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WORKING PARTY ON
MECHANICAL PROPERTIES OF INTERFACES

23 AUGUST - 3 SEPTEMBER 1993

"Grain-Boundary Brittleness and Ductility Improvement in Intermetallic Alloys" (Part I)

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

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Grain-Boundary Brittleness and Ductility Improvement in Ordered Intermetallics

Part I: fcc-ordered intermetallics
Part II: bcc-ordered intermetallics

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Working Party on Mechanical Properties of Interfaces
ICTP
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Outline

- Characteristics of brittle grain-boundary (GB) fracture in ordered intermetallics

- Causes of GB brittleness

    a) intrinsic factor: poor GB cohesion
    b) extrinsic factor: moisture-induced hydrogen embrittlement

- Beneficial effect of boron additions

- GB engineering

    a) control of GB chemistry
    b) control of grain size and shape
    c) control of GB character
    d) control of deviations from alloy stoichiometry

Ordered Intermetallic Alloys Offer Many Advantages for Engineering Use

- Excellent high-temperature strength
- Resistance to oxidation and corrosion
- Low density and high melting point
- Special properties [e.g. shape-memory behavior, vibration cavitation resistance, magnetic properties ($Nd_2Fe_{14}B$)]

In many cases, poor fracture resistance and fabricability limit their use as engineering materials

- Brittle intergranular fracture is a major cause of low ductility in many $L1_2$ and B2 intermetallics

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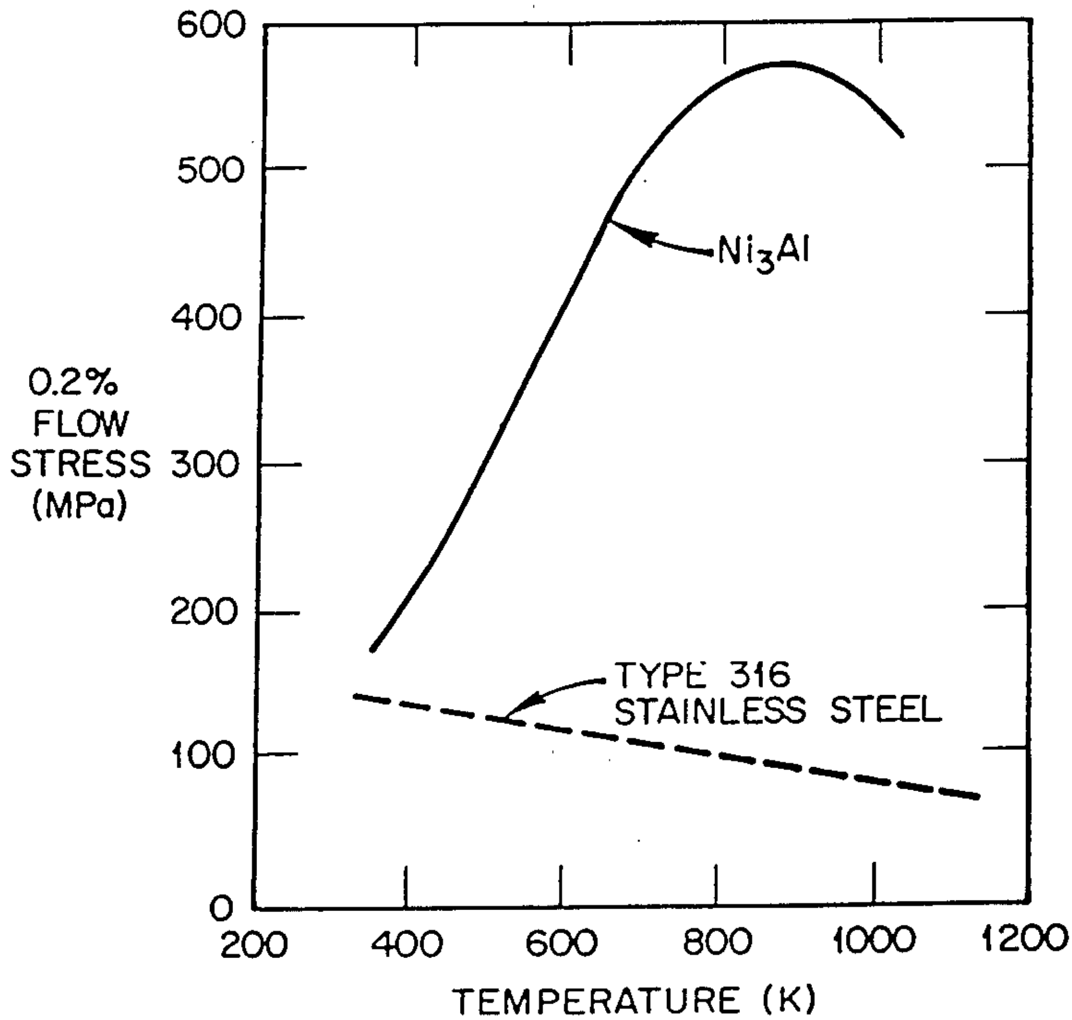
THE YIELD STRENGTH OF Ni_3Al INCREASES WITH TEMPERATURE AND REACHES A MAXIMUM AROUND 830 K



- BECAUSE OF THE INCREASE IN YIELD STRENGTH WITH TEMPERATURE, Ni_3Al IS MUCH STRONGER THAN TYPE 316 STAINLESS STEEL AT ELEVATED TEMPERATURES.

Brittle GB fracture in ordered intermetallics with high-crystal symmetry

I. fcc-ordered intermetallics ($L1_2$)

Ni_3Al
Ni_3Si
Ni_3Ga
Ni_3Ge
$(Ni,Co,Fe)_3V$
Co_3Ti

II. bcc-ordered intermetallics

FeAl (B2)
Fe_3Al ($D0_3$)
NiAl (B2)
CoFe (B2)

Characteristics of brittle GB in ordered intermetallics

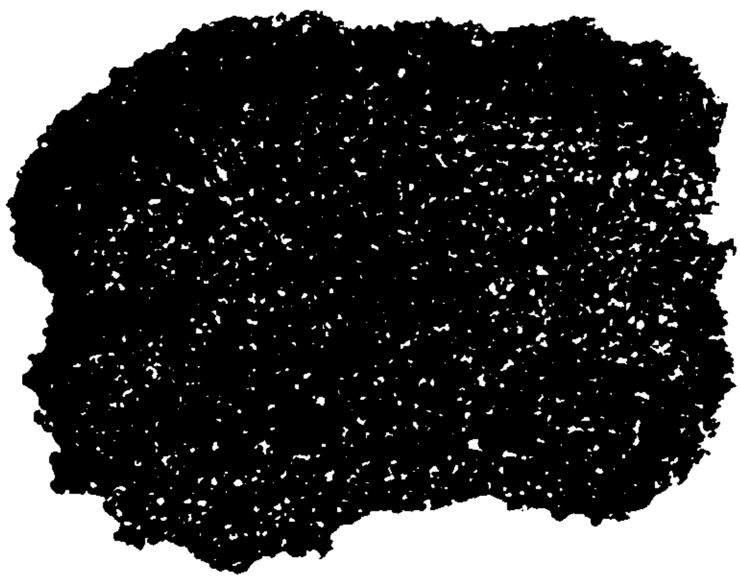
- Brittle GB fracture with no detectable impurity segregation (based on Auger analyses)
- GBs in ordered intermetallics had been considered to be intrinsically brittle until recently
- Brittle fracture and tensile ductility are sensitive to deviations from alloy stoichiometry

ORNL PHOTO 3430-83

POLYCRYSTALLINE Ni_3Al SHOWS POOR DUCTILITY AND BRITTLE GRAIN-BOUNDARY FRACTURE

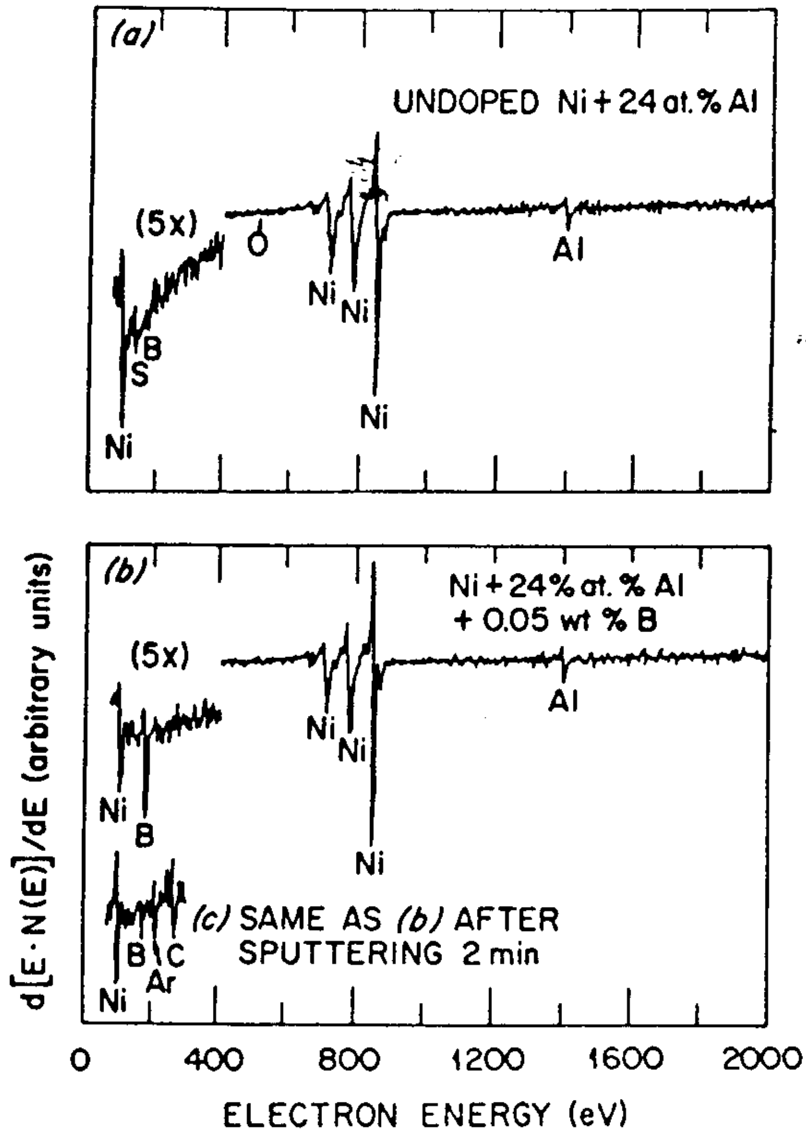
- SINGLE CRYSTALS OF Ni_3Al ARE DUCTILE
- POLYCRYSTALLINE Ni_3Al IS EXTREMELY BRITTLE BECAUSE OF GRAIN-BOUNDARY WEAKNESS

BRITTLE GRAIN BOUNDARY FRACTURE AT ROOM TEMPERATURE



EXTENSIVE CRACKING ALONG GRAIN BOUNDARIES IN Ni_3Al CAST INGOT HOT ROLLED AT 1200°C

Auger Analyses Indicate That Grain Boundaries in Ni_3Al are Clean and Free from Detectable Impurities.



- **Boron Dopants Segregate Strongly to Ni_3Al GBs.**

VG090392.3

Ni_3Al is Susceptible to Moisture- Induced Hydrogen Embrittlement at Room Temperature

Alloy composition (at. %)	Test environment	Tensile ductility (%)	Strength (Mpa)		Fracture mode
			Yield	Tensile	
Ni-24Al	Air	2.6	280	333	GBF
Ni-24Al	Oxygen	7.2	279	439	GBF
Ni-23.5Al	Air	2.5	193	230	GBF
Ni-23.5Al	Oxygen	8.2	194	351	GBF

- Environmental embrittlement appears not to be the sole source of grain boundary brittleness.

