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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

ORDERED INTERMETALLICS AND NICKEL-BASE SUPERALLOYS
(Part I)

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ORDERED INTERMETALLICS AND NICKEL-BASE SUPERALLOYS

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OUTLINE

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 - (C) GENERAL MECHANICAL BEHAVIOR OF ORDERED INTERMETALLICS
 - (D) RECENT DEVELOPMENT IN DUCTILE ORDERED INTERMETALLIC ALLOYS
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 - (B) THE GIBB'S PHASE RULE AND PHASE DIAGRAM
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 - (D) COMPLEX NICKEL-BASE SUPERALLOYS: PHYSICAL METALLURGY AND ALLOY DESIGN
- III. INNOVATIVE MATERIALS SYNTHESIS
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 - (C) MECHANICAL ALLOYING
 - (D) DIRECTIONAL SOLIDIFIED EUTECTICS

THE STRUCTURE OF INTERMETALLIC PHASES

1. DEFINITION: AN INTERMETALLIC COMPOUND IS A PHASE WHICH CRYSTALLIZES WITH A STRUCTURE DIFFERENT FROM THOSE OF ITS COMPONENTS.
AB, AB₂, AB₃, AB₅, AB₇, A₃B₅ ...
2. ATOMIC BONDING: METALLIC, COVALENT, IONIC, OR COMBINATIONS AMONG THESE THREE.
3. THREE GROUPS OF INTERMETALLIC COMPOUNDS:
 - (A) ELECTROCHEMICAL COMPOUNDS (VALENCE COMPOUNDS)
 - (B) ELECTRON COMPOUNDS (HUME-ROTHERY PHASES)
 - (C) SIZE-FACTOR COMPOUNDS.

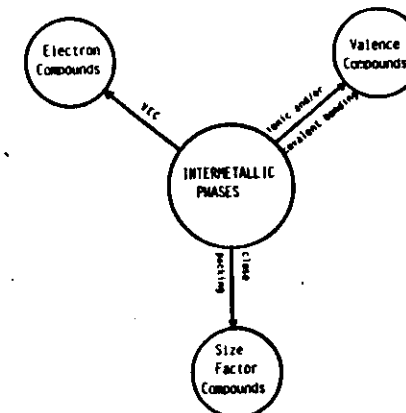


Fig. 4. Simple representation of the three main categories of intermetallic compounds.

ELECTROCHEMICAL COMPOUNDS (VALENCE COMPOUNDS)

- *THE COMPOUNDS ARE FORMED WHEN ONE ELEMENT IS STRONGLY ELECTROPOSITIVE AND THE OTHER IS STRONGLY ELECTRONEGATIVE.
- *ALL ATOMS IN THE COMPOUNDS EITHER ACCEPT OR PROVIDE VALENCE ELECTRONS TO OBTAIN A STABLE OCTET CONFIGURATION, I.E. ALL S&P ORBITALS ARE COMPLETELY FILLED OR COMPLETELY EMPTY.
 - ELECTRONS ARE DONATED TO ONE KIND OF ATOMS BY THE OTHER ONE: IONIC INTERACTION
 - ELECTRONS ARE SHARED BETWEEN THE ATOMS: COVALENT INTERACTION.

*EXAMPLES: Mg_3Sb_2 , Mg_2Si , ZrS , Zn_3P_2 .

*IN GENERAL, THE RANGE OF SOLUBILITY IN THEM IS SMALL.

