, June 15–18, 1987, and to be published
in Advances in Cryogenic Engineering, Vol. 34

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August 1987

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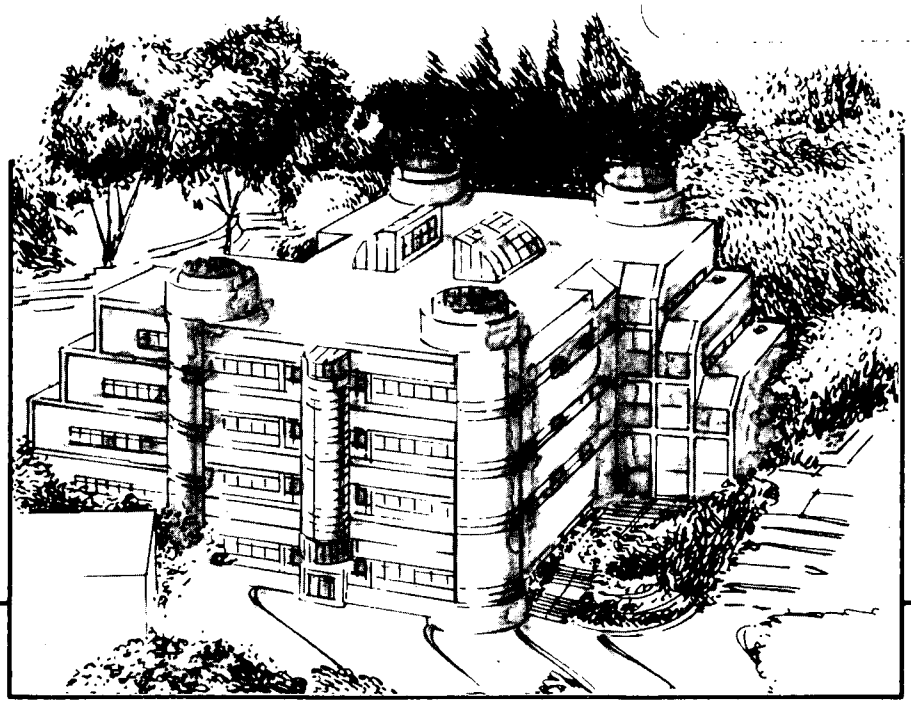

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-23853

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INFLUENCE OF POST-ANNEAL COOLING TREATMENTS ON SUPPRESSION OF CRYOGENIC INTERGRANULAR FRACTURE IN EXPERIMENTAL NI-FREE HIGH-MN AUSTENITIC STEELS

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This work is supported by the Director, Office of Energy Research, Office of Basic Energy Science, Material Sciences Division of the U. S. Department of Energy under Control No. DE-AC03-76F00098

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ABSTRACT

The influence of thermal history on the grain boundary chemistries and cryogenic mechanical properties of two high-Mn austenitic steels are examined.While high-Mn alloys with excellent toughness at 4K have been developed,the Ni-free high-Mn alloys are susceptible to cryogenic intergranular embrittlement. Both the source of this embrittlement and the conditions necessary for its control have remained poorly understood. In quaternary Fe-30Mn-5Cr-0.16N and Fe-30Mn-5Cr-0.22N alloys the cryogenic toughness is strongly dependent on cooling rate. The 77K Charpy impact toughness of Fe-30Mn-5Cr-0.16N increases with decreasing cooling rate from 41 J after a brine-quench to 183 J after air-cooling. The influence of post-quench isothermal tempering treatments between 723K and1023K on the impact toughness are also measured. The grain boundary chemistries of brine-quenched and air-cooled samples were examined by Auger electron spectroscopy. No grain boundary segregation of Mn is observed but both N and slight Cr enrichments are present. While no segregation of common emrittling species occurs, boron segregates to the grain boundaries during slow-cooling.

INTRODUCTION

High-Mn austenitic steels have recently emerged as potential alternatives to traditional 300-series stainless steels for cryogenic structural applications While high-Mn alloys with excellent toughness at 4K have been developed [1], the Ni-free high-Mn austenitic alloys are susceptible to cryogenic intergranular embrittlement [2-5]. The influence of the large Mn additions on the susceptibility to intergranular fracture has remained poorly understood. Examination of grain boundary chemistries and their dependence on thermal history provide insight into the intrinsic or extrinsic nature of the source of brittle intergranular fracture in the high-Mn alloys.