(Liu, 1992)

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Tensile ductility and brittle GB fracture in Ni_3Al* are sensitive to test environment at room temperature

Test Environment	Elongation to Fracture (%)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)
Air	3.1	308	392
Oxygen	15.8	336	681

*Polycrystalline Ni_3Al produced from cold work and recrystallization of single crystals

- Ni_3Al shows a tensile ductility as high as 23% when tested in an Auger vacuum (10^{-10} torr) system
- All specimens exhibited mainly GB fracture; however, the propensity for transgranular fracture increases with increasing ductility (George, Liu and Pope, 1993)

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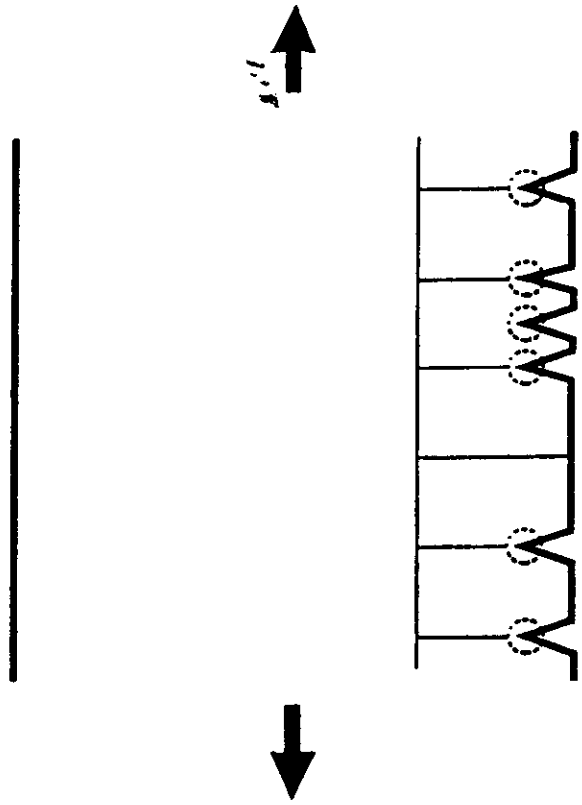
MOISTURE-INDUCED HYDROGEN EMBRITTLEMENT IN ALUMINIDES AT RT



TENSILE TEST IN AIR AT CONVENTIONAL STRAIN RATES

- Hydrogen generated at crack tips
  $2\,Al + 3H_2O_3 \rightarrow Al_2O_3 + 6H$
- Atomic hydrogen penetrates into crack tips and embrittles the material.

Ni_3Si (22.5% Si) Showed Environmental Embrittlement at RT

Alloy	Test environment (%)	Tensile ductility (ksi)	Yield strength (ksi)	Fracture mode
Ni_3Si	Air	0	--	GBF
Ni_3Si	Vacuum	4.7	98.3	GBF
Ni_3Si	Oxygen	7.5	99.4	GBF

- The results suggest that environmental embrittlement is not the sole cause of low ductility and grain-boundary fracture in Ni_3Si

(Liu and Oliver, 1991)

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Major Causes of GB Brittleness in Ni_3Al and Other $L1_2$ Intermetallics at Room Temperature

- Intrinsic factor: poor GB cohesion for strongly ordered intermetallics

- Extrinsic factor: moisture-induced hydrogen embrittlement

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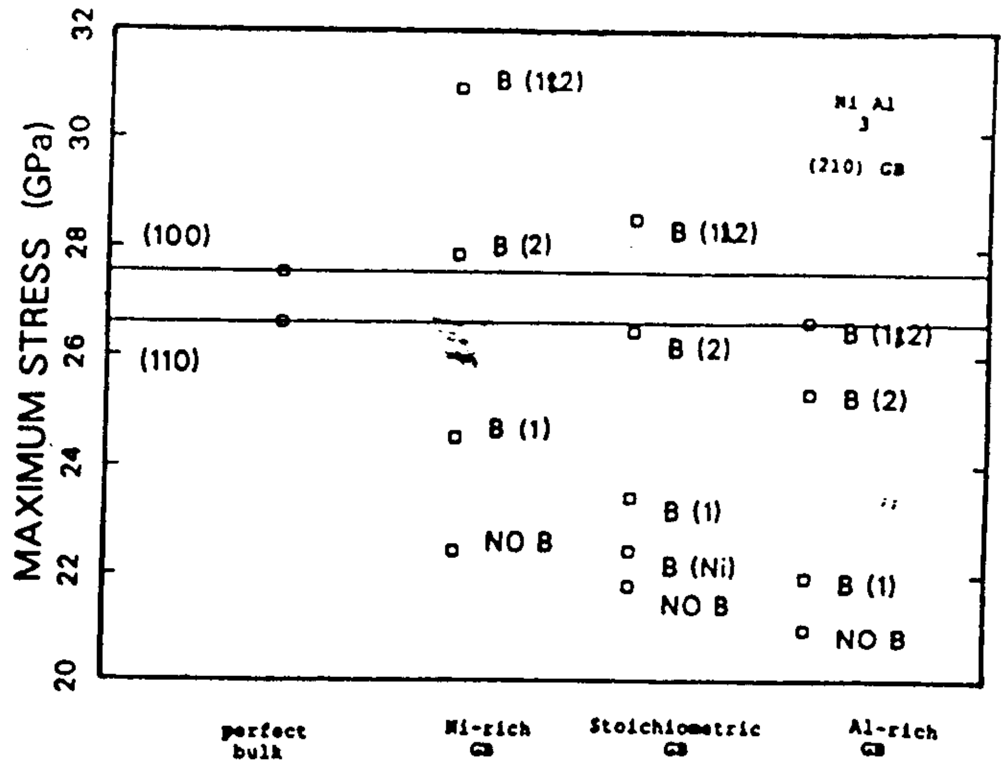
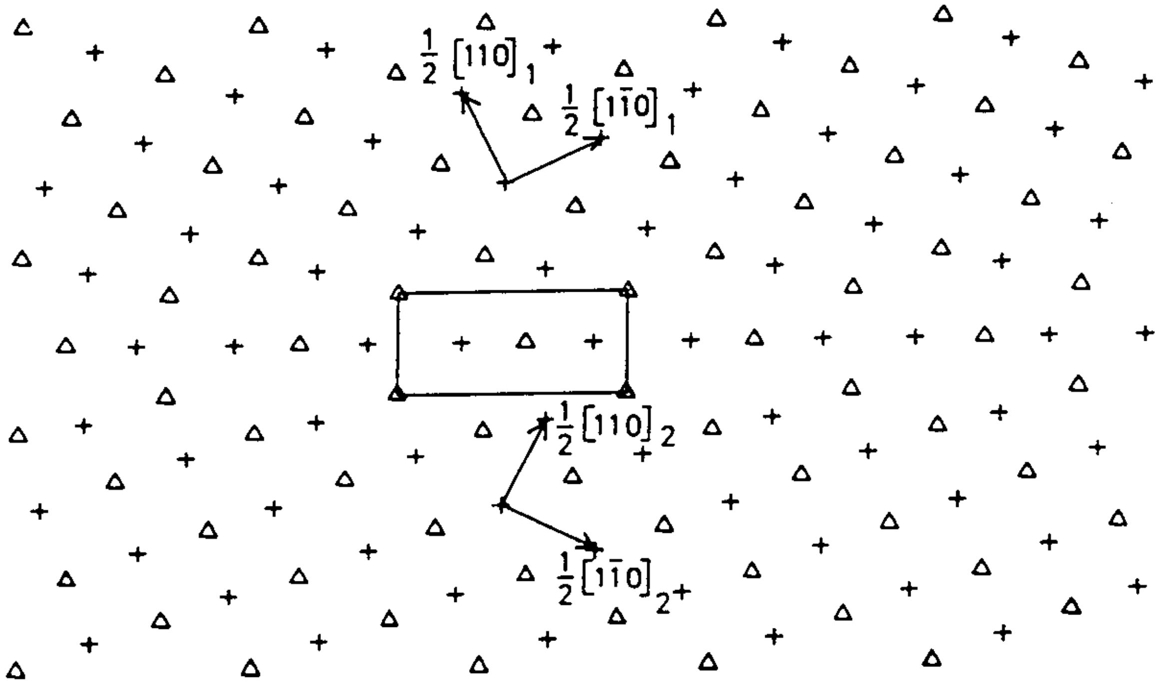
BORON INCREASES THE MAXIMUM STRESS REQUIRED TO SEPARATE (210) SYMMETRIC TILT BOUNDARY IN Ni_3Al



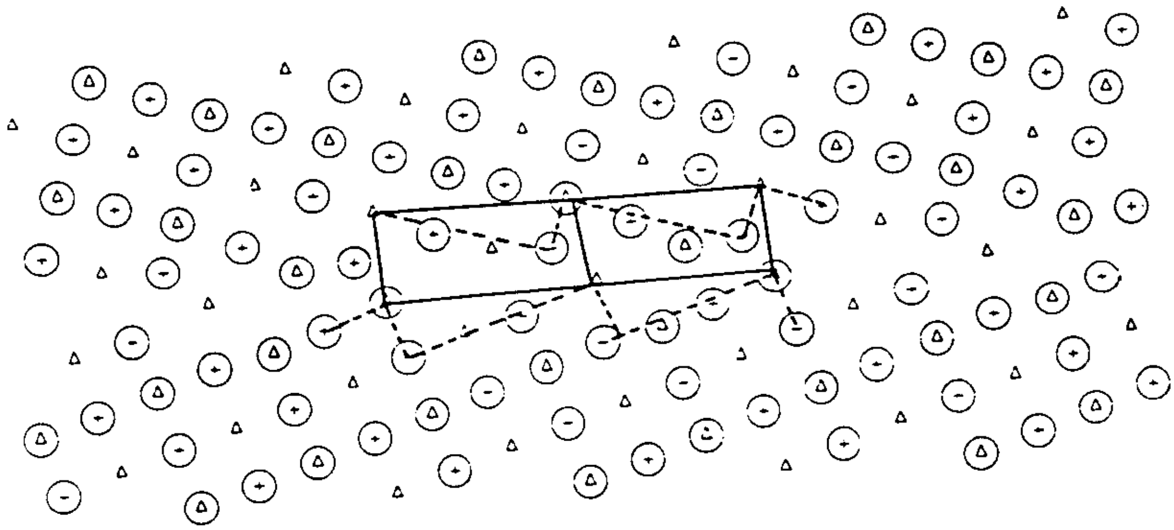
(S. P. CHEN ET AL., J. DE PHYSIQUE, 1988)

Atomic Structures of $\Sigma = 5$ (310) Tilt-Boundary

fcc

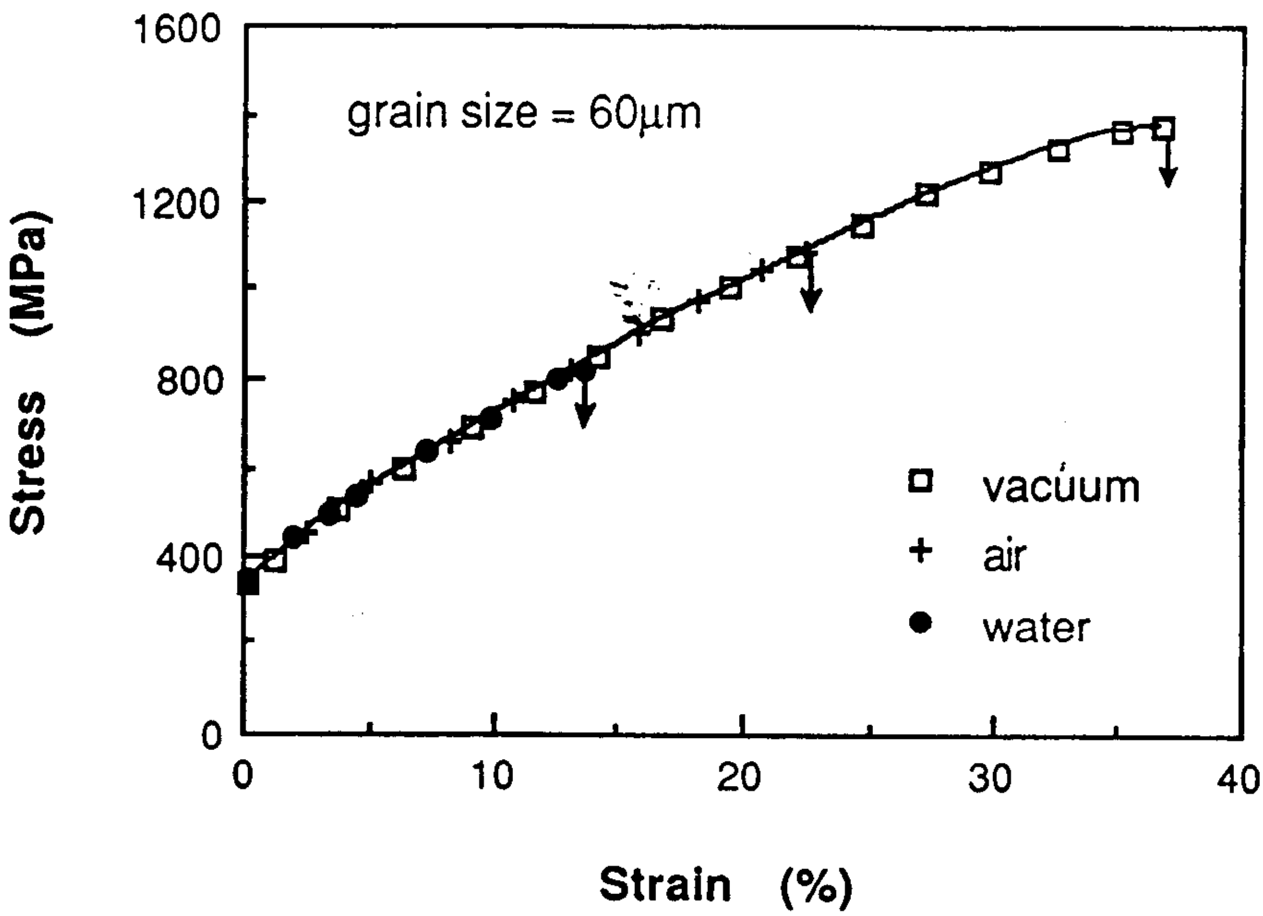


Strongly Ordered $L1_2$



- Columns of Atomic-Size Cavities are Formed in Stoichiometric Boundaries in Order to Preserve the Chemical Order up to the Boundary (Vitek et al., 1988).