Structure of intermetallic compounds

● = f.c.c. CN = 12
○ = hex. CN = 12
■ = b.c.c. CN = 8
● = O or ●
○, ● = deformed O, ●
- = special type

																Zintl-line											
																p1 IIIB	p2 IVB	p3 VB	p4 VIB	p5 VIIB	p6 VIIIB						
																B	C	N	O	F	Ne						
																-	3N4L	-	-	-	-						
1A	2A											3A	4A	5A	6A	7A	8A	9A	10A								
H	He											Li	Be	B	C	N	O	F	Ne								
Na	Mg	d1 IIIT	d2 IVT	d3 VT	d4 VIT	d5 VIIT	d6 VIIT	d7 IXT	d8 XT	d9 IB	d10 IIB	Al	Si	P	S	Cl	Ar										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr										
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe										
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn										
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf																
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	14												

Fig. 2. Structure of the elements. The modifications stable at room temperature are symbolized at the left side of each partition. (After LAVES [1956].)

ELECTRON COMPOUNDS (HUME-ROTHERY PHASES)

- *A LARGE NUMBER OF COMPOUNDS – ELECTRON COMPOUNDS – CRYSTALLIZES WITH THE SAME CRYSTAL STRUCTURE WHEN THEY POSSESS THE SAME AVERAGE NUMBER OF VALENCE ELECTRONS PER ATOM [VALENCE ELECTRON CONCENTRATION (VEC)].
- *METALLIC BONDS

Table 2
The valence electron concentration calculation scheme.

Element	Valence
Transition elements with nonfilled d-shells	0
Cu, Ag, Au (d-electrons)	1
Mg (s-electrons)	2
Zn, Cd, Hg (d-electrons)	2
Sn, Si, Ge (p-electrons)	4
Sb (p-electrons)	5

Table 3
Some representatives of Hume-Rothery phases.

	VEC = 3/2		VEC = 21/13	VEC = 7/4
Body-centred cubic structure	Complex cubic "β-manganese" structure	Close-packed hexagonal structure	"γ-brass" structure ^c	Close-packed hexagonal structure
CuBe	Cu ₃ Si	Cu ₃ Ga	Cu ₃ Zn ₂	CuZn ₃
CuZn	Ag ₃ Al	Cu ₃ Ge	Cu ₃ Cd ₂	CuCd ₃
Cu ₃ Al	Au ₃ Al	AgZn	Cu ₃ Hg ₂	Cu ₃ Sn
Cu ₃ Ga ^b	CoZn ₃	AgCd	Cu ₃ Al ₂	Cu ₃ Ge
Cu ₃ In ^a		Ag ₃ Al	Cu ₃ Ga ₂	Cu ₃ Si
Cu ₃ Si		Ag ₃ Ga	Cu ₃ In ₂	AgZn ₃
Cu ₃ Sn		Ag ₃ In	Cu ₃ Si ₂	AgCd ₃
AgMg		Ag ₃ Sn	Cu ₃ Sn ₂	Ag ₃ Sn
AgZn ^b		Ag ₃ Sb	Ag ₃ Zn ₂	Ag ₃ Al ₃
AgCd ^b		Au ₃ In	Ag ₃ Cd ₂	AuZn ₃
Ag ₃ Al ^b		Au ₃ Sn	Ag ₃ Il ₂	AuCd ₃
Ag ₃ In ^b			Ag ₃ In ₂	Au ₃ Sn
AuMg			Au ₃ Zn ₂	Au ₃ Al ₃
AuZn			Au ₃ Cd ₂	Cu ₃ Sb & Ag ₃ Sb ^d
AuCd			Au ₃ In ₂	
FeAl			Mn ₃ Zn ₂₁	
CoAl			Fe ₃ Zn ₂	
NiAl			Co ₃ Zn ₂₁	
NiIn			Ni ₃ Be ₂₁	
PdIn			Ni ₃ Zn ₂₁	
XTI ^c			Ni ₃ Cd ₂₁	
			Rh ₃ Zn ₂₁	
			Pd ₃ Zn ₂₁	
			Pt ₃ Be ₂₁	
			Pt ₃ Zn ₂₁	
			Na ₃₁ Ph ₂	

