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I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

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WORKING PARTY ON
MECHANICAL PROPERTIES OF INTERFACES

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"Enviromental Embrittlement and Intergranular Fracture in Intermetallic Alloys" (Part II)

Chain T. LIU
Oak Ridge National Laboratory
Metals & Ceramics Division
P.O. Box 2008
Building 4500S, MS115
Oak Ridge, TN 37831-6115
U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

MAIN BUILDING STRADA COSTIERA, 11 TEL. 22401 TELEFAX 224163 TELEX 460392 ADRIATICO GUEST HOUSE VIA GRIGNANO, 9 TEL. 224241 TELEFAX 224531 TELEX 460449
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Environmental Embrittlement and Brittle Grain-Boundary Fracture in BCC-Ordered Intermetallics

C. T. Liu
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6115

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Outline

- Environmental embrittlement and brittle fracture in iron aluminides (Fe_3Al-FeAl)
- Brittle GB fracture and boron additions in Fe_3Al-FeAl
- Alloy design of ductile iron aluminides
- Brittle GB fracture and boron additions in NiAl
- Conclusions

Environmental Embrittlement in Iron Aluminides (FeAl and Fe_3Al)

- Materials Scientists Had Been Puzzled for More Than 45 Years by the RT Brittleness of FeAl Aluminides
- In 1989, Liu et al. First Demonstrated That FeAl is Intrinsically Ductile, and the Low Ductility and Brittle Fracture in the Aluminide is Caused by Environmental Embrittlement at RT.
- The Embrittlement Involves Moisture in Air.

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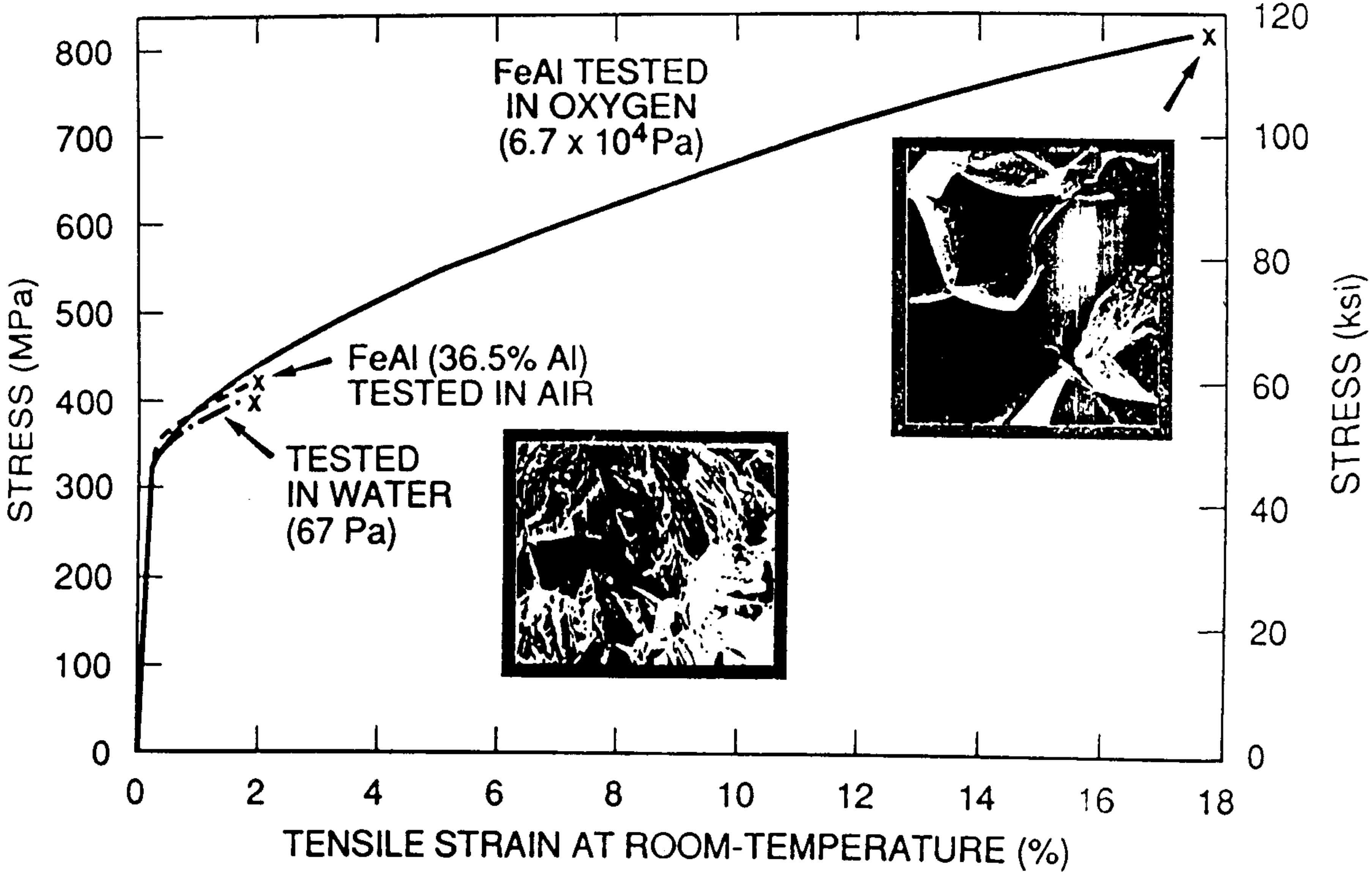
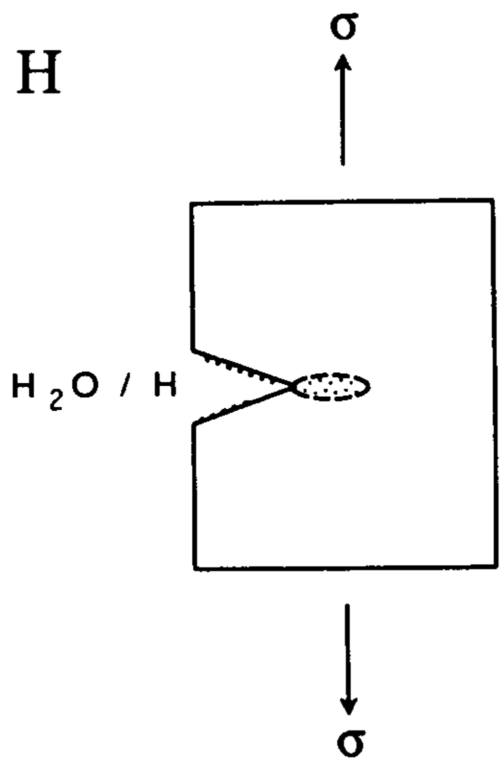
FeAl IS BRITTLE AT ROOM TEMPERATURE BECAUSE OF SEVERE EMBRITTLEMENT BY WATER VAPOR IN AIR



- The identification of the mechanism for the low ductility is critical for alloy design of FeAl