$(Co,Fe)_3V$ Alloys Exhibited Environmental Embrittlement at RT



- Test environments do not affect work hardening and slip behavior of $(Co_{78}Fe_{22})_3V$

(Nishimura and Liu, 1991)

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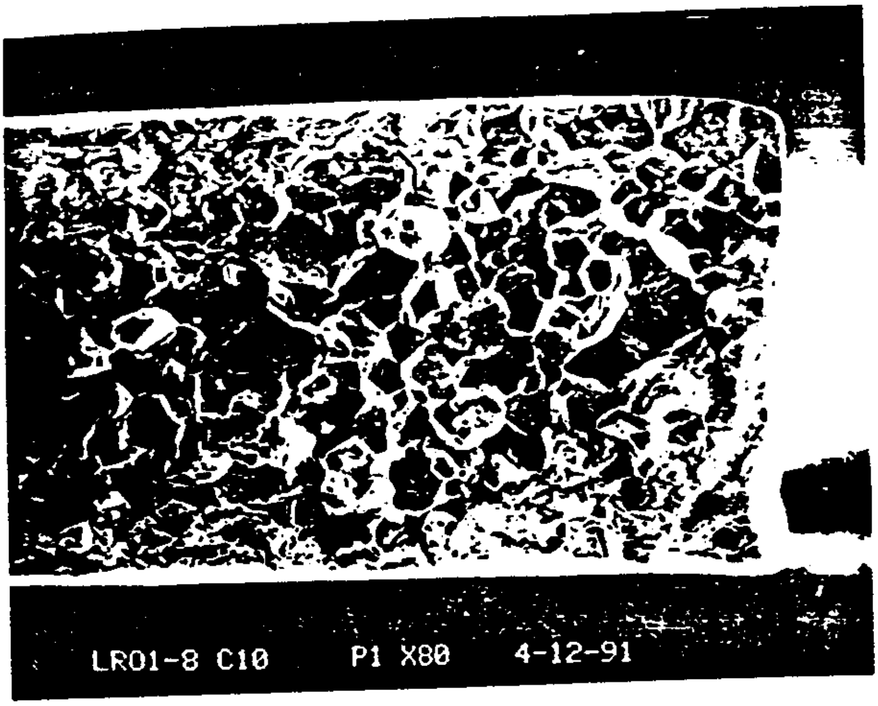
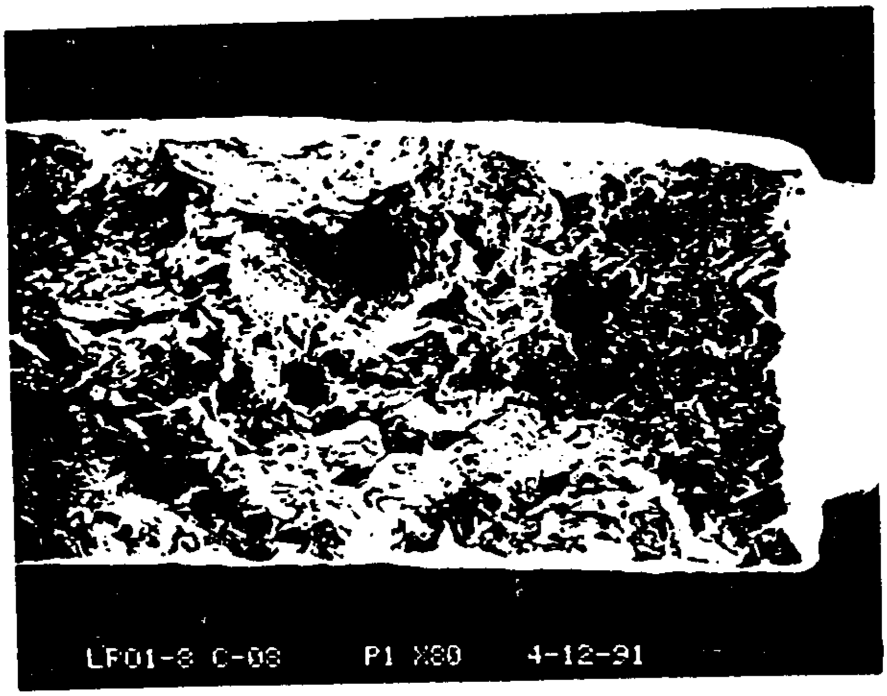
Environmental Embrittlement in $(Co_{78}Fe_{22})_3V$ Can Be Completely Suppressed by Increasing Strain Rates at RT

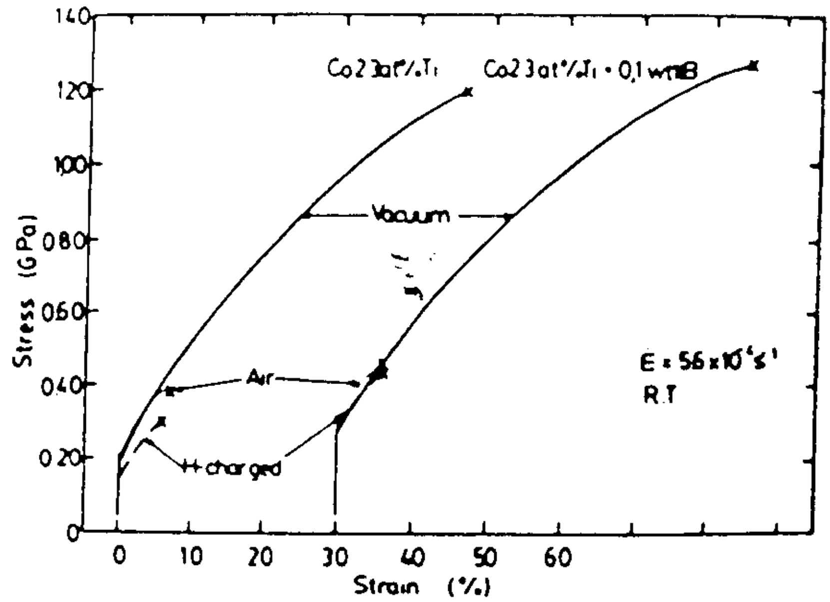


$\varepsilon = 3.3 \times 10^{-5}\ s^{-1}$
$\varepsilon = 10\%$
intergranular fracture



$\varepsilon = 3.3 \times 10^{-1}\ s^{-1}$
$\varepsilon = 35\%$
transgranular fracture

RT Ductility and Fracture in Co3Ti (23% Ti) Alloys are Sensitive to Test Environments



- With Decreasing the Ductility, the Fracture Mode Changes From Transgranular to Intergranular.
- The Embrittlement is Attributed to Hydrogen Effects.
- Boron Addition Has No Affect on the Hydrogen Embrittlement.
- The Alloys with Lower Ti are Less Susceptible to Hydrogen Embrittlement.

(Takasugi and Izumi, 1986)

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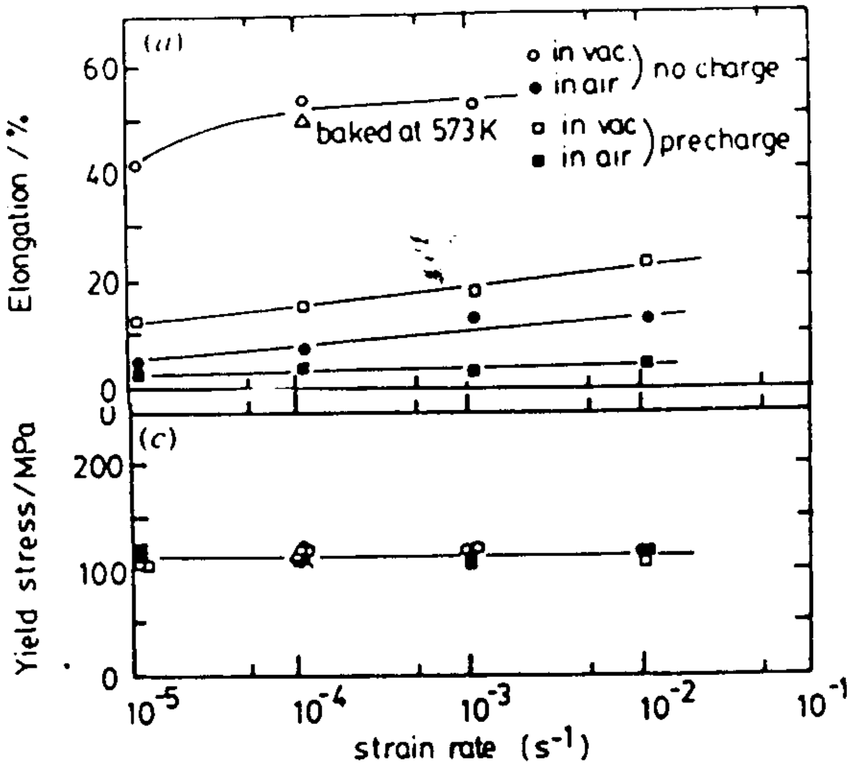
RT Ductility and Fracture Behavior of Ni3(Al0.4Mn0.6) Are Sensitive to Test Environments



- With Decreasing Elongation, the Fracture Mode Changes Gradually From Transgranular to Intergranular.
- The Loss In Ductility is Due to Hydrogen Embrittlement

(Masahashi, Takasugi, and Izumi, 1988)

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Beneficial effect of boron additions

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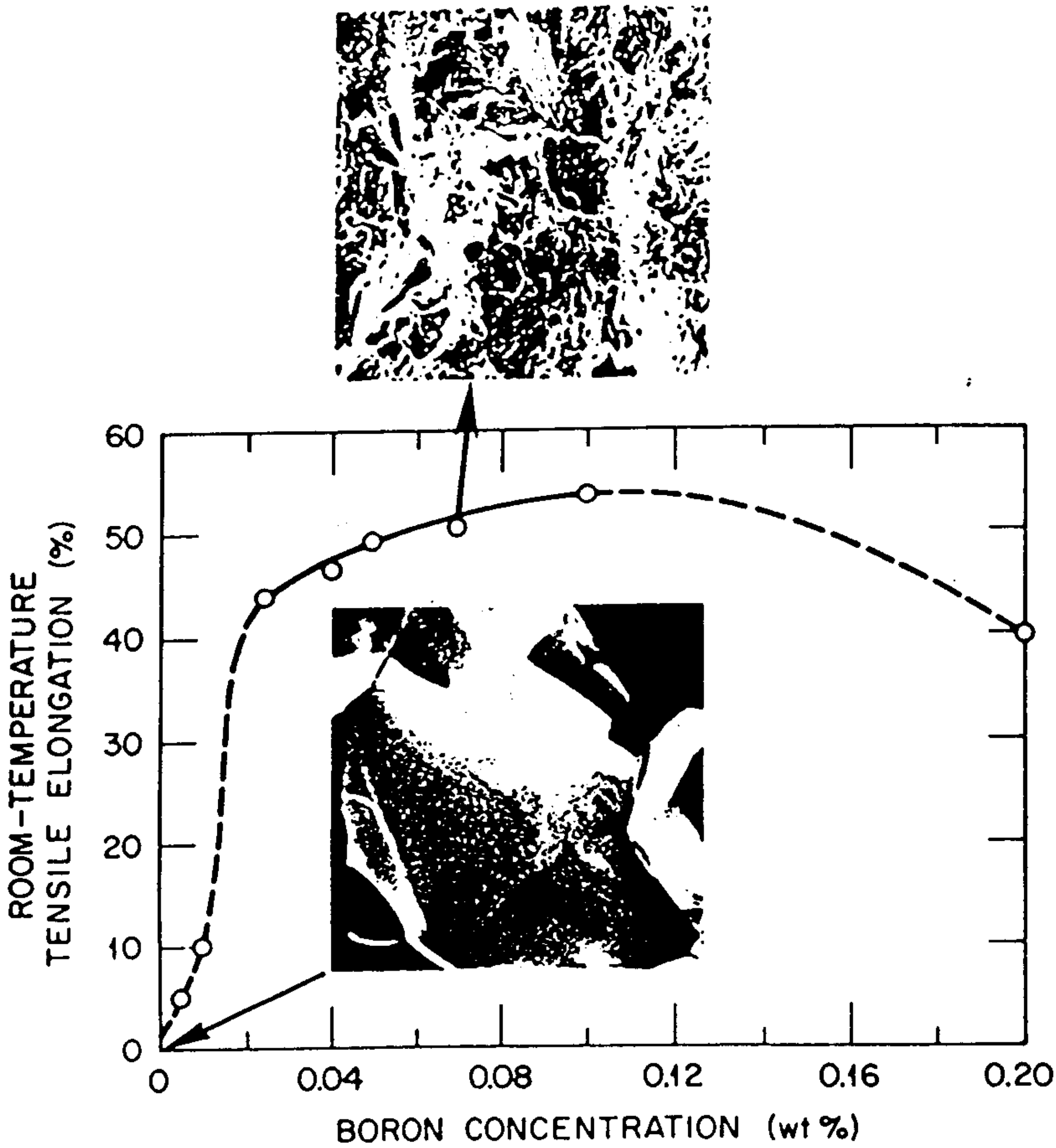
MICROALLOYING WITH BORON DRAMATICALLY IMPROVES THE TENSILE DUCTILITY AND SUPPRESSES BRITTLE GRAIN-BOUNDARY FRACTURE IN Ni_3Al (24 at. %)