SIZE-FACTOR COMPOUNDS

- * SIZE-FACTOR COMPOUNDS ARE FORMED, IN WHICH ONE ATOM IS MUCH SMALLER THAN THE OTHER (E.G. 20-30%).
- * AN IMPORTANT GROUP OF THE COMPOUNDS ARE THE LAVES PHASES WITH AB_2 COMPOSITIONS. THE DIFFERENCE IN A AND B ATOMS BY ABOUT 22.5%.
- * LAVES PHASES: $MgCu_2$, $MgNi_2$, $MgZn_2$, $AgBe_2$, $TiFe_2$, ...
- * INTERSTITIAL PHASES: HYDRIDES, NITRIDES, CARBIDES, AND BORIDES OF TRANSITION METALS.
: SMALL NON-METALLIC ATOMS TAKE UP INTERSTITIAL POSITIONS BETWEEN THE METALLIC ATOMS.

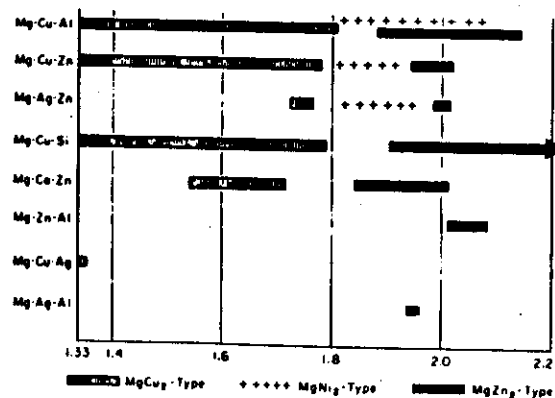


Fig. 22. The ranges of homogeneity in terms of electron concentration of several ternary magnesium alloys which possess the three typical Laves structures (from MASSALSKI (1956) after LAVES and WITTE (1936)).

J. H. WERNICK

TABLE 3

Some examples of laves phase intermetallic compounds.

MgCu ₂ structure-type	MgZn ₂ structure-type	MgNi ₂ structure-type
MgCu ₂	MgZn ₂	MgNi ₂
CuBe ₂	MnBe ₂	UPt ₂
CoAl ₂	CaMg ₂	U(Fe, Ni) ₂
UAl ₂	NbFe ₂	U(Mn, Ni) ₂
BiAu ₂	ZrCr ₂	CuMg ₂ Zn ₂
KBi ₂	ZrMn ₂	
NaAu ₂	HfMn ₂	
CeCo ₂	TiMn ₂	
UMn ₂	UNi ₂	
HfCo ₂	KNa ₂	
ZrCr ₂	CoCrTa	
TaCr ₂	CoTaTi	
TiCr ₂		
ZrCo ₂		
CdCuZn		
CuTaV		
MgNiZn		

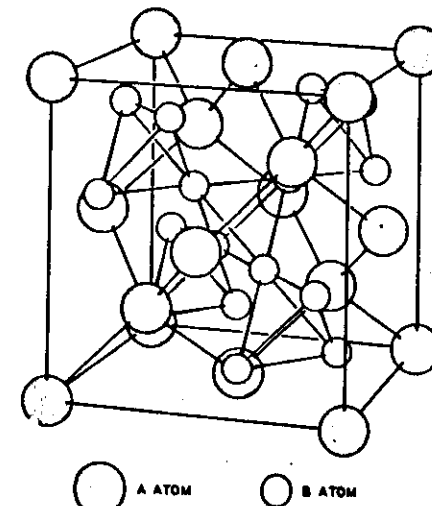


Fig. 4. The $MgCu_2$ structure (AB_2).

STRUCTURAL FEATURES OF ORDERED INTERMETALLICS

- * LONG-RANGE ORDERED CRYSTAL STRUCTURES.
- * ANTIPHASE BOUNDARIES (APB) AND DOMAIN STRUCTURES.
- * SUPERLATTICE DISLOCATIONS.