Environmental Embrittlement in Aluminides

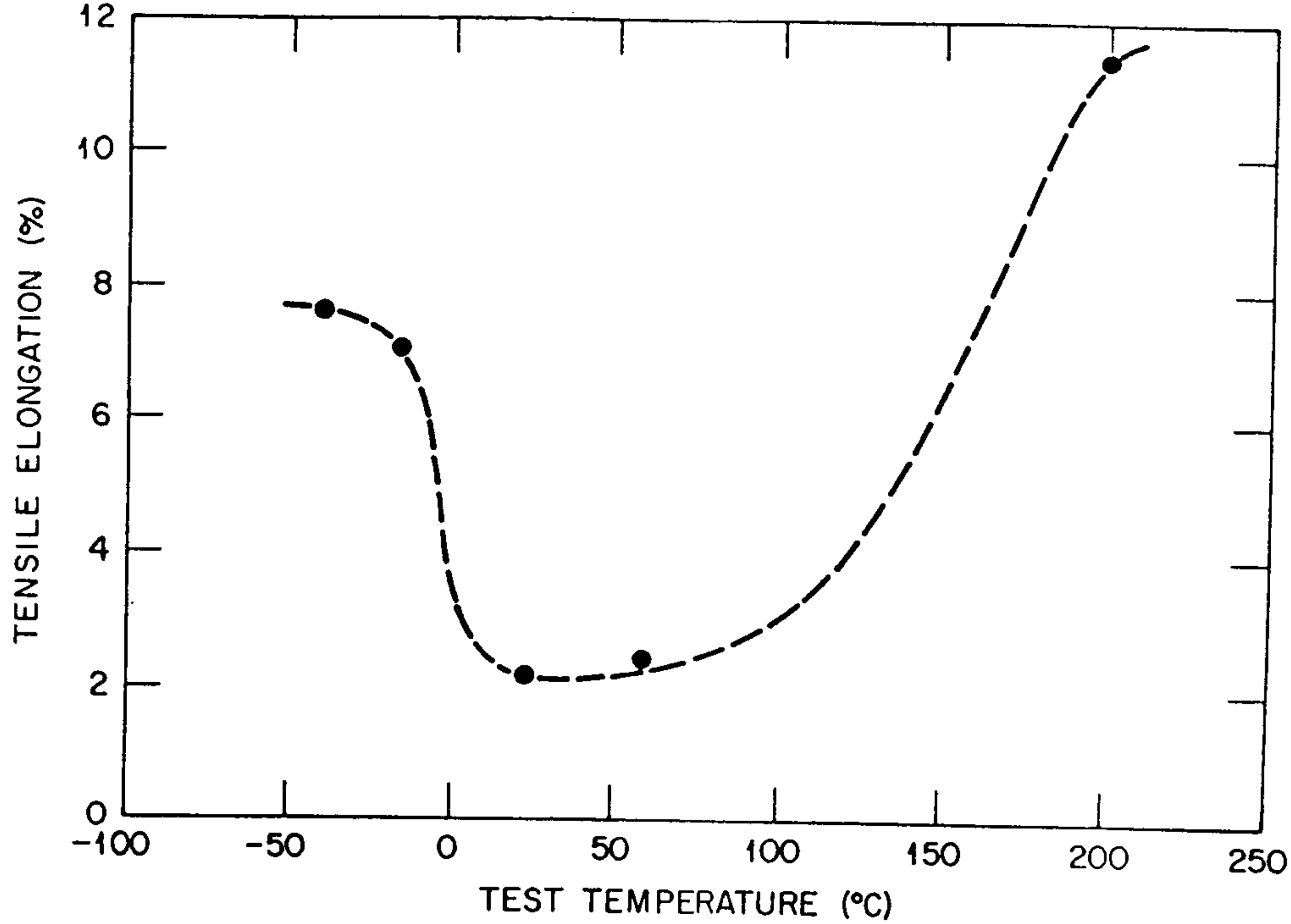
- $2\ Al + 3\ H_2O \rightarrow Al_2O_3 + 6\ H$
- Atomic hydrogen drives into metals and causes room temperature embrittlement
- FeAl shows much less embrittlement when exposed to molecular hydrogen