Investigations of brittle intergranular fracture in many other alloy systems have successfully correlated intergranular embrittlement with changes in grain boundary chemistry [6]. The decreases in grain boundary cohesion due to the segregation of deleterious species to the grain boundaries result in the change from a transgranular to an intergranular fracture mode resulting in dramatically decreased fracture energies. Such embrittlement mechanisms are termed extrinsic. In alloy systems such as Ni3Al which fail by intergranular fracture without observed grain boundary segregation [7], the mechanism of intergranular fracture can be termed intrinsic. Inherently low intergranular cohesion (and/or difficulties in strain accomodation due to an insufficient number of slip systems or slip localization) may be responsible for intrinsic intergranular failure.

When diffusion-controlled grain boundary segregation alters the intergranular cohesion, the thermal history of the material can control the ductile-to-brittle transition behavior. Therefore the influence of cooling rate and temper treatments on the cryogenic mechanical properties can be significant. In addition to mechanical property measurements, the associated changes in grain boundary chemistry with thermal history are examined by

Auger electron spectroscopy (AES). Together they provide insight into the cause of intergranular fracture in high-Mn austenitic alloys and the means to control the cryogenic fracture mode.

EXPERIMENTAL PROCEDURE

The alloys used in this investigation were experimental heats of fully-austenitic Ni-free high-Mn steels [2]. The austenitic phase was stabilized through additions of approximately 30%Mn and strengthened by interstitial N additions. Chromium additions further increased the N solubility. The chemical compositions of the alloys are given in Table 1.

The 9 kg heats were melted under Ar in a vacuum induction furnace and cast into 80 mm diameter Cu molds. After homogenization at 1473K, the ingots were hot-rolled at 1373K into 20 mm plates. Mechanical property specimens were machined after subsequent 35% cold-roll and 1273K recrystallization/anneal treatments followed by water-cooling. For subsequent heat treatments, individual specimen blanks were encapsulated in protective quartz tubes partially back-filled with Ar. Annealing treatments consisted of 1hr at 1273K followed by either an air- cool within the sealed quartz tubes or a rapid quench obtained by breaking the tubes in an iced-brine solution. Isothermal tempering treatments between 723K and 1023K were performed on previously water-quenched specimens. The 77K mechanical behavior was evaluated in impact using standard Charpy v-notch specimens and in uniaxial tension using flat-plate specimens nominally 3.2 mm thick with a gage region 3.2 mm wide and 25 mm long. Yield strengths were determined by the 0.2% offset strain method from extensometer data.

Grain boundary chemistries were measured by Auger electron spectroscopy (AES). Notched impact specimens were cooled by conduction to 117K within the ultra-high vacuum chamber and broken in-situ. A probe diameter of 1 to 2 um allowed surface chemical analysis of specific features on the fracture surfaces. The degree of grain boundary segregation was measured by direct comparison of transgranular and intergranular surface chemistries on the mixed-mode as-fractured surfaces. Depth-profile analysis by Ar-ion sputtering proved to be of limited usefullness in this alloy system due to the preferential sputtering of Mn with respect to Fe, high interstitial mobility, and variations in adsorbed oxygen levels.

RESULTS

1. Fracture behavior.

While both of the alloys used in this investigation fracture in a fully-ductile manner at room temperature, they also both undergo a transition in fracture mode with decreasing temperature such that at 77K the fracture is predominantly intergranular (Fig.1) The brittle nature of the intergranular fracture mechanism results in significantly reduced fracture energies.

The dependence of the fracture behavior in these alloys on the cooling rate from the annealing temperature (1273K) was measured in notched-impact tests. Unlike alloys exhibiting segregation-induced embrittlement, the amount of intergranular fracture at 77K increases for increasing cooling rates. The results of 77K Charpy impact tests for three cooling rates are shown in Table 2. Impact energies increase continuously as the cooling rates decrease from an ice-brine quench to a water-quench and to an air-cool treatment.