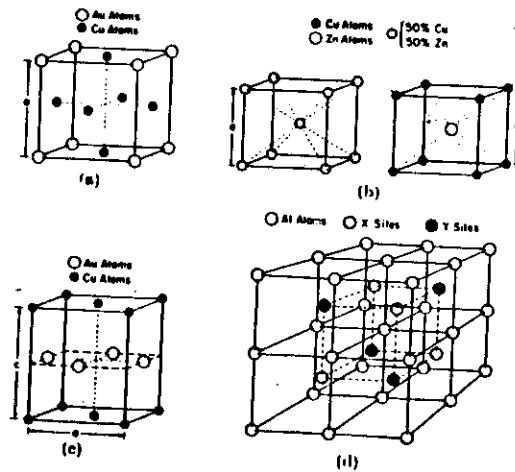
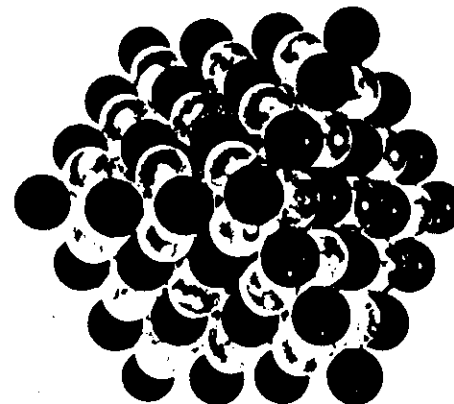
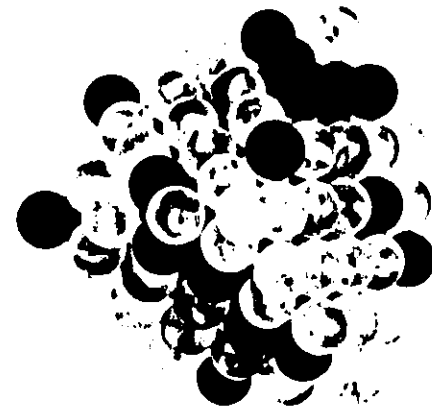


Fig. 14. Various types of ordered superlattices: (a) ordered cubic superlattice Cu_3Au ; (b) disordered and ordered structures of β brass; (c) the tetragonal superlattice of AuCu ; (d) the structure of Fe_3Al and FeAl . Al atoms fill the X sites in Fe_3Al and the X and Y sites in FeAl .

LONG-RANGE ORDERED (LRO) ALLOYS AND INTERMETALLIC COMPOUNDS
(IC) ARE DIFFERENT FROM 'CONVENTIONAL' ALLOYS IN ATOMIC ARRANGEMENT

CONVENTIONAL ALLOYS

LRO AND IC



DISORDERED CRYSTAL
STRUCTURE

ORDERED CRYSTAL
STRUCTURE

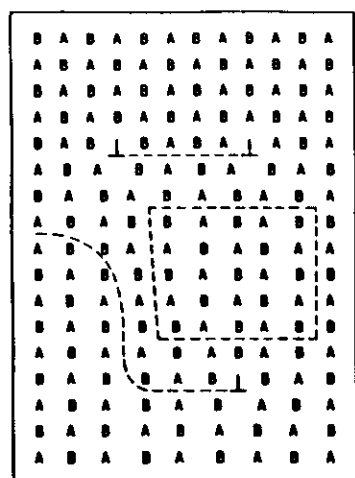


Fig. 4. Schematic representation of a superlattice dislocation in an ideal simple cubic lattice, along with two thermally produced antiphase boundaries, one of which terminates on an ordinary dislocation (from Marcinkowski⁽¹⁰⁾).