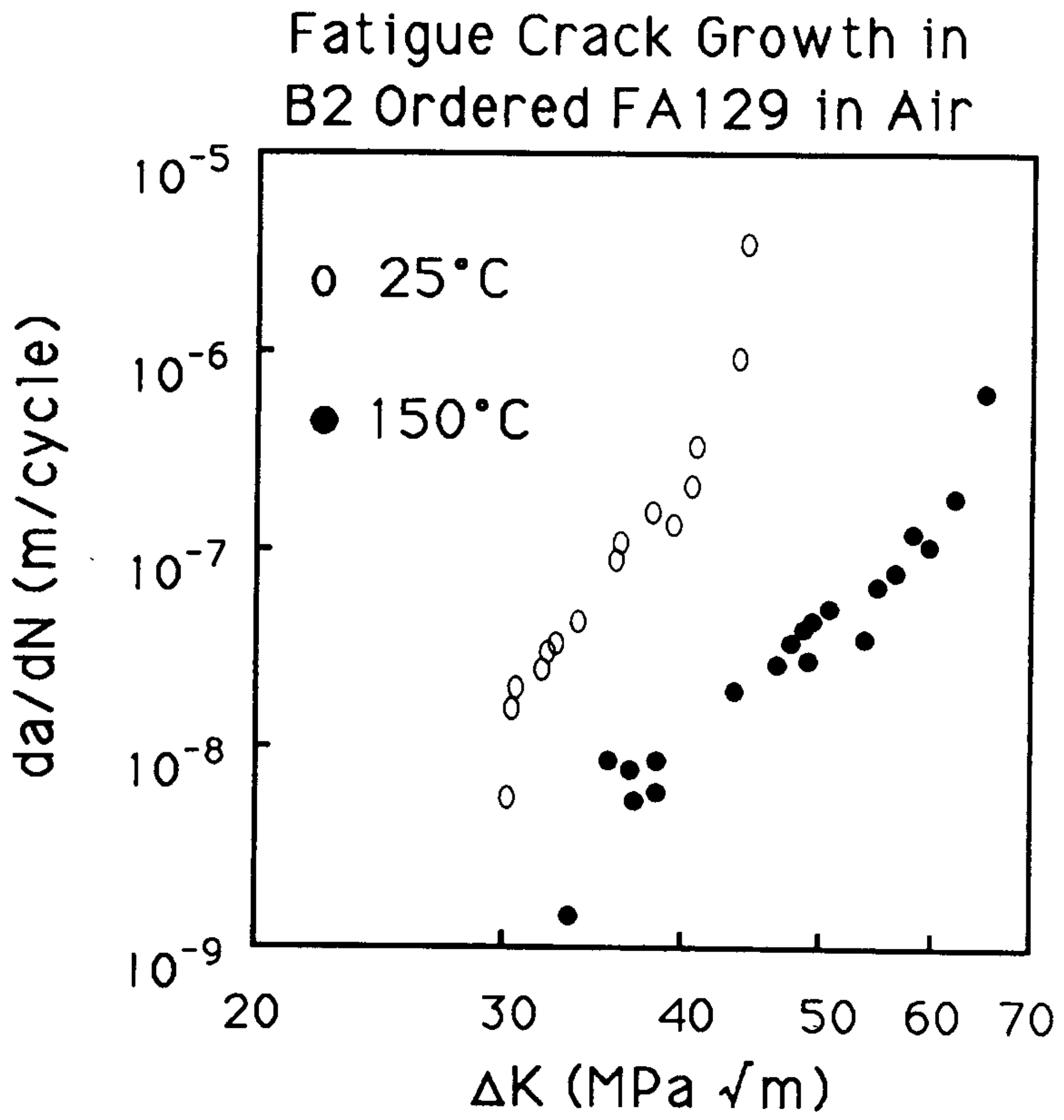


- Oxygen reduces the moisture-induced embrittlement

$$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$$

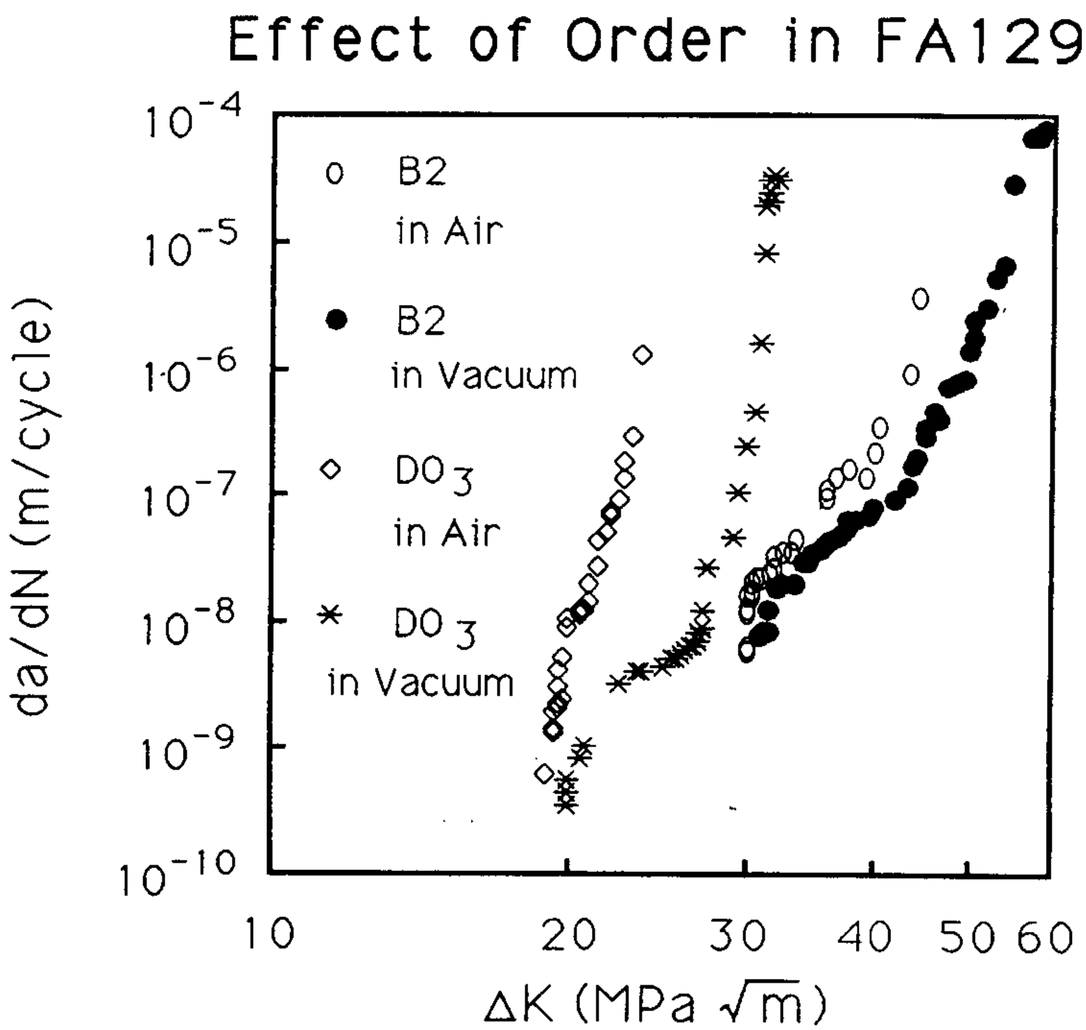
Worst Embrittlement Occurs Around Ambient Temperatures for FeAl (36.5% Al)





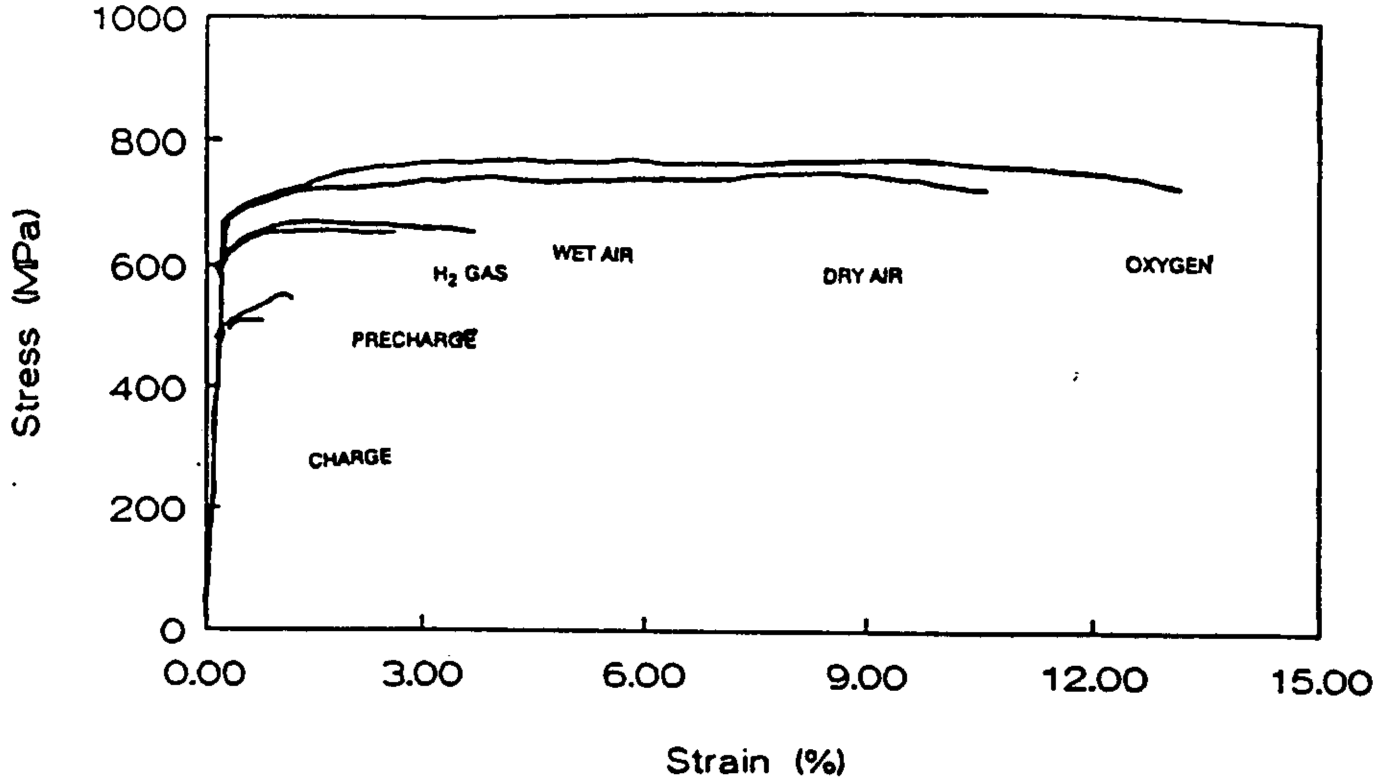
(Stoloff et al., 1992)

Both Crystal Structure and Test Environment Affect the Crack Growth Behavior of Fe3Al Alloys



(Stoloff et al., 1992)

Effect of Test Environment on the Stress-Strain Behavior of D0₃ Fe₃Al (24% Al)



- Hydrogen charging appears to soften Fe_3Al and lower σ_y

(Stoloff, 1992)