Intergranular fracture is nearly completely suppressed in the air-cooled 0.16N alloy. A mixed-mode fracture remains in the higher strength 0.22N alloy after air- cooling treatments.

The influence of strength level on the onset of brittle intergranular fracture after these treatments must also be considered. Therefore the uniaxial tensile properties of air-cooled and brine-quenched specimens were measured at 77K. The yield strengths remain very similar in these two conditions (see Table 3). The ductility, however, decreases significantly in the brine-quenched condition resulting in a reduced tensile strength.

While air-cooling treatments promote ductility, no information on the beneficial temperature regime or kinetics of potential solute redistributions are provided from the continuous cooling treatments. Therefore isothermal tempering treatments were performed on quenched samples. The results of short-term treatments between 723K and 1023K are shown in Table 4. While the low-temperature treatments are effective, the 1023K treatments result in re-embrittlement.

2. Surface Analysis.

Surface chemical analysis was performed by AES on fracture surfaces created in-situ under ultra-high vacuum. Both rapid quenched and intermediate air-cooled samples of the 0.22N alloy were examined. Use of the higher-N alloy allowed examination of grain boundary chemistries in the air-cooled condition (which is fully transgranular in the 0.16N alloy). Grain boundary segregation was investigated using both sputter and direct-comparison techniques.

Removal of surface layers below the original boundary by Ar-ion sputtering is often used to measure differences in grain boundary and bulk chemistries. Comparison of

the increased N contents after quenching, and the grain boundary segregation of B during the air-cool treatment.

The increased grain boundary N content after quenching is a non-equilibrium condition. No N segregation is observed after slower cooling treatments which must approach equilibrium. It is well known that N contents held in solution decrease at high temperatures. It is not unusual to expect N accumulation at the relatively disordered grain boundary sites which are then quenched-in during rapid-cooling treatments. Grain boundary porosity has been observed after annealing high-N21Cr-6Ni-9Mn alloys for example [11]. While solid solution N is predicted by the pair-potential model to improve cohesion, molecular N should dramatically reduce the cohesion. The strong mechanical influences of N in the bulk material are well known. High grain boundary N contents may also help to increase localized stress concentrations or flow stresses.

The predicted influence of B segregation to the grain boundaries is consistent with the observed temper-toughening of these high-Mn steels. The quasi-chemical model predicts a large remedial effect of B additions. Likewise, B additions have been experimentally observed to improve resistance to intergranular fracture in Ni3Al [7] and Fe-12Mn ferritic steel [12,13]. Boron is present in these high-Mn alloys only as an impurity. The beneficial influence of intentional B additions is expected to be limited by interactions with the N used to raise strength levels.

SUMMARY

The reduction of post anneal cooling rates from a rapid brine-quench to air-cooling suppresses the intergranular fracture mode at 77K. The 77K Charpy impact energies in Fe-

Mn contents at grain boundary and transgranular fracture regions both before and after the sputter-removal of several hundred Angstroms from the surface are shown in Table 5. Although grain boundary segregation of Mn is indicated by the decreased Mn content after sputtering, a similar decrease occurs in sputtered transgranular regions. Both the original and the sputtered transgranular surfaces, however, should represent bulk material. The significance of this preferential sputtering of Mn will be presented in the discussion. Direct comparison of Mn concentrations from transgranular and intergranular regions on the asfractured surfaces reveal the absence of Mn segregation.

Fracture surface chemistries from the quenched and intermediate air-cooled 0.22N specimens are compared in Table 6. No grain boundary segregation of common deleterious species such as S or P were observed after either treatment. With respect to alloying element segregation there is no evidence of grain boundary Mn segregation. Slight Cr enrichments are present at the grain boundaries in both the quenched and slowly-cooled samples. In the quenched condition the grain boundary N contents are significantly higher than the bulk (transgranular) levels. After slow-cooling, however, no nitrogen segregation is present.