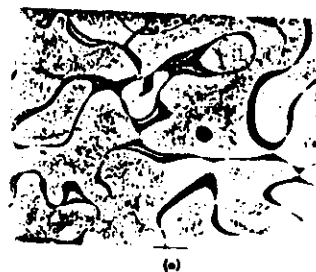
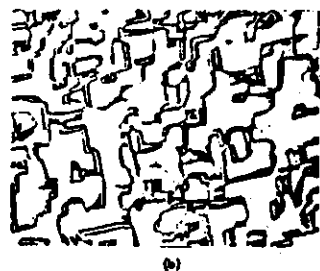
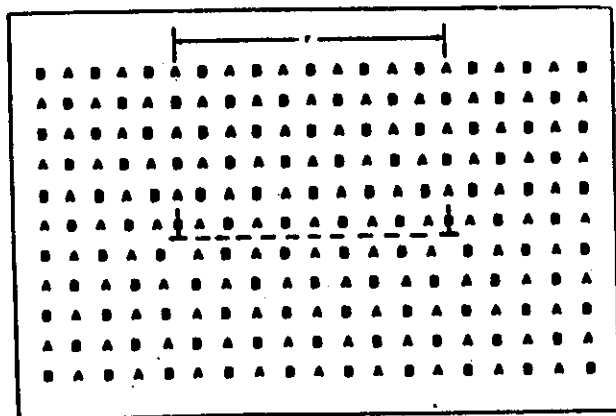


Fig. 5. Thermally produced antiphase boundaries in (a) Fe₃Al-L2₁ Schmatz⁽¹⁰⁰⁾, (b) Cu₃Au-L1₂ structure (from Kear⁽¹⁰⁾), (c) Mg₂Cd-DO₁₉ Blackburn⁽¹⁰¹⁾.



GENERAL MECHANICAL BEHAVIOR OF ORDERED INTERMETALLICS

I. GOOD HIGH-TEMPERATURE PROPERTIES.

(1) GOOD CREEP RESISTANCE DUE TO SLOW DIFFUSION IN ORDERED LATTICES.

(2) GOOD HIGH-TEMPERATURE STRENGTH: INCREASE IN YIELD STRENGTH WITH INCREASING TEMPERATURE (ANOMALOUS TEMPERATURE DEPENDENCE OF YIELD STRENGTH).

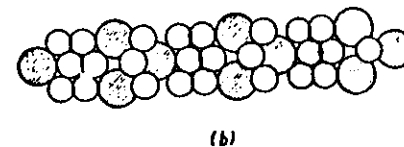
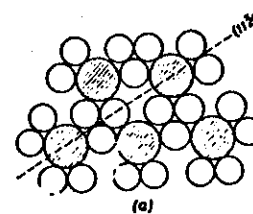
II. LOW DUCTILITY AND BRITTLE FRACTURE.

(A) LACK OF SUFFICIENT DEFORMATION MODES.

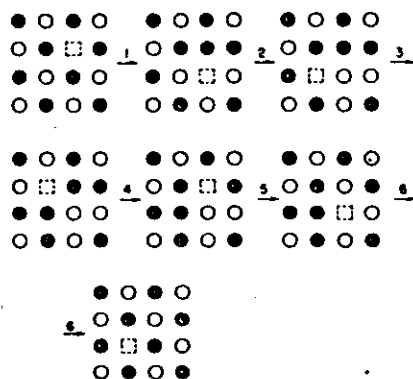
(B) BRITTLE GRAIN BOUNDARIES.

(C) LOW MOBILITY OF DISLOCATIONS.

(D) HIGH LOCALIZED STRESS CONCENTRATION: PLANAR SLIP.