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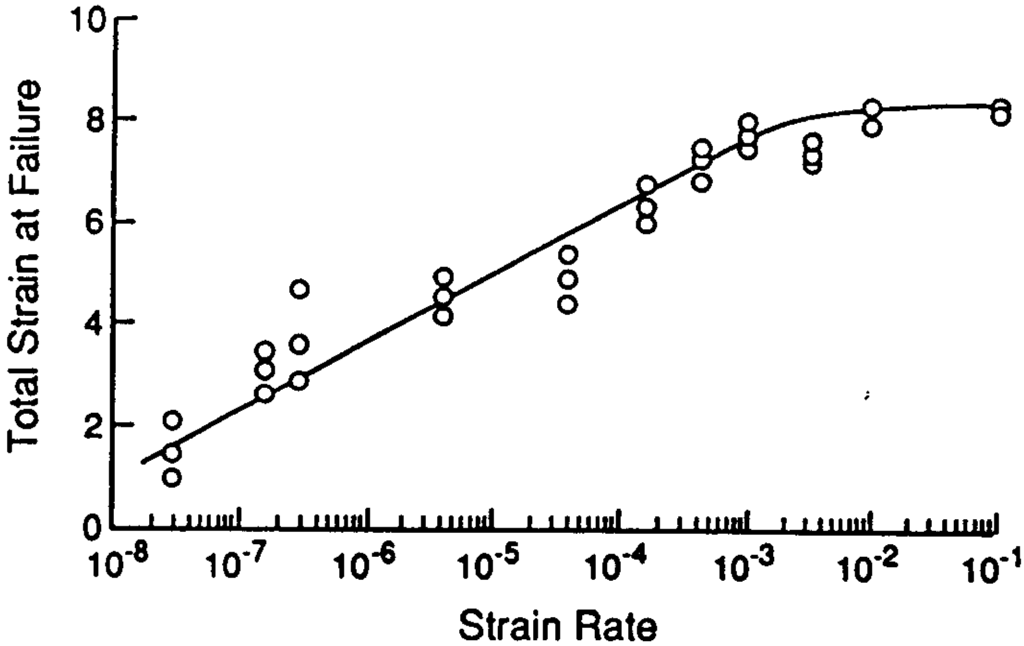
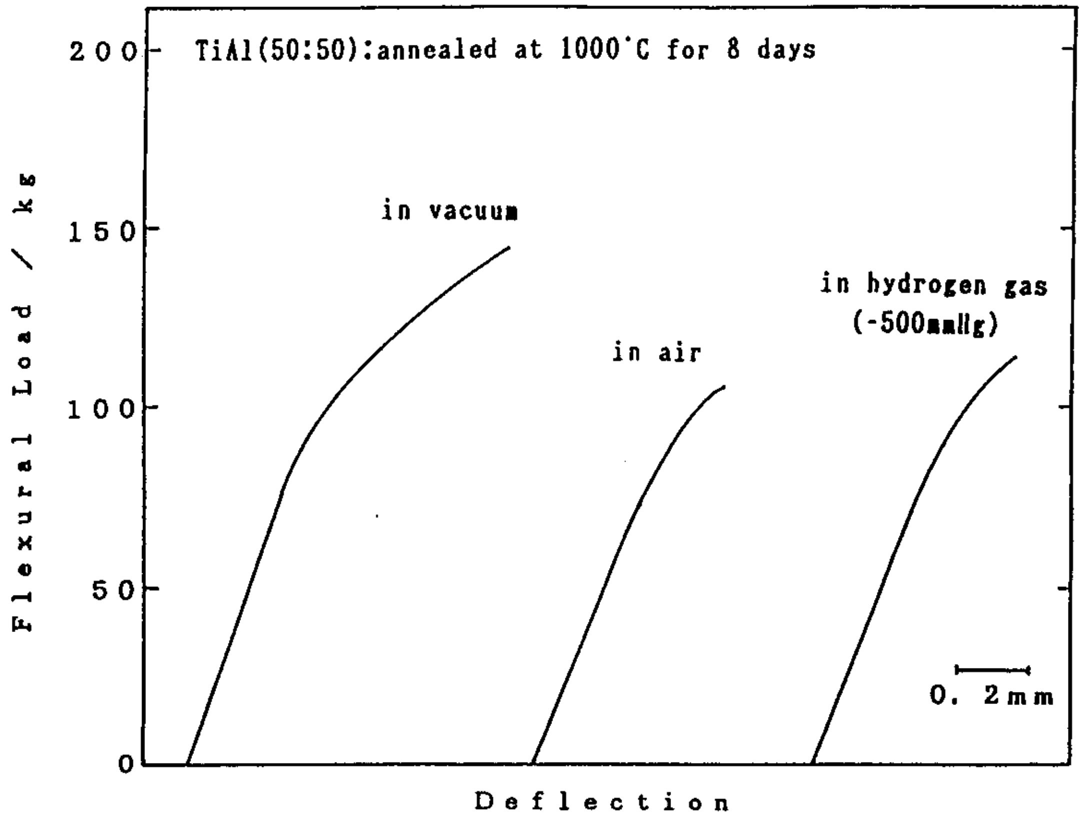
Effect of Strain Rate on Elongation of PM Fe_3Al ($D0_3$) Tested in Air



- Grain size = 30 μm

(Stoloff et al., 1993)

Bend Tests Indicate Environmental Embrittlement of TiAl (50% Al) in Air and H_2 at RT



(Nakamura, NRIM, 1991)

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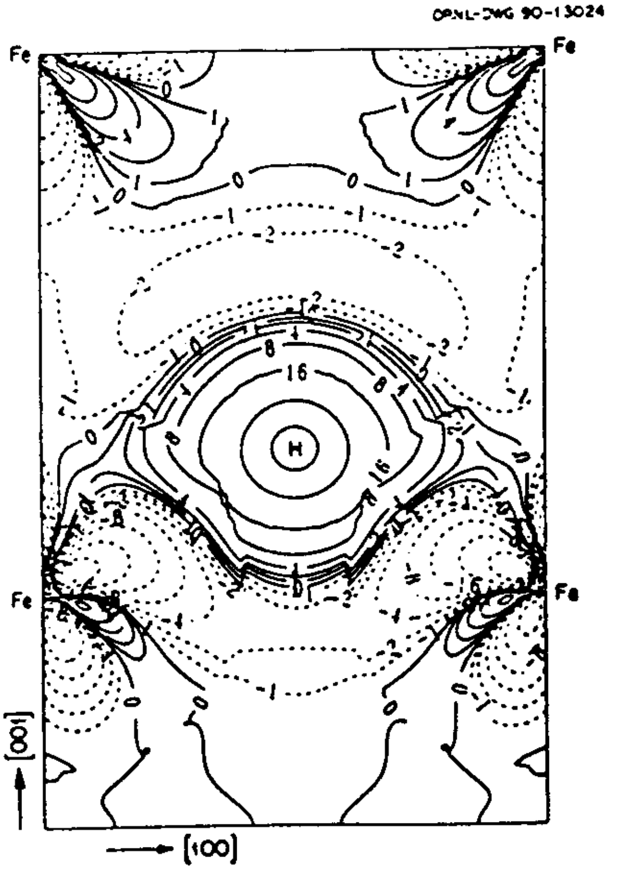
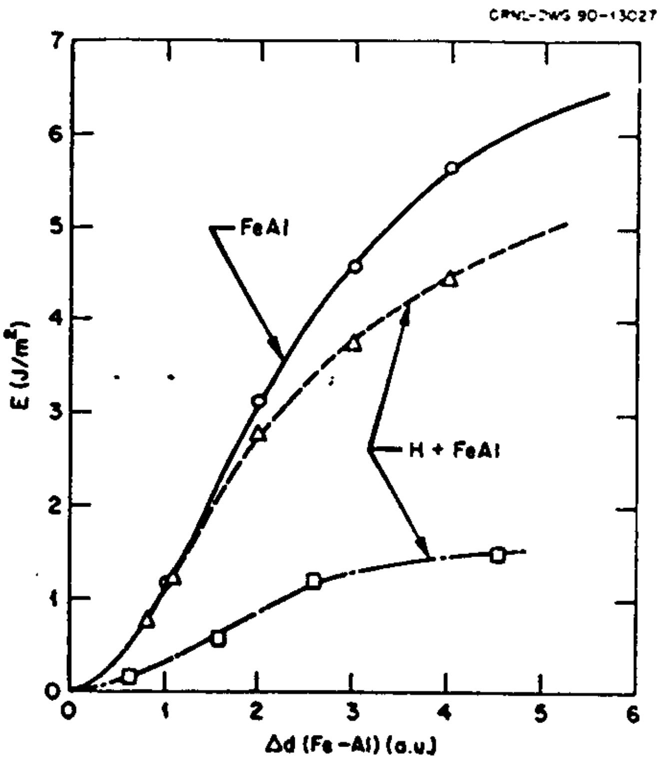
First-Principles Total-Energy Calculations[a] are Capable of Predicting Cleavage Fracture in Ordered Intermetallics

Alloy	Cleavage Strength (GPa)	Ideal Cleavage Energy (J/m^2)
Al_3Sc	19	3.5
Ni_3Al	30	6.0
FeAl	35	6.5

[a]FLAPW: Full-potential linearized augmented plane-wave (Fu, Painter, and Yoo; 1990 & 1991)

Interstitial Hydrogen Absorbs Electrons From Iron and Reduces Fe-Fe Bonding by as Much as 70% (Hydrogen Embrittlement)





The charge density contour plot of FeAl+H on (010) plane

(Fu and Painter, 1990)

Hydrogen Diffusion Affects the RT Fracture Mode in bcc- and fcc-Ordered Intermetallics

- **Hydrogen diffusion in conventional materials**

Material	Hydrogen diffusivity, D (cm^2/s)	
	Grain boundary	Lattice
αFe (bcc)	6.3×10^{-5}	3.1×10^{-5}
304 SS (fcc)	1.0×10^{-4}	8.6×10^{-13}

- **Estimation of hydrogen diffusion from environmental studies of intermetallic alloys**

Alloy	Estimated hydrogen diffusivity, D (cm^2/s)	
	Grain boundary	Lattice
$(Co,Fe)_3V$	2.0×10^{-5}	--
$Ni_3(Si,Ti)$	1.8×10^{-5}	--

(Chou, Liu and Miura, 1992)

Boron Enhances GB Cohesion But Does Not Reduce Moisture-Induced Hydrogen Embrittlement in FeAl (40% Al)

Alloy	Test environment	**Ductility (%)**	Yield strength (MPa)	Fracture mode
FeAl	Air	**1.2**	390	GBF
FeAl	Oxygen	**3.2**	402	GBF
FeAl+B	Air	**4.3**	391	TF
FeAl + B	Oxygen	**16.8**	392	TF

- Boron tends to segregate strongly to GBs and suppresses intergranular fracture
- However, B-doped FeAl still shows environmental embrittlement in air.