In addition to alloying element segreation, the presence of B has been clearly identified at the grain boundaries in the air-cooled specimen as shown in the transgranular and intergranular spectra in Fig. 2. In the quenched specimen only a small amount of B is present at the grain boundaries. No B was detected at the transgranular regions of the asfractured surfaces in either specimen. Due to the relatively high inclusion contents in these alloys, an inclusion particle is often present within the surveyed region. While most intergranular regions are S-free, the S present on many fracture surfaces has been identified as localized to MnS inclusions [2]. Carbon appears in all spectra due to adsorption from residual CO in the vacuum chamber.

DISCUSSION

The transition from transgranular to intergranular fracture in these alloys results in large decreases in cryogenic impact toughness. As shown in Fig.1 intergranular fracture occurs by a brittle verses a ductile process. Unlike the strain-controlled ductile fracture process, brittle intergranular fracture is stress-controlled. Intergranular crack initiation only requires that the stress across the grain boundary exceeds the grain boundary cohesive strength. Brittle intergranular cracking interrupts the ductile fracture process, reducing absorbed energies. Changes in either the grain boundary cohesive strength or applied stresses will alter the susceptibility to brittle intergranular fracture.

Changes in strength levels can have significant influences on the fracture mode. Examples are the increased amounts of intergranular fracture in the higher strength 0.22N alloy as well as in the higher-strength condition at decreased temperatures. Due to the similar flow strengths of the air-cooled and quenched specimens strength considerations are not expected to modify the transition behavior. Deformation heterogeneity is difficult to quantify beyond the macroscopic stress-strain behavior and is not examined here. Although localization of slip is observed in these alloys, it is not qualitatively affected by the range of alloy levels investigated here [2], and is assumed to be a minor influence on variations in fracture mode transition behavior with heat treatment.

Changes in grain boundary chemistries are often associated with variations in intergranular fracture susceptibility. The grain boundary cohesive strength is determined by the grain boundary chemistry. Therefore the thermal history of a material can strongly influence the grain boundary cohesive strength through its effect on the diffusion-controlled

segregation of alloy and impurity elements to the grain boundaries. In extrinsic embrittlement, the grain boundaries are weakened by segregation of deleterious species to the grain boundaries.

An extrinsic embrittlement mechanism cannot be supported in the high-Mn alloys. Chemical analysis by AES has shown no evidence of the segregation of common embrittling impurities such as S and P to the grain boundaries. In addition, slow-cooling or tempering treatments which are known to promote segregation-induced embrittlement actually toughen the high-Mn alloys. An intrinsic susceptibility is therefore implicated.

Support for an intrinsic cause of embrittlement can be found by considering the predictions of available models on the influence of alloy additions to the interfacial cohesion. The predictions of two such models will be discussed. Both consider changes in the ideal interfacial cohesion.

In the thermo-chemical model the change in fracture work necessary to create two new surfaces is calculated from the balance of resulting changes in grain boundary and surface energies. An embrittling segregant must lower the product of twice the surface energy by an amount larger than the corresponding decrease in the grain boundary energy. As equilibrium segregation will always reduce the interfacial energies, an embrittling element will segregate more strongly to surfaces than to grain boundaries.

A measure of the segregation tendencies of Mn were obtained by AES analysis. By direct comparison of transgranular and intergranular regions, it is clear that no grain boundary segregation of Mn occurs in either heat treatment condition. There is, however, a significant decrease in surface Mn contents after Ar-ion sputtering. The occurence of preferential sputtering is now known to be correlated to chemical bonding [8,9]. Moreover, the reduced surface concentration measuredafter sputtering is the result of preferential segregation to the surface. The concurrent processes of surface segregation and surface

sputtering result in Mn depletion at the surface. From the thermo-chemical theory the presence of grain boundary Mn should therefore lower the grain boundary cohesive strength.

An alternative approach used is the pair-potential model [10]. The energy of fracture is calculated from a pair-bonding approximation of the energy required to break the bonds across the interface. The reduction in fracture energy due a fractional coverage of solute is proportional to the difference in sublimation enthalpies for the matrix and solute. The fracture energy will decrease with the addition of solutes whose sublimation enthalpies are lower than that of the matrix. This theory correctly predicts nearly all experimentally observed grain boundary segregation effects including the embrittlement of Fe by such elements as Sb, S, Sn, and P. The model also predicts that Mn additions to an Fe matrix decrease the grain boundary cohesion. Although Mn is predicted to be a less potent embrittling addition to Fe than the commonly observed embrittling species such as S, P, Sb, or Sn, the calculated reduction in fracture energy from a 30%Mn addition to an Fe matrix is large relative to the corresponding effect calculated due to observed impurity concentrations of S or P in heavily embrittled low-alloy steels [6].