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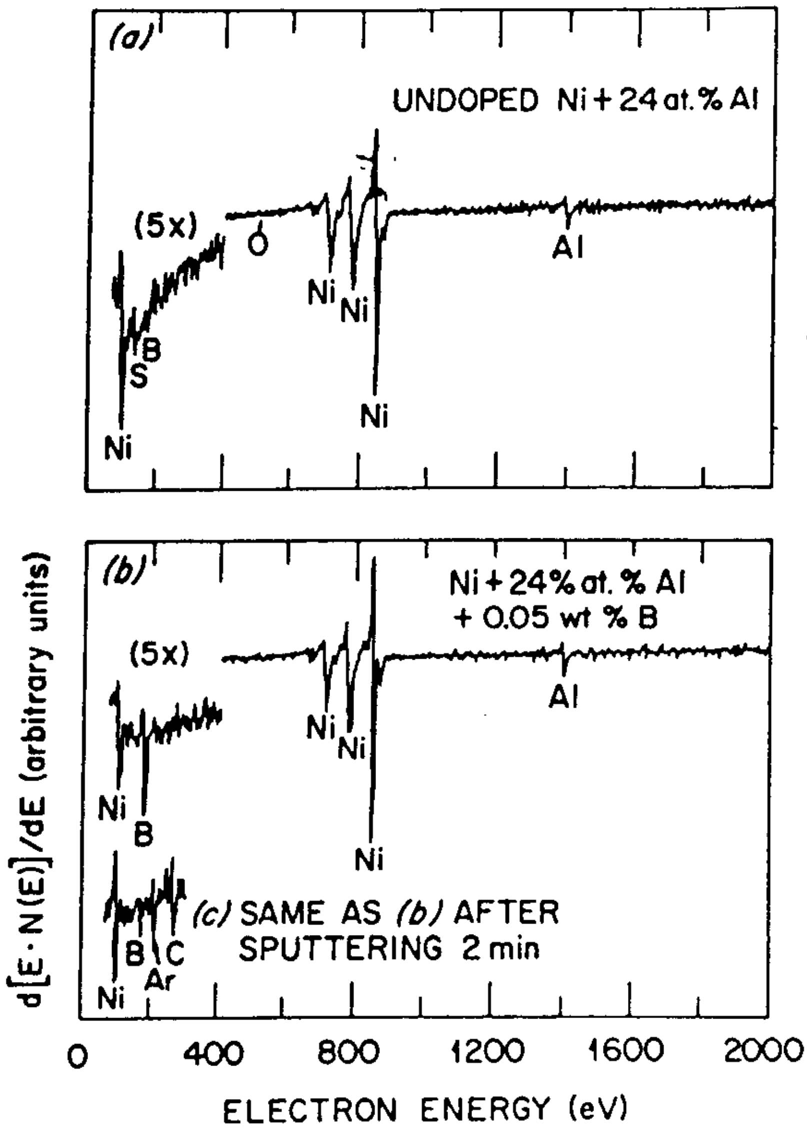
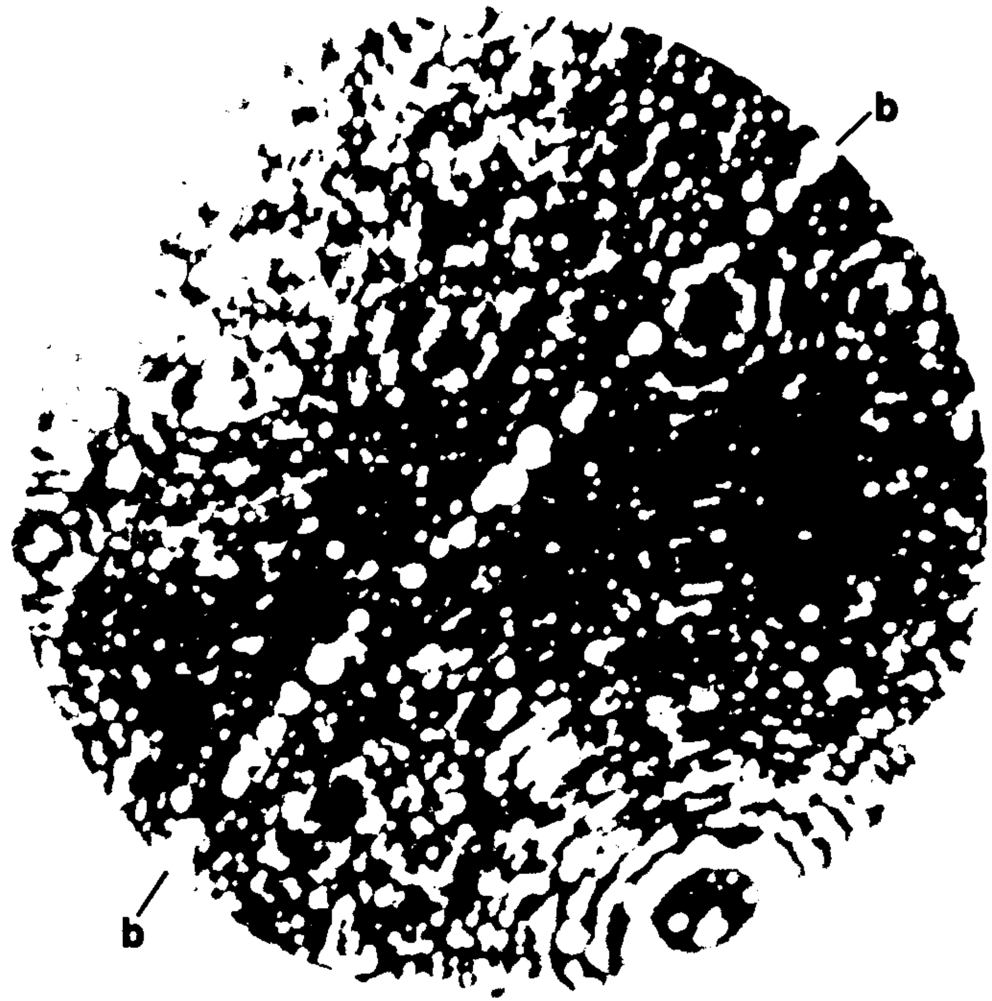
Auger Analyses Indicate That Grain Boundaries in Ni_3Al are Clean and Free from Detectable Impurities.



- **Boron Dopants Segregate Strongly to Ni_3Al GBs.**

ORNL-PHOTO 6690-86



BORON SEGREGATES TO HIGH ANGLE GRAIN BOUNDARIES (Σ27)

- After anneal for 9 min at 1000 °C,
- Boron present in a band along gb
- Coverage highly variable

Boron-Doped Ni_3Al (24% Al) Showed Excellent Ductility at Room Temperature in Various Environments.

Test environment	Elongation (%)	Strength (ksi)	
		Yield	Ultimate
Oxygen	42.8	41.9	190.8
Air	39.3	40.6	180.1
Water	36.8	41.8	174.0

- **Beneficial Effect of Boron**

  (1) Blocking H Diffusion and Eliminating Moisture-Induced Hydrogen Embrittlement

  (2) Enhancing GB Cohesion

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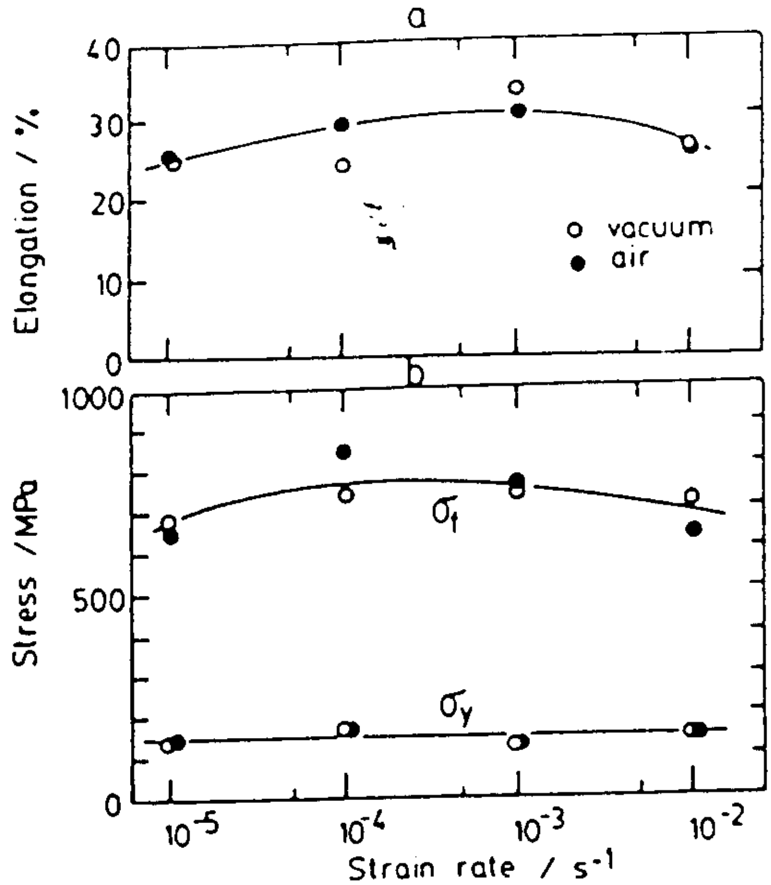
Effect of Environment on RT Ductility and Fracture in Ni3Al Doped with B or Be

- Tensile Properties of B-Doped Ni3Al (24% Al) Appear Not Sensitive to Test Environment and Strain Rate.