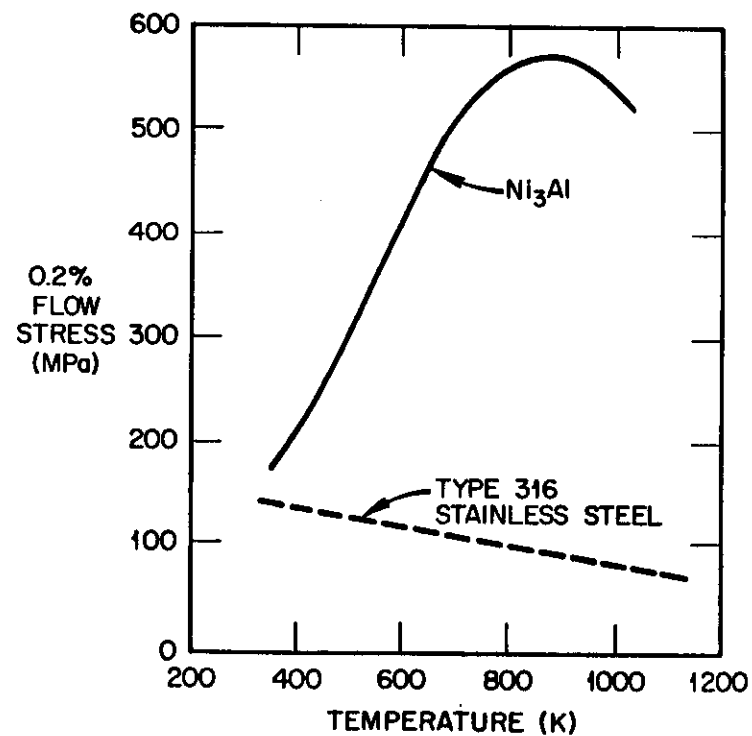


VACANCIES IN ORDERED LATTICE ARE "TRAPPED"
IN THEIR ORIGINAL SITES



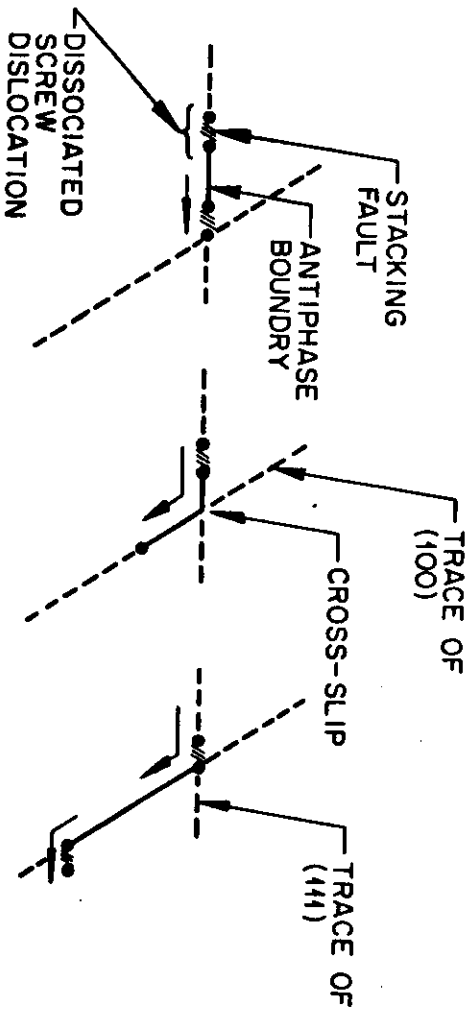
ORNL-DWG 82-9862

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.

RECENT DEVELOPMENT IN ORDERED INTERMETALLIC ALLOYS



Cross-slip of a Superlattice Dislocation from the
(111) Slip Plane Into (100) (from Kear)

Y 138773

ORNL-DWG 80-8994R

ORDERED INTERMETALLICS BASED ON ALUMINIDES AND SILICIDES OFFER
POTENTIAL ADVANTAGES FOR HIGH-TEMPERATURE STRUCTURAL USE

- GOOD HIGH-TEMPERATURE STRENGTH
- SLOW KINETIC PROCESSES
- RESISTANCE TO OXIDATION AND CORROSION
- HIGH MELTING POINT
- LOW MATERIAL DENSITY