The detrimental influence of increasing Mn contents on the susceptibility of fully-austenitic Fe-Mn binary alloys to intergranular fracture has also been observed experimentally. The 77K fracture mode of 30 to 45%Mn binary alloys becomes increasingly intergranular as the Mn content is increased [5].

While high Mn contents may increase the susceptibility of these alloys to intergranular embrittlement, they do not account for the thermal history dependence. Grain boundary Mn contents remain at bulk levels after air-cool or rapid quench treatments. The minor segregation of Cr to the grain boundaries is also independent of cooling rate. The most significant differences in grain boundary chemistries between the two treatments are

30Mn-5Cr-0.16N increase from 41 J in the brine-quenched condition to 183 J in the air-cooled condition. The cryogenic ductility.can be recovered in rapidly cooled material by isothermal aging treatments between 673 and 873K.

Grain boundary chemical analysis by Auger electron spectroscopy (AES) shows no evidence of grain boundary segregation as the primary source of cryogenic intergranular embrittlement. The strong tendency for Mn surface segregation is evident from its preferential sputtering behavior. Reductions in grain boundary cohesive strengths with increasing Mn additions are expected from both thermo-chemical and pair-bonding models.

Nitrogen enrichments of 65% at the grain boundaries are measured after a brine quench in Fe-30Mn-5Cr-0.22N while no N accumulation is present after an air-cool treatment. Boron, a well-known cohesive enhancer, segregates to the grain boundaries during air-cooling to concentrations of approximately 1at.%, relative to levels of 0.1at.% after a brine quench. No B was detected at the transgranular regions of either sample.

ACKNOWLEDGEMENTS

This research was supported by the Director, Office of Energy Research, Office of Fusion Energy, Development and Technology Division of the U.S. Department of Energy under contract #DE-AC03-76SF00098.

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Table 1. Chemical analysis.

Alloy	Composition, wt.%									
	Fe	Mn	Cr	Ni	Si	N	C	S	P	O
.16N	bal.	31	5	-	-	0.158	0.003	0.014	<0.005	0.006
.22N	bal.	31	5	-	-	0.223	0.001	0.012	<0.005	-

Table 2. Cooling rate dependence of Charpy impact values.

Alloy Composition	77K Charpy Impact Value, Joules		
	ice brine quench	water quench	air cool
Fe-31Mn-5Cr-.16N	41	92	183
Fe-31 Mn-5Cr-.22N	8	23	49

Table 3. 77K Tensile properties.

Treatment	Yield Strength ksi, (MPa)	Tensile Strength ksi, (MPa)	Elongation* %
brine quench	90 (620)	146 (1005)	27
air-cool	89 (615)	155 (1070)	57

* from 1 in (25 mm) gage length

Table 4. Influence of temper treatments on 77K impact energies.

Treatment * (Fe-31Mn-5Cr-0.14N)	77K Charpy Impact Energy, Joules
+450°C/30 min —> water quench	129
+600°C/30 min —> air cool	156
+600°C/30 min —> water quench	146
+600°C/16 hrs —> water quench	45
+750°C/30 min —> water quench	37

*initial condition 1000 C/1 hr -> water quench

Table 5. Sputtering-induced compositional changes.

Condition	Survey Region	Composition, At.% Fe	Mn
as fractured	intergranular	bal.	31.2
	transgranular	bal.	31.4
Ar^+ sputtered	intergranular	bal.	20.8
	transgranular	bal.	21.0

Table 6. AES fracture surface analysis.