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Fracture Behavior of Fe3Al-FeAl With and Without Boron Addition at RT

No B, Air Tests

Fe-25Al ______ Cleavage ______ 38Al ______ GBF ______ 51Al

No B, Dry Oxygen (or Vacuum) Tests

Fe-25Al ______ Mixed Fracture ______ 32Al ______ GBF ______ 51Al

B-Doped, Air or Dry Oxygen

Fe-25Al ______ Cleavage ______ 45Al ______ GBF ______ 51Al

Comparison of the Fracture Behavior of FeAl at RT

35%, air

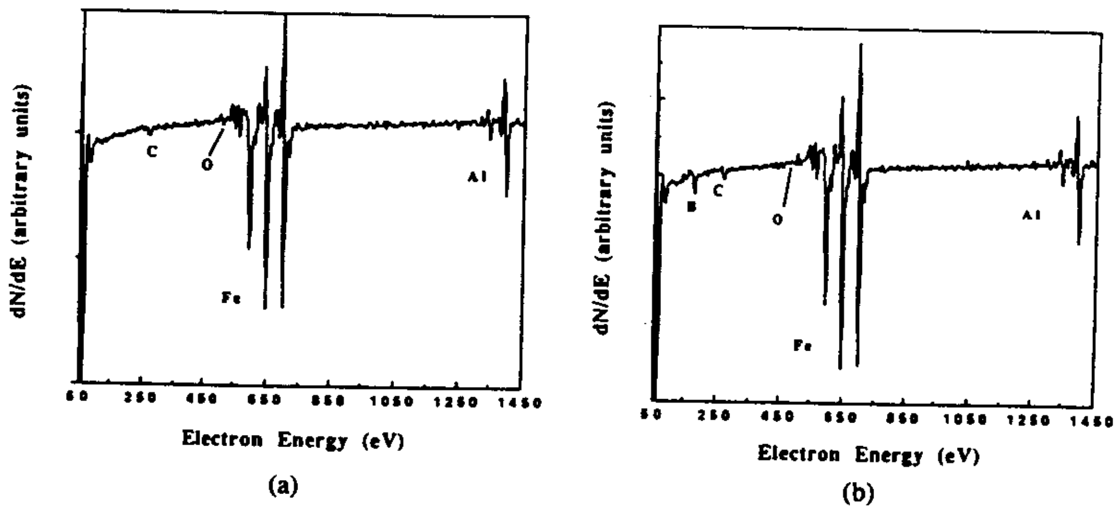
35%, oxygen

43% Al, air

43% Al, oxygen

(Liu and George, 1991)

Boron Segregates Strongly to GBs in FeAl (40% Al)



Undoped Boron-doped

- GBs in FeAl are clean and free from detectable impurities
- The average boron level on GBs in FeAl is estimated to be 2.6 at. % (segregation factor = 43)

(Liu and George, 1991)

Metallurgical Solutions to Environmental Embrittlement

- To control surface composition, thereby reducing the kinetics of generation of moisture-induced hydrogen
- To reduce hydrogen solubility and hydrogen diffusion
- To refine grain structure, resulting in reduced stress concentrations during plastic deformation
- To lower yield and flow stresses

EFFECT OF SURFACE TREATMENT ON RT TENSILE PROPERTIES OF FeAl Alloy (FA-350)

Surface treatment	Ductility (%)	Yield strength (ksi)	Tensile strength (ksi)
1 h/700°C/Vac	10.7	47.2	110
1 h/700°C/Vac/Oil	13.4	47.8	123
30 min/700°C/Air +6 times	14.2	51.8	134

- Formation of protective oxide scales increases the RT tensile ductility by 33%.

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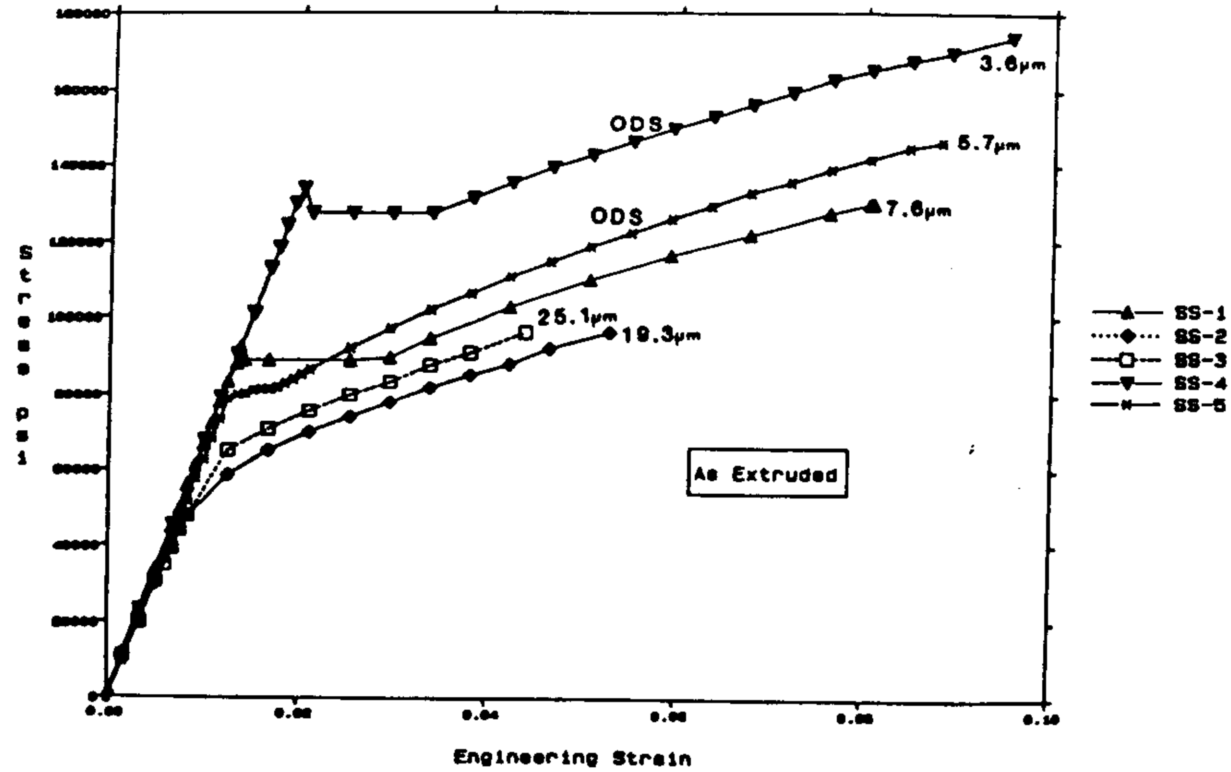
Grain Refinement Improves the RT Ductility of FeAl (40 at. % Al) Prepared by Mechanical Alloying (Strothers and Vedula, 1987)