- The Test Environment Has a Moderate Effect on Tensile Ductility of Be-Doped Ni3Al ($\varepsilon = 5\%$ in vac; $\varepsilon = 1\%$ in air)

(Masahashi, Takasugi, and Izumi, 1988)

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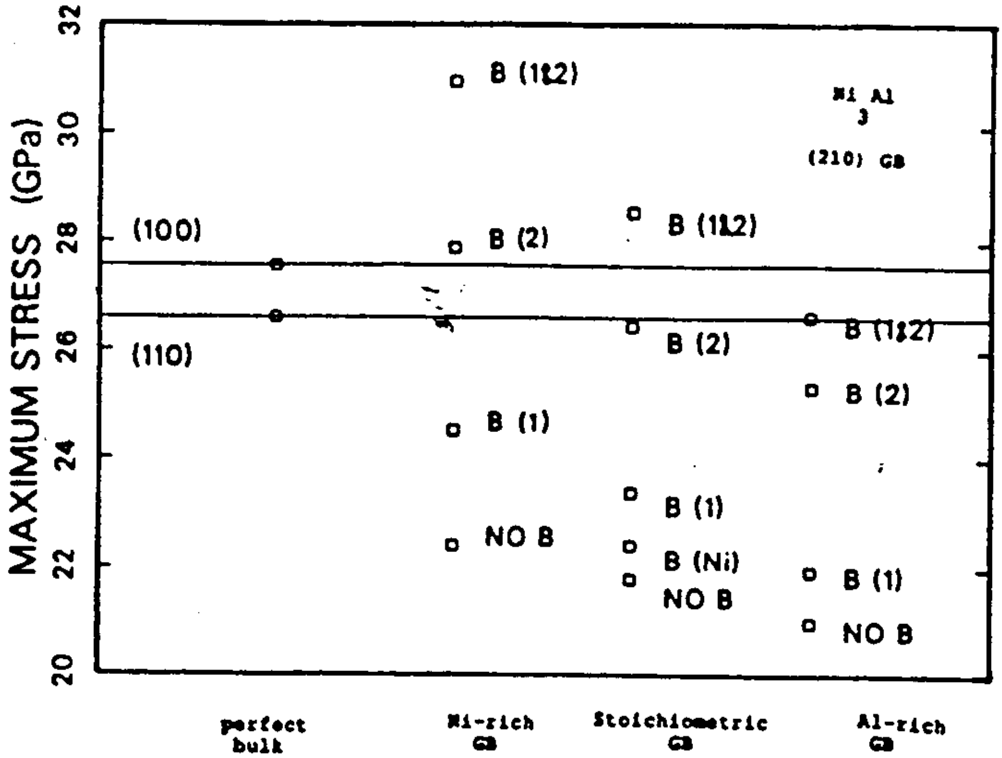
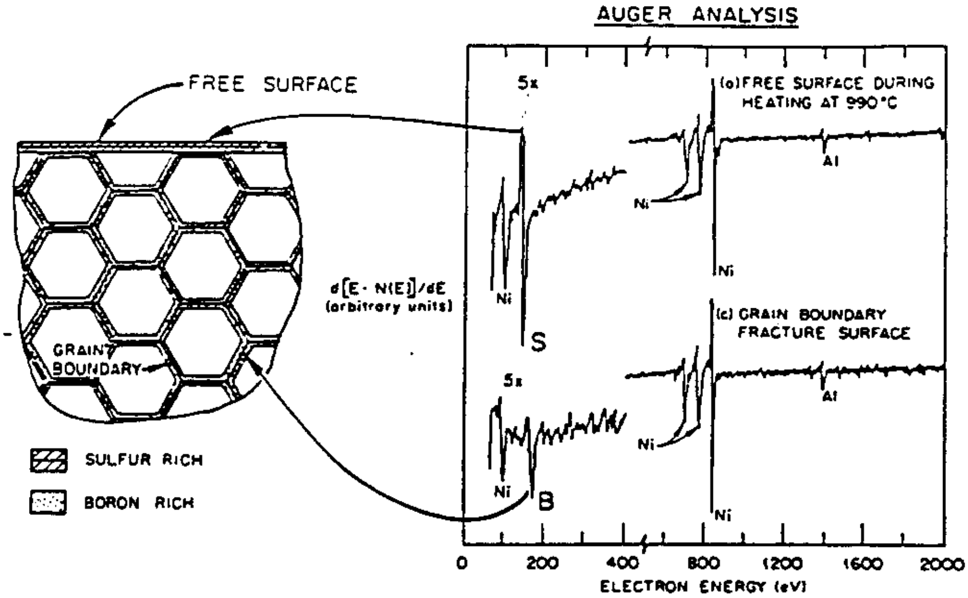
Effect Of Boron On
The Bonding Charge Density of Ni_3Al

BORON INCREASES THE MAXIMUM STRESS REQUIRED TO SEPARATE (210) SYMMETRIC TILT BOUNDARY IN Ni_3Al



(S. P. CHEN ET AL., J. DE PHYSIQUE, 1988)

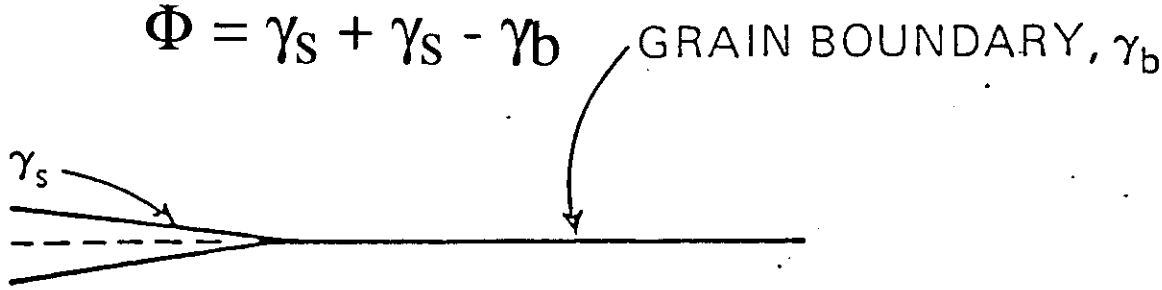
BORON EXHIBITS AN UNIQUE SEGREGATION BEHAVIOR - STRONG SEGREGATION TO GBs BUT NOT TO FREE SURFACES



- IN CONTRAST, SULFUR, AN EMBRITTLING ELEMENT, SEGREGATES MUCH MORE STRONGLY TO FREE SURFACES THAN TO GBs.

- ACCORDING TO RICE'S SEGREGATION THEORY (1976), THE BORON SEGREGATION LEADS TO INCREASE THE GB COHESIVE ENERGY:

$$\Phi = \gamma_s + \gamma_s - \gamma_b$$



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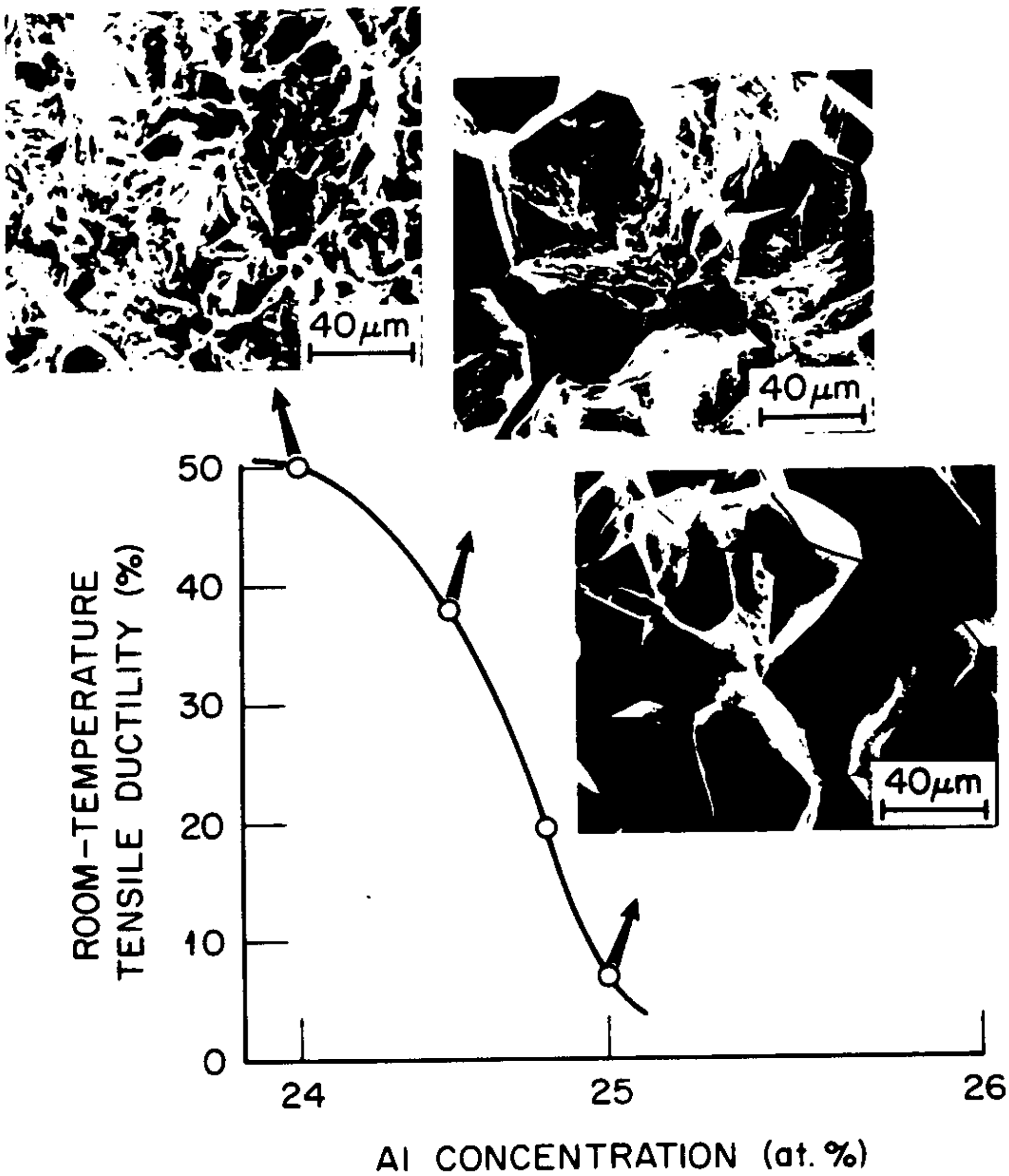
INCREASING Al CONTENT FROM 24 TO 25% SHARPLY DECREASES TENSILE DUCTILITY AND PROMOTES GRAIN-BOUNDARY FRACTURE IN Ni_3Al ALLOYS DOPED WITH 0.2% BORON