Heat Treatment	Survey Region	Chemical Composition, At.% Fe	Mn	Cr	N	B
1000 °C/1 hr → WQ	intergranular	61.3	31.4	5.7	1.5	0.1
	transgranular	62.6	31.2	5.3	0.9	-
1000 °C/1 hr → 500 °C/10 min → air cool	intergranular	60.9	31.4	5.7	0.9	1.1
	transgranular	62.8	31.0	5.3	0.9	-

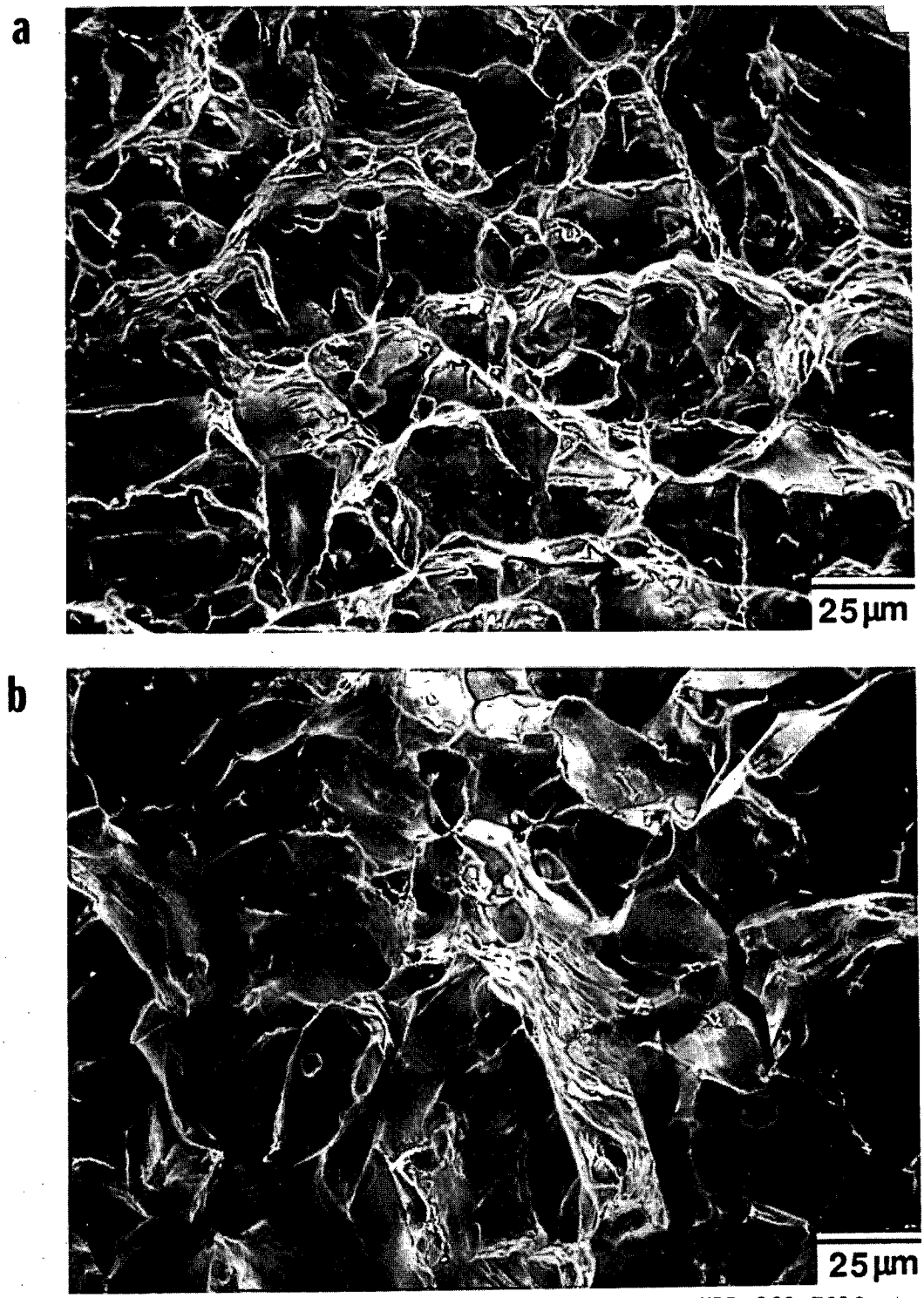

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Fig 1: SEM fractographs of 77K Charpy impact specimens: a) alloy Q1; b) alloy Q2.