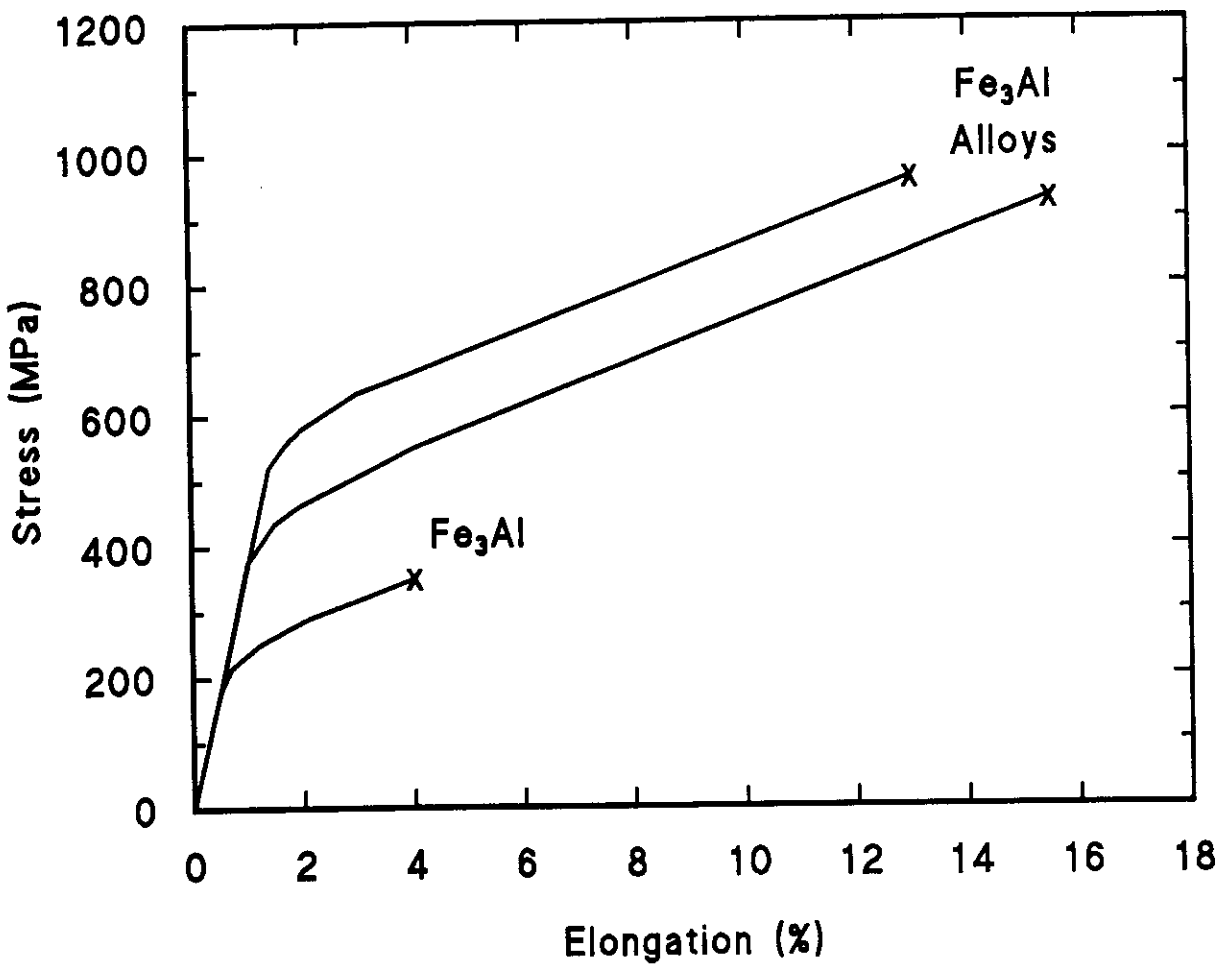
Tensile behavior of as-extruded alloys at room temperature.

The BES Effort on Environmental Studies Led to a New Approach to Alloy Design of Iron Aluminides for Industrial Use Under Energy Conservation and Fossil Programs

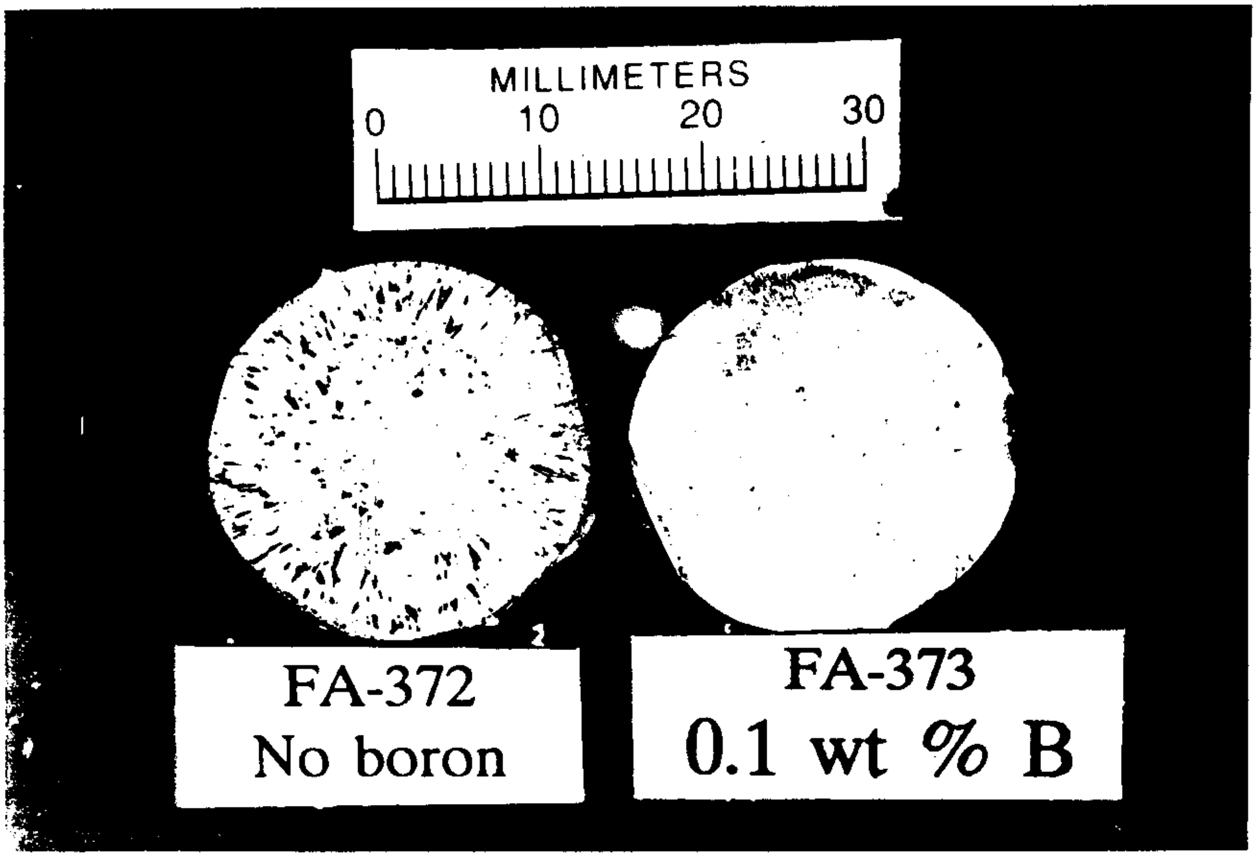
Alloy composition (at. %)	RT elongation in air (%)	Strength (ksi) Yield	Strength (ksi) Tensile
FeAl (35.8Al)	2.2	51.6	59.4
FeAl+0.05Zr+0.24B	10.7	48.2	109.6
FeAl+0.05Zr+0.24B + preoxidation[a]	14.2	51.8	134.0

[a]To form protective oxide scales at 700°C.

TENSILE PROPERTIES OF Fe_3Al HAVE BEEN SUBSTANTIALLY IMPROVED BY CHANGES IN COMPOSITION AND PROCESSING



Boron Additions Dramatically Reduce Cast Cavities in FeAl Alloys Prepared by Arc Melting and Drop Casting



- It is possible that boron occupies interstitial sites and reduces the solubility of H/H_2O.

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Intergranular Fracture in NiAl

- NiAl has the B2 crystal structure

- Stoichiometric NiAl showed ~2% tensile elongation and GB fracture at RT (Hahn and Vedula, 1988; Rozner and Wasilewski, 1966)

- GBs are clean, with compositions similar to bulk compositions (George and Liu, 1990)