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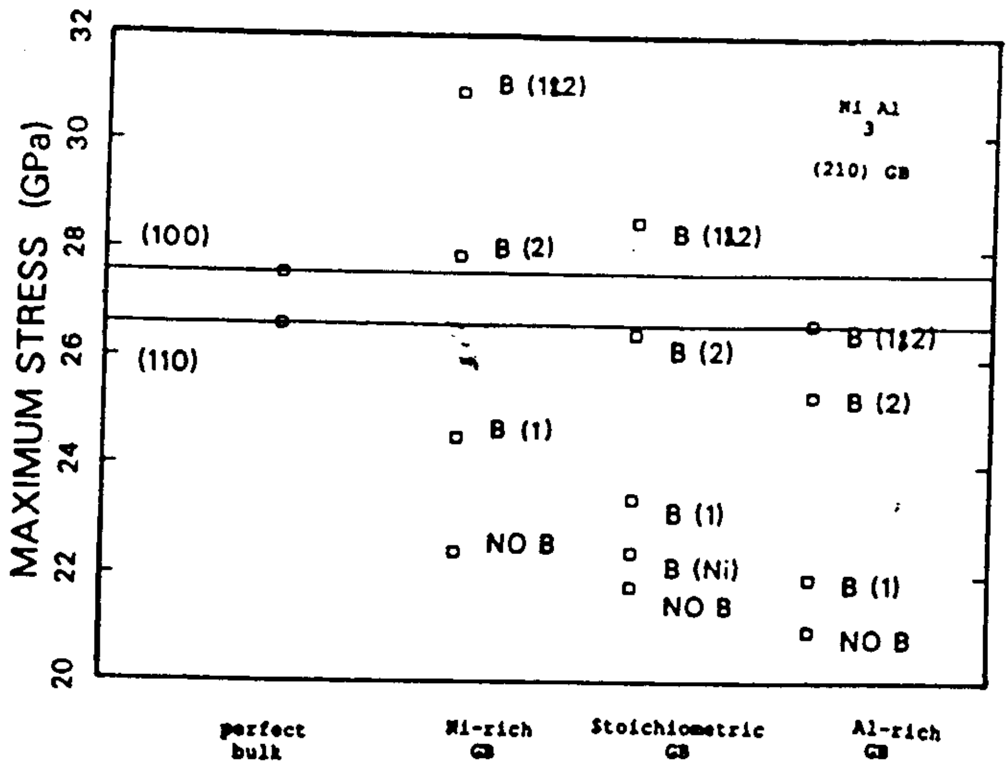
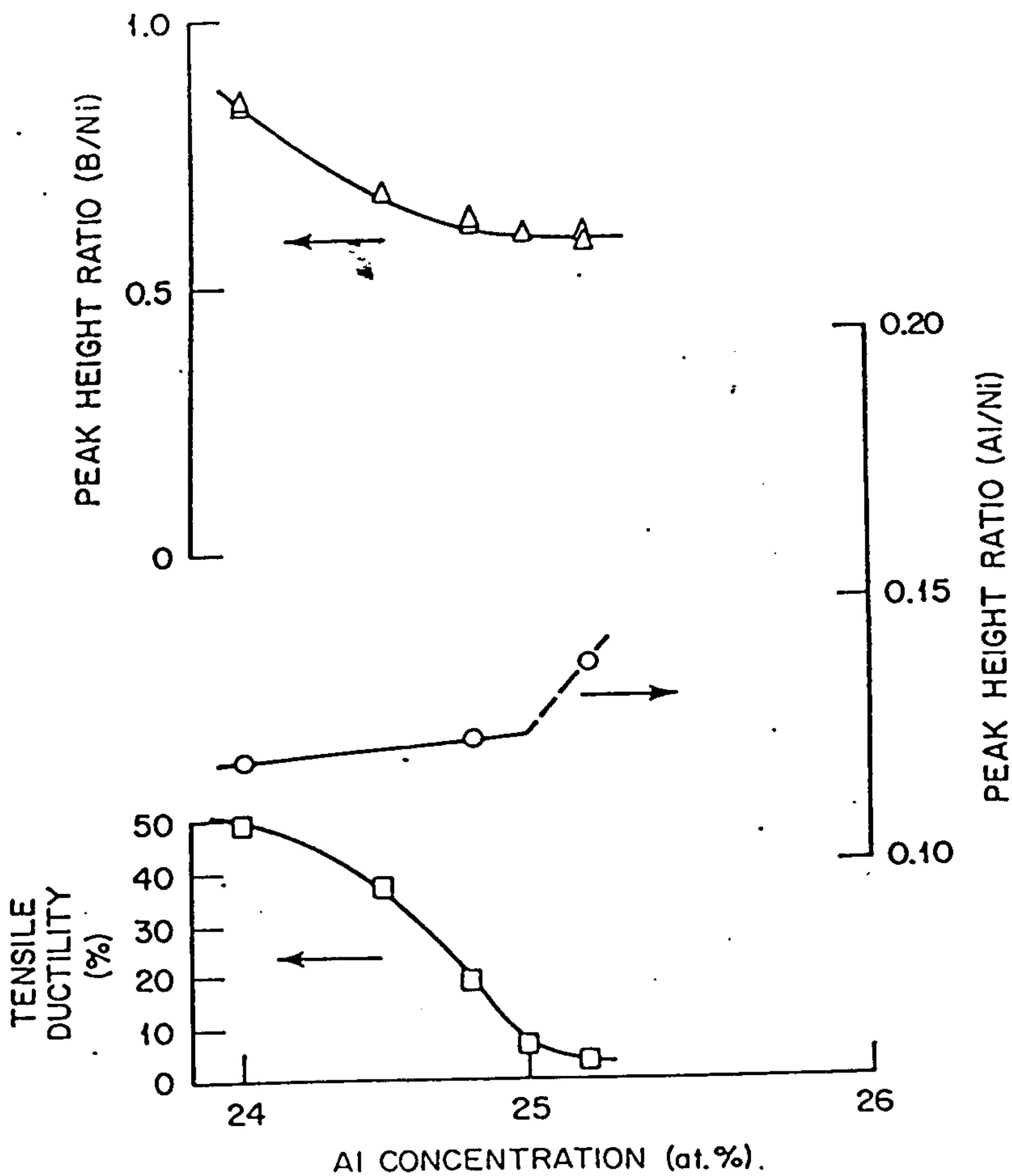
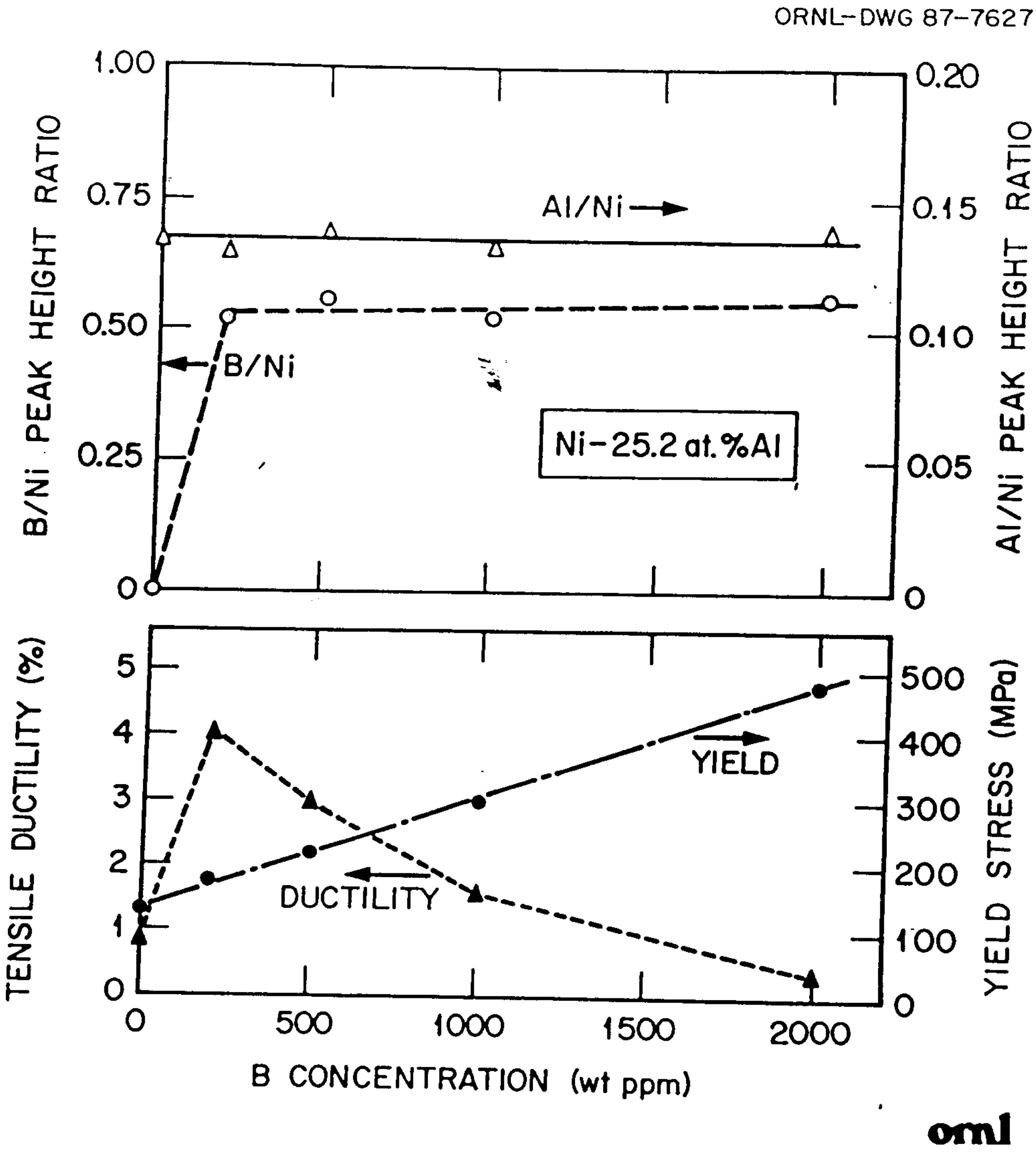
BORON INCREASES THE MAXIMUM STRESS REQUIRED TO SEPARATE (210) SYMMETRIC TILT BOUNDARY IN Ni_3Al



(S. P. CHEN ET AL., J. DE PHYSIQUE, 1988)

ORNL-DWG 87-11289




ORNL-DWG 87-7627
B/Ni PEAK HEIGHT RATIO
Al/Ni PEAK HEIGHT RATIO
1.00
0.75
0.50
0.25
0
0.20
0.15
0.10
0.05
0
Al/Ni
B/Ni
Ni-25.2 at.%Al
TENSILE DUCTILITY (%)
YIELD STRESS (MPa)
5
4
3
2
1
0
500
400
300
200
100
0
YIELD
DUCTILITY
0
500
1000
1500
2000
B CONCENTRATION (wt ppm)
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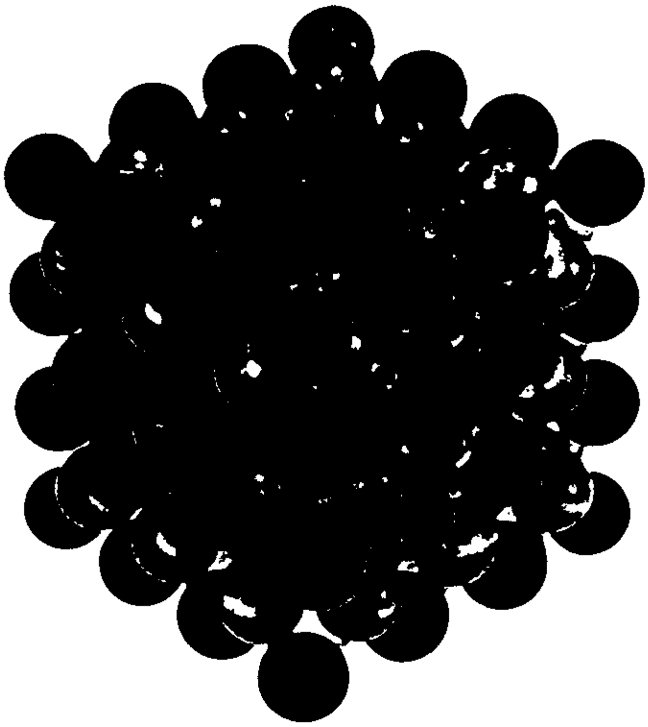
Major Causes of Intrinsic GB Brittleness

- High ordering energy
- Large difference in electronegativity/valency

CRYSTAL STRUCTURE OF $L1_2$ Ni_3X



• Ni
o X

ALLOY	T_C, CRITICAL ORDERING TEMPERATURE	FRACTURE MODE
Ni_3Fe	516°C	TRANSGRANULAR
Ni_3Mn	440°C	TRANSGRANULAR
Ni_3Al	1395°C	INTERGRANULAR
Ni_3Ga	1210°C	INTERGRANULAR
Ni_3Si	1035°C	INTERGRANULAR
Ni_3Ge	1132°C	INTERGRANULAR

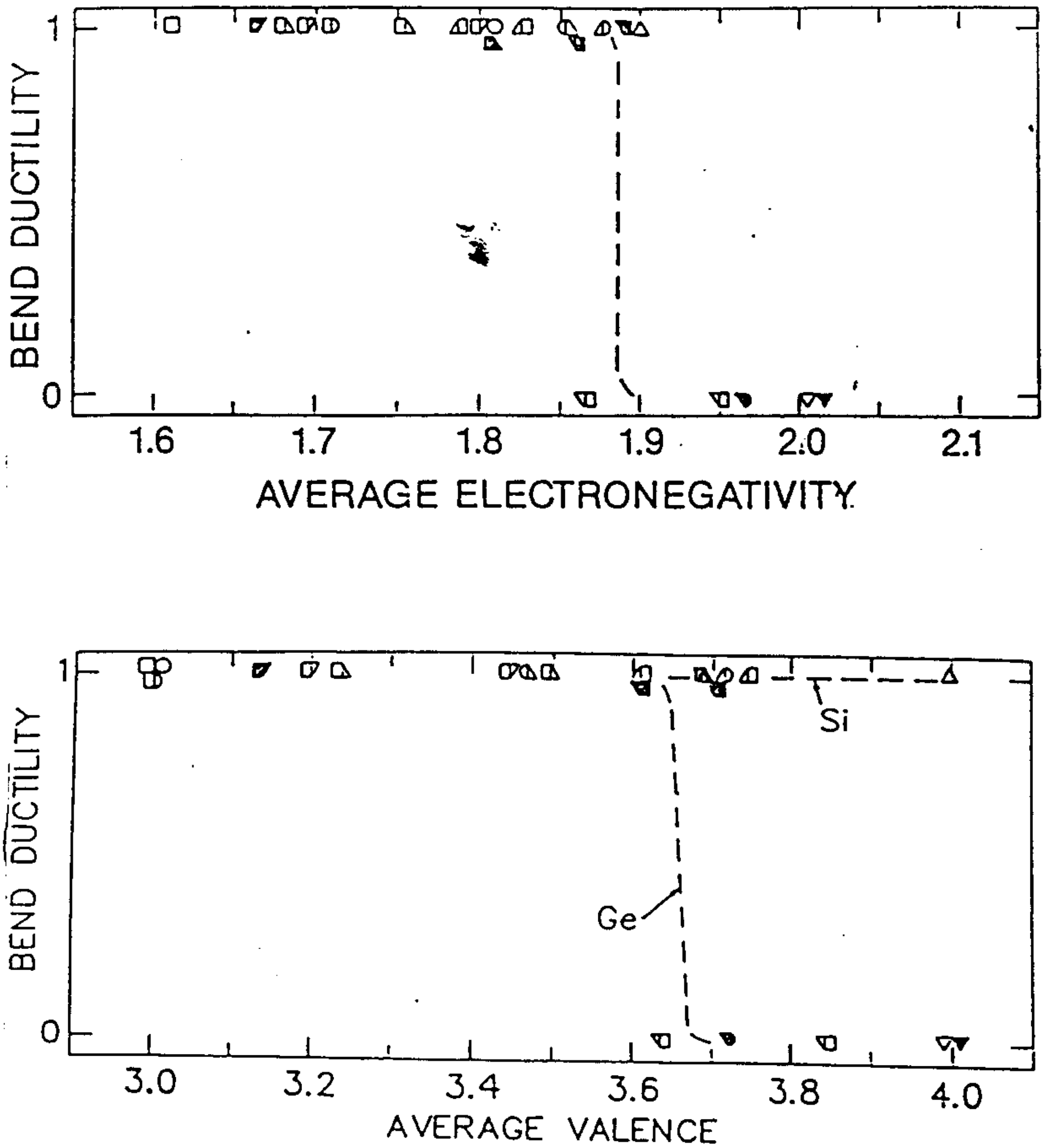
VALENCY-SIZE EFFECT-ELECTRONEGATIVITY CORRELATION WITH DUCTILITY IN THE $L1_2$ Ni_3X ALLOYS (TAUB AND BRIANT, 1987)