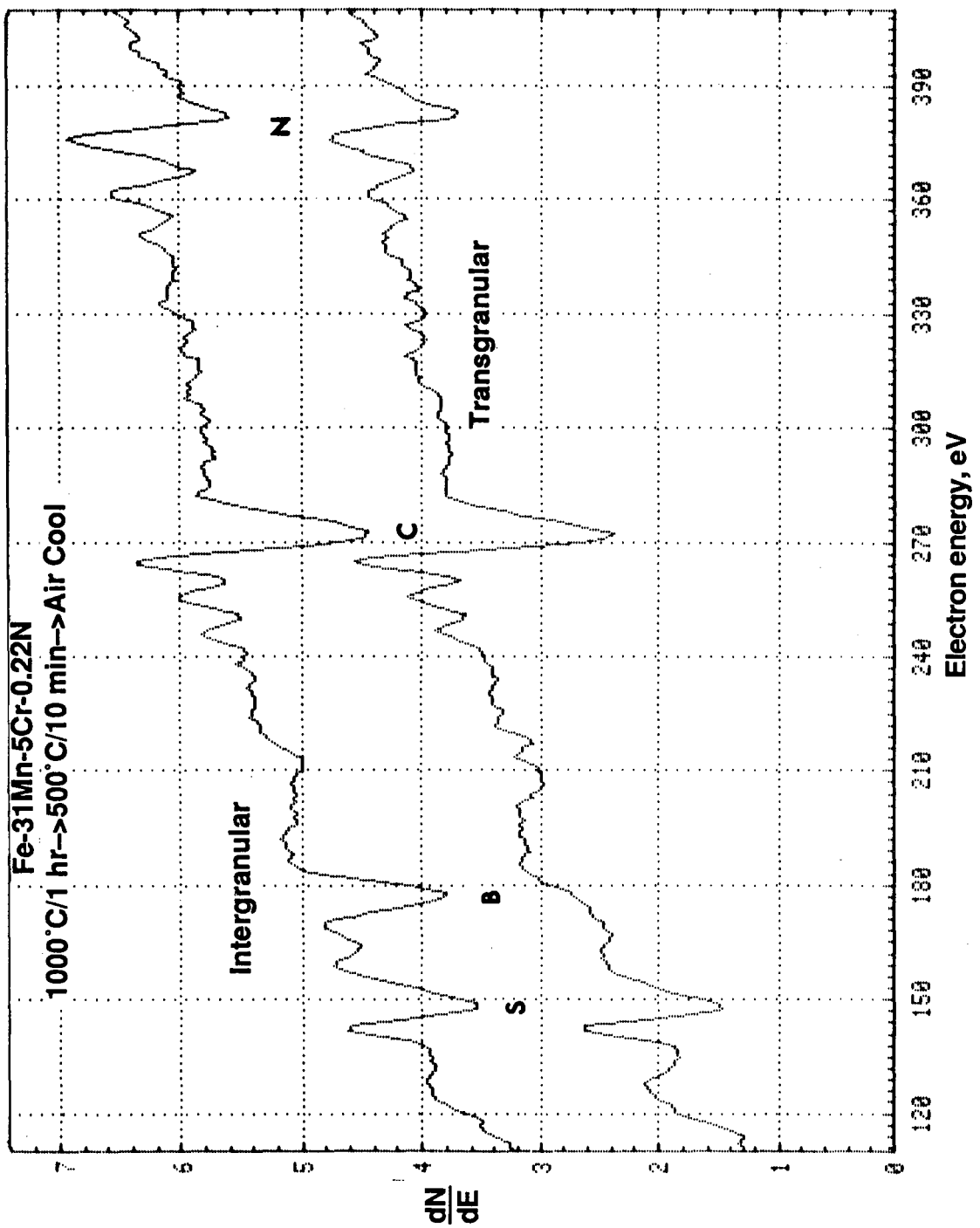

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Fig. 2: Expanded AES spectra comparing the as-fractured grain boundary boron content with that from a transgranular region.

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