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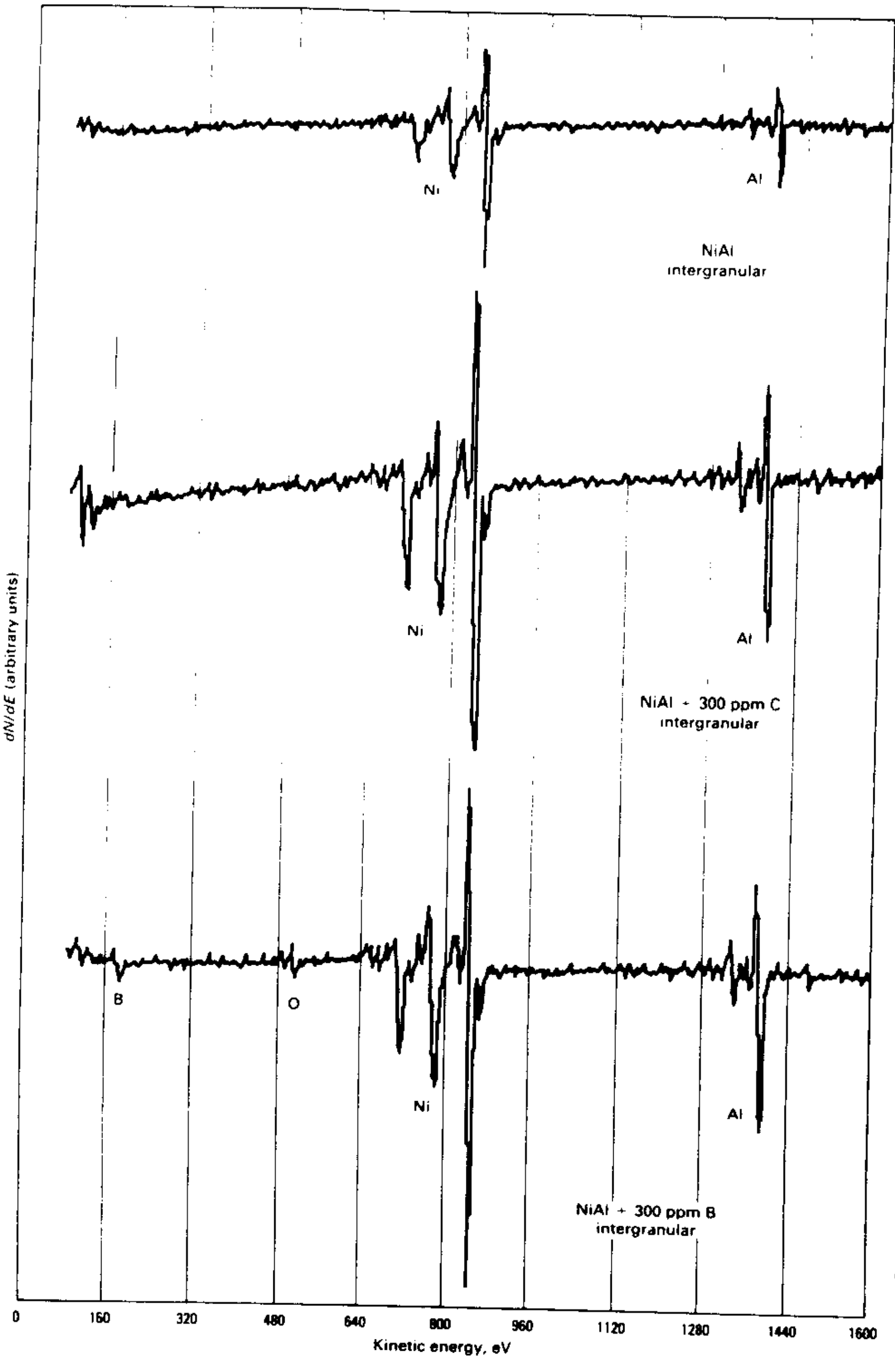
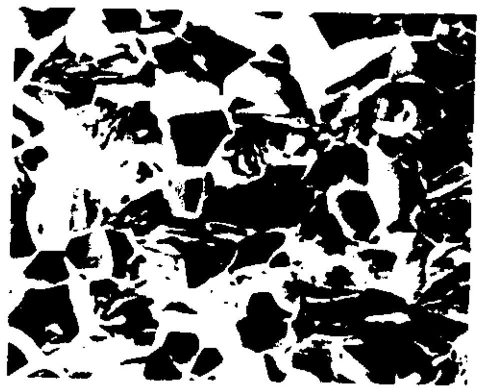


NiAl



NiAl + 300 ppm C

NiAl + 300 ppm B

Microalloying of NiAl

Suppression of GB Fracture Does Not Impart RT Ductility to NiAl

- The Weak GB is a Part of the Brittleness Problem in NiAl, But Not the Only Problem
- Other Causes of Brittle Fracture in NiAl
  - — Insufficient Deformation Modes <100> vs <111> Slip
  - — Poor Cleavage Strength
- Ductility Improvement in NiAl Requires to Increase Deformation Modes and to Enhance Cleavage Strength, in Addition to Strengthening GBs

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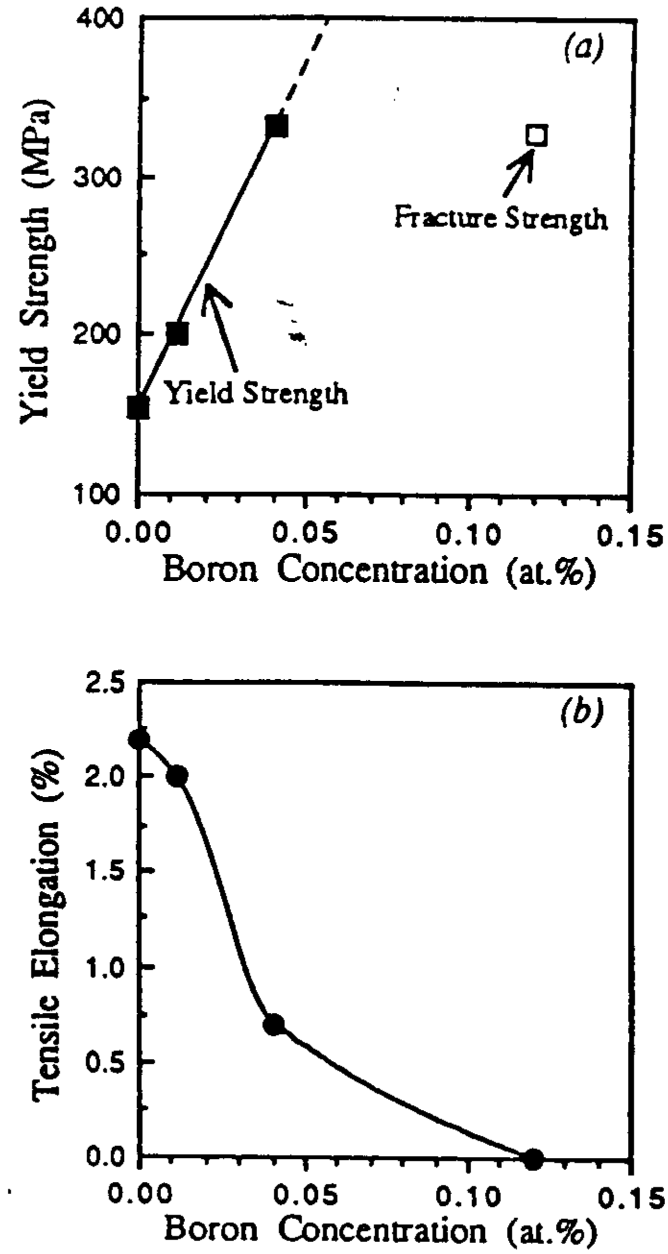
Boron Additions Dramatically Increase the Yield Strength and Lower the Tensile Ductility of NiAl at RT



(George and Liu, 1990)

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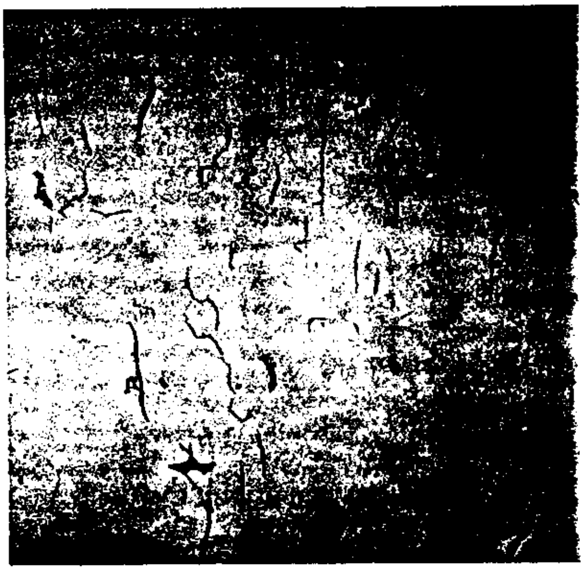
Boron Addition Strengthens GBs and Reduces Their Crack Tendency in Compression Deformed NiAl