X SPECIES	VALENCY[a] DIFFERENCE (Δz)	LATTICE DILATION ($a-a_{Ni}/a_{Ni}$)	ELECTRONEGATIVITY DIFFERENCE (PAULING'S)	UNDOPED ALLOY	BORON-DOPED ALLOY
Fe	0.2	+1.0%		T	-
Mn	0.9	+2.2%	–0.36	T	-
Al	3.0	+1.5%	–0.30	I	T
Ga	3.0	+1.6%	–0.10	I	T
Si	4.0	–0.04%	–0.01	I	M
Ge	4.0	+1.5%	+0.10	I	I

[a]TAKASAGI AND IZUMI, ACTA METALL. 33, 1247 (1985).

T = TRANSGRANULAR, I = INTERGRANULAR, M = MIXED MODE.

THE AVERAGE ELETRONEGATIVITY APPEARS TO CONTROL THE BEND DUCTILITY OF B-DOPED Ni_3X ALLOYS (WHERE X = AL, GA, SI, AND/OR GE)



(Taub & Briant, 1987)

Grain-Boundary Engineering

- Control of GB chemistry
- Control of grain size and shape
- Control of GB character
- Control of deviations from alloy stoichiometry

Boron Completely Eliminates Environmental Embrittlement in $(Co,Fe)_3V$ Alloys.

Test environment	Elongation (%)	Strength (MPa)	
		Yield	Ultimate
	$(Co_{85}Fe_{15})_3V$ without B		
Air	6.3	342	642
Vacuum	18.8	353	1233
Oxygen	24.2	366	1429
	$(Co_{85}Fe_{15})_3V$ + 200 wt ppm B		
Water	35.3	259	1608
Air	33.8	235	1564
Vacuum	36.5	268	1586
Oxygen	33.9	259	1609

(Pike and Liu, 1992)

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Effect of alloying addition on RT ductility and fracture behavior of Ni3Al alloys*

Alloying element	Alloy composition (at. %)	Tensile ductility (%)	Fracture mode
	Ni_3Al (24% Al)	1 to 3	Intergranular
B	Ni-24 Al-0.5 B	35 to 54	Transgranular
B, Fe	Ni-20 Al-10 Fe-0.2 B	50	Transgranular
Mn	Ni-16 Al-9 Mn	16	Transgranular
Fe	Ni-10 Al-15 Fe	8	Mixed
Pd	Ni-23 Al-2 Pd	11	Intergranular
Pt	Ni-23 Al-2 Pt	5	Intergranular
Co	Ni-23 Al-2 Co	4	Intergranular
Cu	Ni-23 Al-2 Cu	6	Intergranular
Zr	Ni-22.65Al-0.26 Zr	13	Intergranular

*Prepared by conventional melting and casting.

Environmental Embrittlement Identified as the Major Cause of Low Ductility of Zr-Doped Ni3Al (Ni-22.65Al-0.26Zr, at. %)

Test environment	Elongation to Fracture (%)	Yield strength (MPa)	Ultimate tensile strength (MPa)
Water	8.7	322	528
Air	13.2	324	661
Oxygen	50.6	326	1451

Microstructure

Fracture Surface (Water)

Fracture Surface (Oxygen)

(George, Liu and Pope, 1992)

Boron Segregates to GBs and Eliminates Environmental Embrittlement in Ni_3Si Alloys

Alloy	Test environment	Tensile ductility (%)	Yield strength (ksi)	Fracture mode
Ni_3Si	Air	0	--	GBF
Ni_3Si	Vacuum	4.7	98.3	GBF
Ni_3Si	Oxygen	7.5	99.4	GBF
Ni_3Si+B	Air	7.0	88.6	GBF
Ni_3Si+B	Oxygen	6.6	85.6	GBF
Ni_3(Si,Ti)*	Air	7	88	GBF + TF
Ni_3(Si,Ti)*	Vacuum	29	85	TF
Ni_3(Si,Ti)+B*	Air	36	86	TF
Ni_3(Si,Ti)+B*	Vacuum	34	89	TF

*Ni-11% Si-9.5% Ti, Takasugi, Suenaga and Izumi, 1991.

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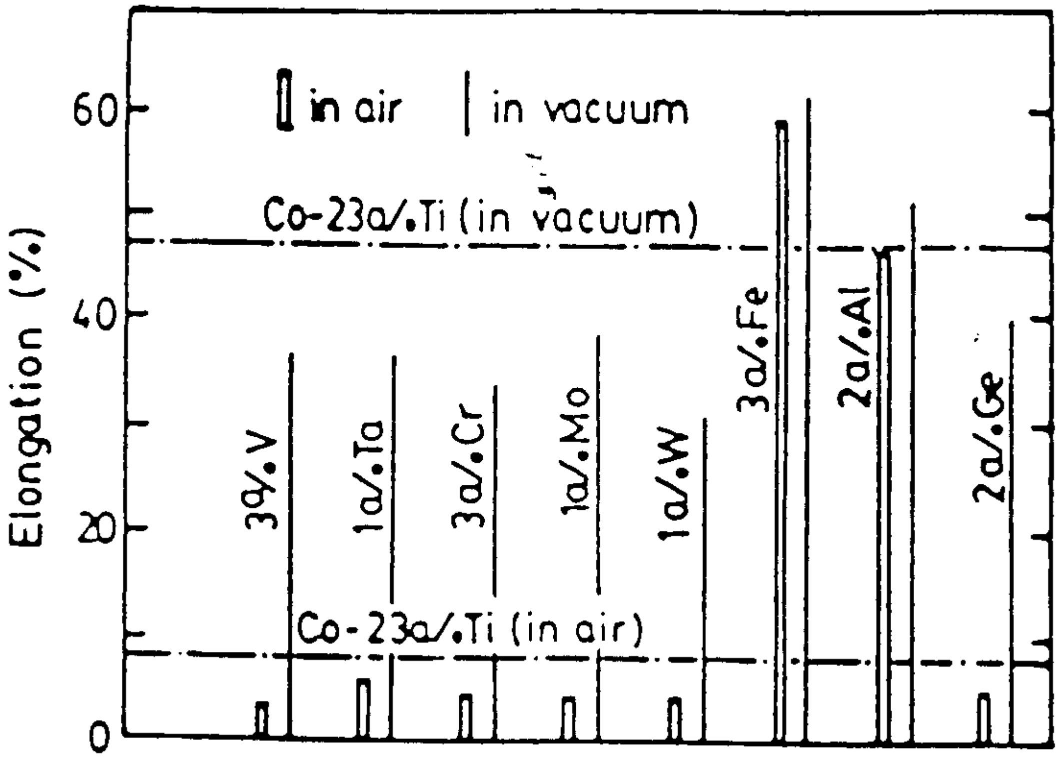
The Embrittlement in Co3Ti (23% Ti) Can be Completely Eliminated by Alloy Additions



- The Beneficial Effect of Fe Has Been Attributed to Creation of a More Homogeneous Electronic Distribution at Grain Boundaries in Co3Ti (Co-Ti Bond vs Co-Fe Bond)

(Izumi and Takasugi, 1988)

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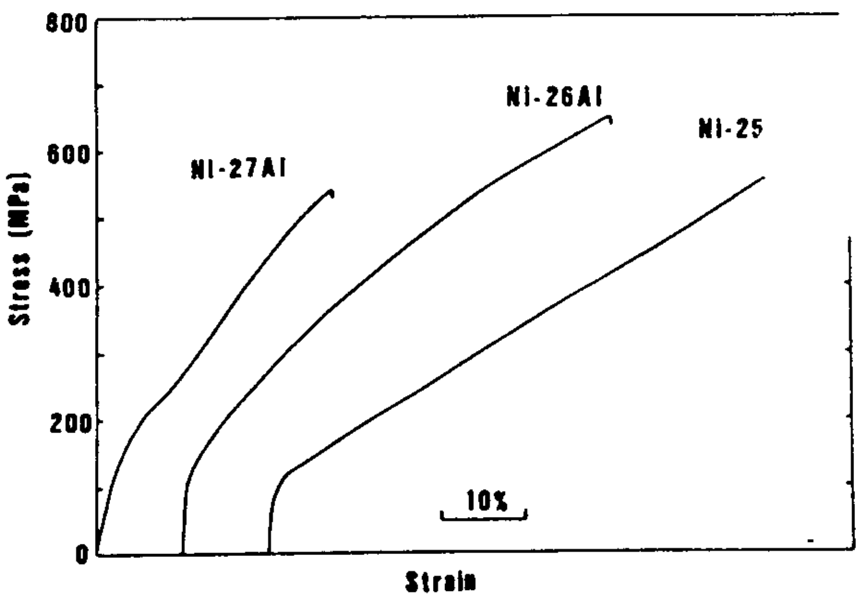
DS Ni_3Al Alloys Show Excellent Ductility at RT in Air



Stress-strain curves of the Ni_3Al grown by FZ-UDS at room temperature.

- Characterization of GB indicates that the majority of GBs in DS Ni_3Al alloys is of low angles

(Hirano et al., 1991).

Ductile Ni_3Al Alloys Developed for Structural Use

- Fabricable alloys (at. %)

IC-50: Ni-23%Al-0.5%Zr/Hf-0.1B

IC-218
IC-221: Ni-16.6±0.6%Al-8±1%Cr-0.6±0.5%Zr-0.1B

- Cast alloy (at. %)

IC-221M
IC-396M: Ni-16.0±0.5%Al-8±1%Cr-1.0±0.3Mo
-1.0±0.25%Zr-0.03B

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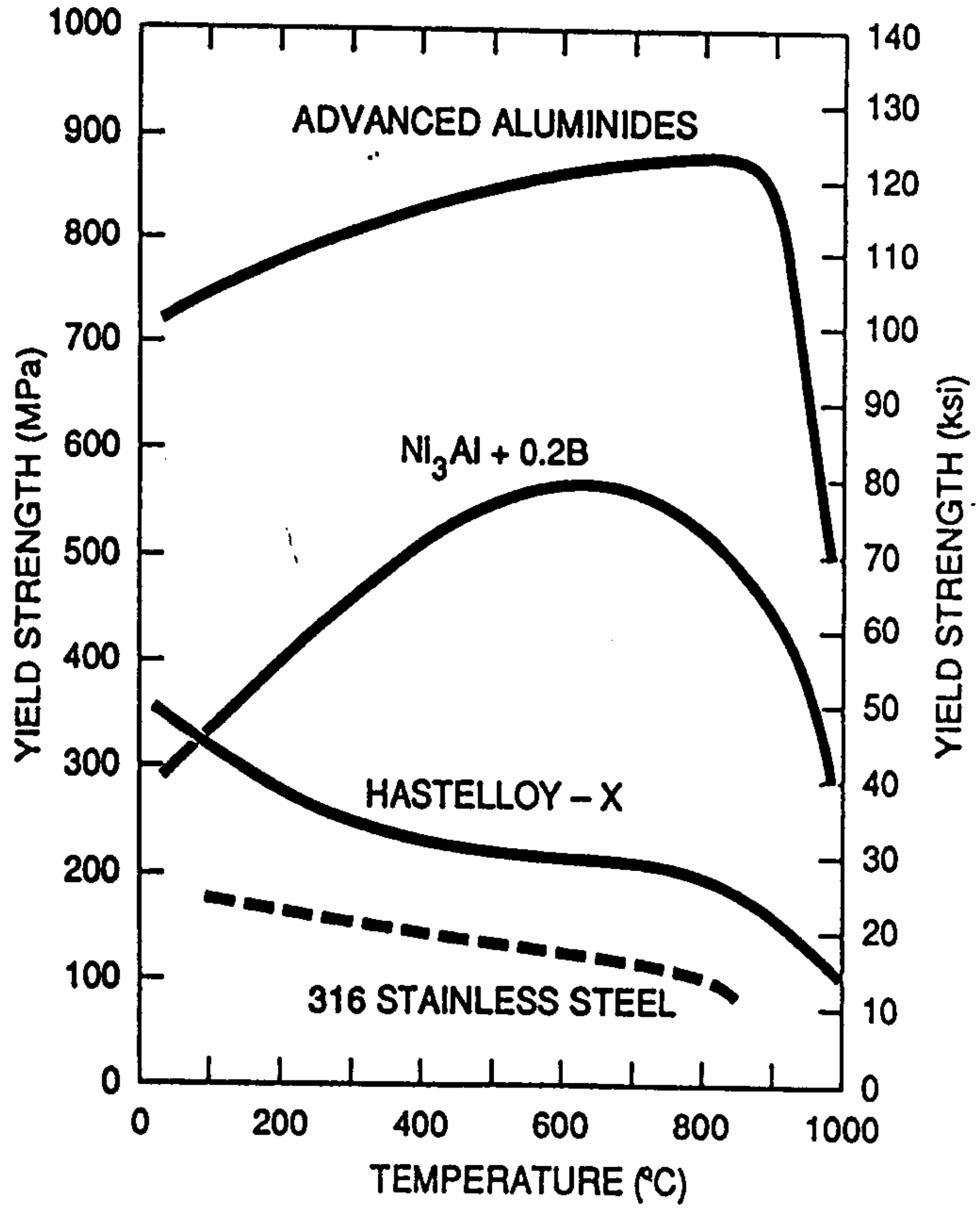
ORNL-DWG 88M-10236

Advanced Aluminide Alloys are much Stronger than Stainless Steels and Superalloys at High Temperatures



U. S. Industries are Very Interested in Nickel Aluminide Alloys Developed at ORNL

- License Agreements with U. S. Companies

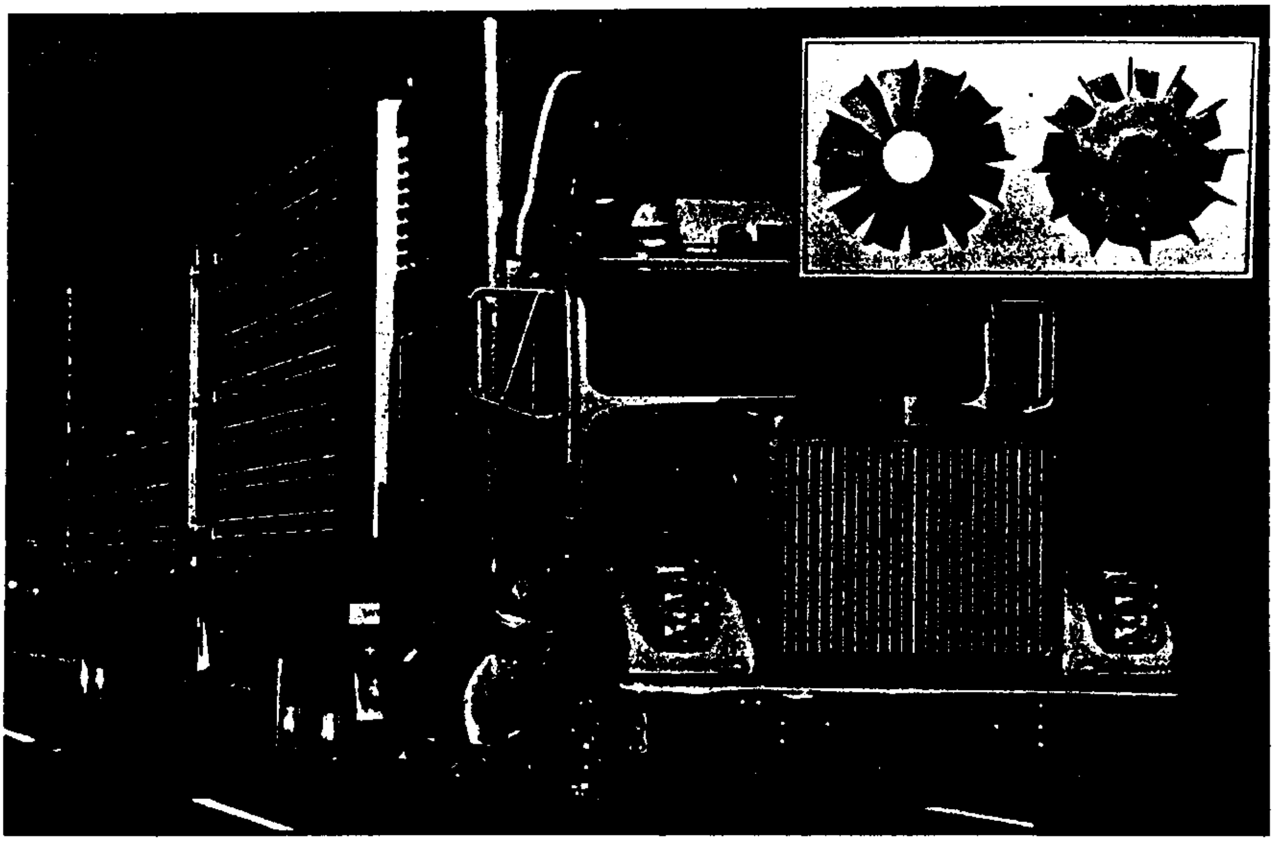
  Cummins Engine Company
  Armco Research and Technology
  Harrison Alloys
  Hoskins Manufacturing Company
  Ametek Specialty Metals Products Division
  Valley-Todeco, Inc.
  Metallamics

- Potential Applications

  TurboCharger
  High-Temperature Dies
  Permanent Molds
  Cutting Tools
  Aircraft Fasteners
  Heating Elements and Cutters
  Water Turbines

ornl

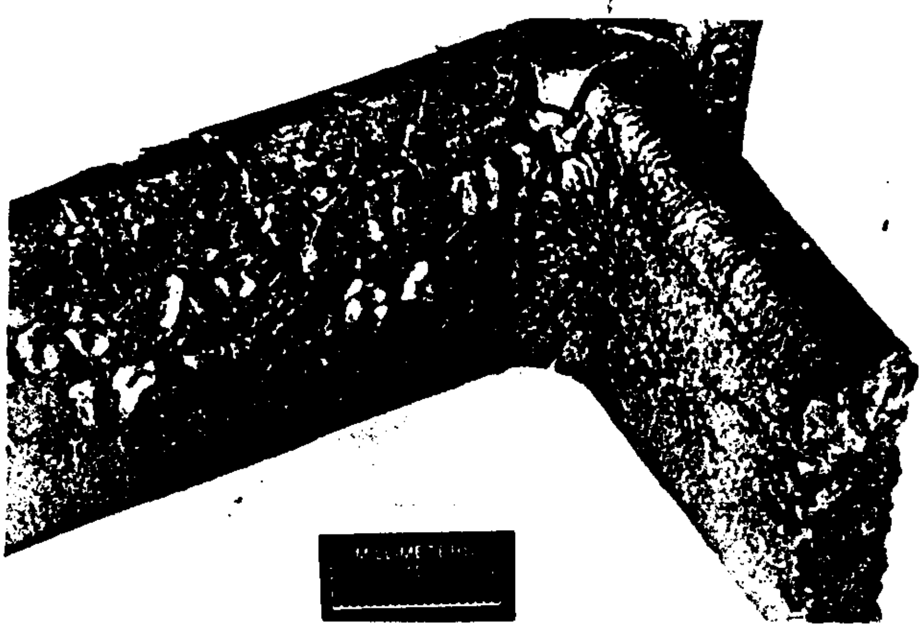
Cummins/PCC/ORNL are at the last stage of developing Ni_3Al alloy turbocharger rotors for diesel-engine applications



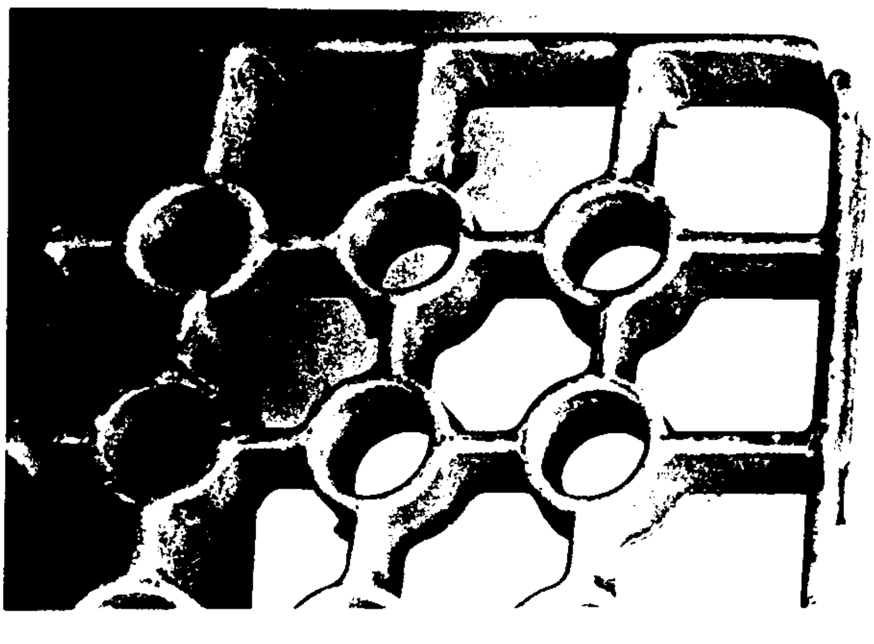
- Ni_3Al turbocharger rotors are successfully fabricated by investment casting
- The cast Ni_3Al alloy (IC-221M) has excellent fatigue properties at 650°C
  $Nf=2x10^4$ cycles for IN-713C; $Nf>4x10^6$ for IC-221M

GM and ORNL are jointly developing Ni_3Al alloy furnace fixtures for heat treating auto parts

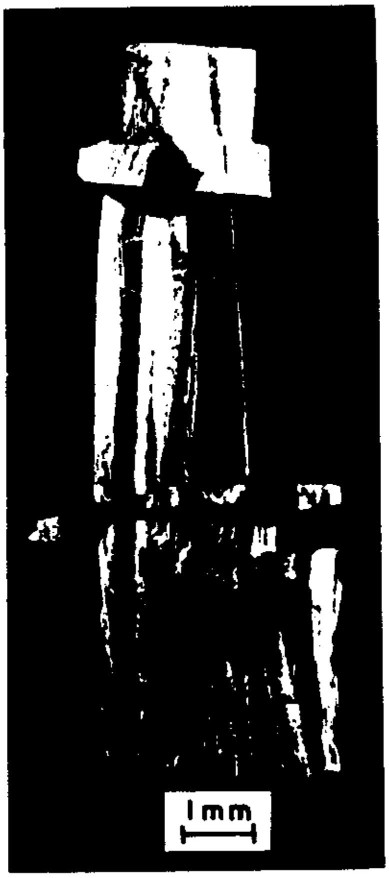
- Heat treatment capacity at Saginaw/GM = 6,000 T/day
- HU alloy furnace fixture cracked badly after 500 thermal cycles



- Ni_3Al alloy furnace fixture made by sand cast



DS Ni_3Al Alloys Have the Potential to be Used as Turbine-Blade Material



- Alloy composition: Ni-16.3Al-8.2Mo-0.24B, at. %
- The alloy shows excellent strength and creep resistance at temperatures above 1000°C

(Han et al., 1992)

Conclusions

- Many $L1_2$-ordered intermetallics show brittle grain-boundary fracture and low ductility at ambient temperatures

- Brittle GB fracture is caused by two major factors
  - Intrinsic factor: poor GB cohesion for strongly ordered intermetallics
  - Extrinsic factor: moisture-induced hydrogen embrittlement

- Boron additions are effective in reducing environmental embrittlement and/or enhancing GB cohesion

- The tensile ductility of $L1_2$ intermetallics can be improved by GB engineering via control of GB composition, grain geometry, GB character, and deviations from alloy stoichiometry