Boron-free NiAl   Boron-doped NiAl

- Specimens were deformed 5% under compression in air (Liu et al., 1993)
- Zr-doping also reduces GB cracking tendency in NiAl (Bowman et al., 1992)

Fracture Behavior of NiAl With and Without Boron Addition at RT

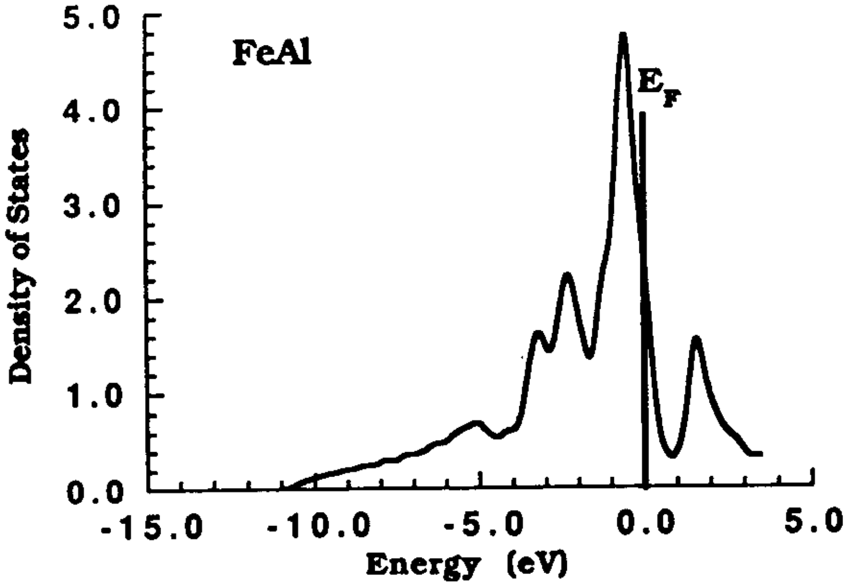
<u>No B, Air Tests</u>

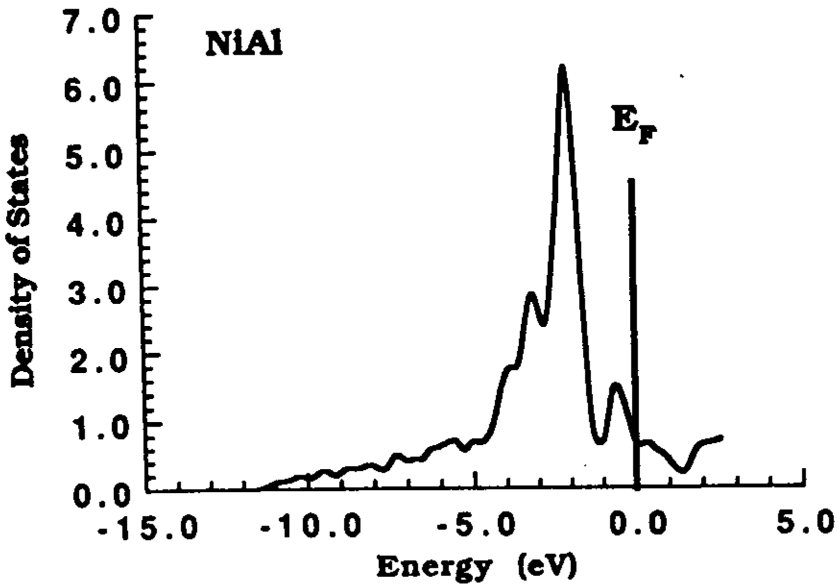
Ni-40Al		42Al		50Al		51Al
	Cleavage		Mixed Fracture		GBF	

<u>B-Doped, Air Tests</u>

Ni-40Al		50Al		51Al
	Cleavage		GBF	

Reduction in Electron Concentration Lowers Atomic Bonding in FeAl But Not in NiAl.





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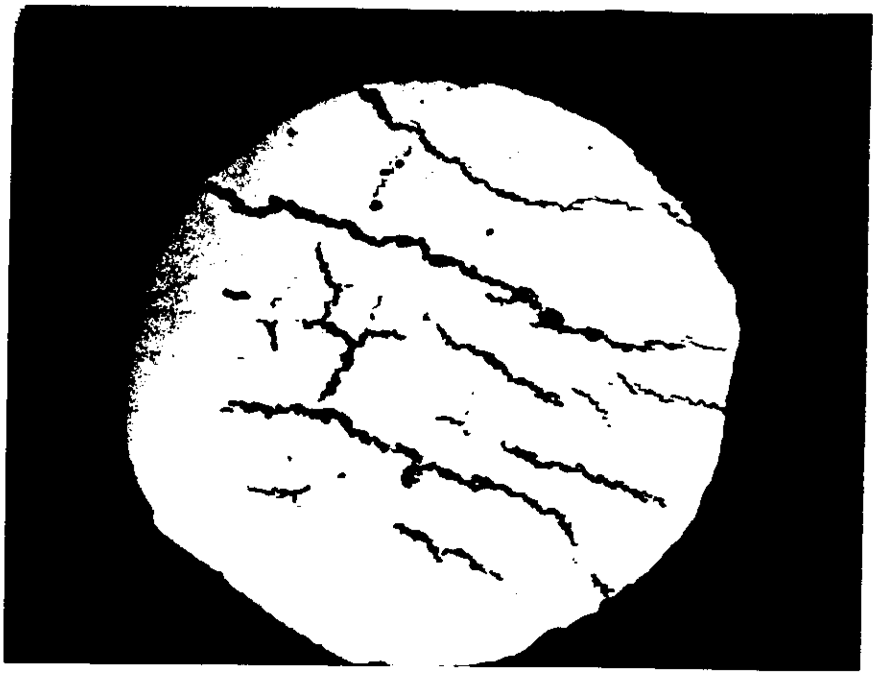
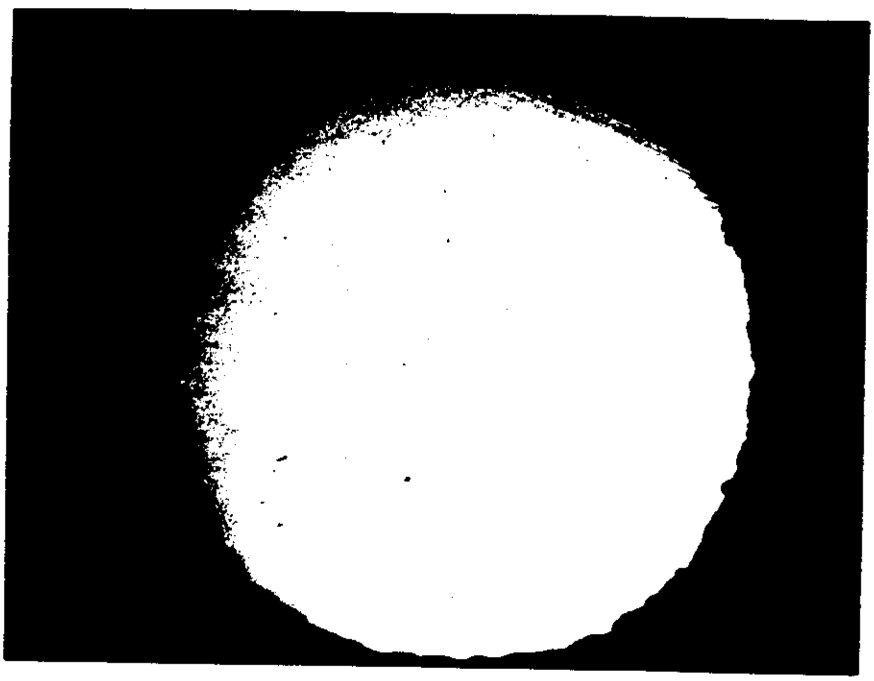
The Environmental Study Has Led to Solve Some Industrial Problems of Using Iron Aluminides



Cut with water lubricant



Cut with oil lubricant

Conclusions

- The GB strength of iron and nickel aluminides decreases with increasing aluminum concentration
- Boron tends to segregate strongly to GBs in iron and nickel aluminides and suppresses intergranular fracture
- Iron aluminides show severe environmental embrittlement whereas NiAl exhibits no indication of such embrittlement at ambient temperatures
- The embrittlement of iron aluminides involves the following chemical reaction

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H$$

- The embrittlement can be reduced by metallurgical means