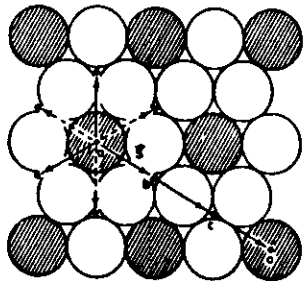
MOST ORDERED INTERMETALLICS EXHIBIT
BRITTLE FRACTURE AND LOW DUCTILITY

- THE BRITTLENESS IS PRIMARILY CAUSED BY
 - LACK OF SUFFICIENT DEFORMATION MODES
 - GRAIN BOUNDARY WEAKNESS
 - LOW MOBILITY OF SUPERLATTICE DISLOCATIONS
 - DIFFICULTY IN CROSS SLIP (PLANAR SLIP)
- THE BRITTLENESS HAD LIMITED THE USE OF
INTERMETALLICS AS ENGINEERING MATERIALS

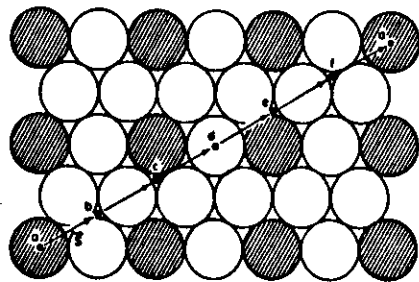
DESIGN OF DUCTILE ORDERED INTERMETALLIC THROUGH CONTROL OF ORDERED CRYSTAL STRUCTURE IN AB_3 ALLOY SYSTEMS

1. STRUCTURAL FEATURES OF AB_3 ORDERED PHASES

- IN RECENT YEARS CLOSE-PACKED ORDERED STRUCTURES WITH AB_3 COMPOSITION HAVE BEEN OBSERVED IN MANY BINARY AND PSEUDOBINARY ALLOY SYSTEMS.
- ALL THESE STRUCTURES ARE BUILT UP FROM CLOSE-PACKED ORDERED AB_3 LAYERS BUT DIFFER IN STACKING SEQUENCE.
- TWO BASIC STRUCTURES OF ORDERED LAYERS.



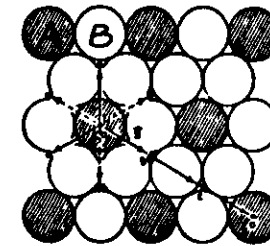
a.
 $AuCu_3$ -type "T-mesh" with
"triangular ordering"



b.
 $TiAl_3$ -type "R mesh" with
"rectangular ordering"

II. CHARACTERIZATION OF CLOSE-PACKED ORDERED CRYSTAL STRUCTURES IN AB_3 ALLOY SYSTEM

1. Basic Structure - Close-packed ordered layer



2. Ordered Crystal Structure

	<u>Stacking Sequence</u>	<u>Hexagonality</u>
Simple Hexagonal Ordered Structure	abababab...(hhh...)	100%
Simple Cubic Ordered Structure	abcabcabc...(ccc...)	0%
Transition Ordered Structure	abcbacab...(hchhchhch...)	66.7%

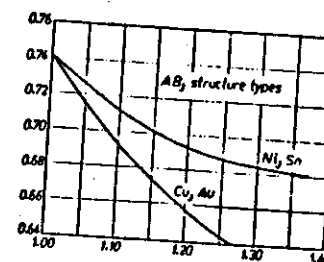
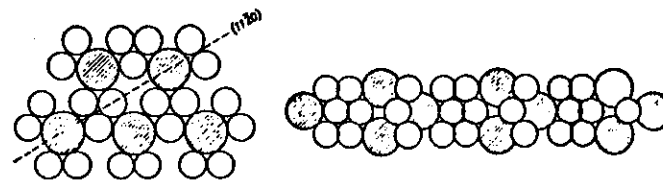
III. FACTORS CONTROLLING THE RELATIVE STABILITY OF THE VARIOUS ORDERED STRUCTURE



1. ATOMIC SIZE EFFECT (VAN VUCHT'S RULE)

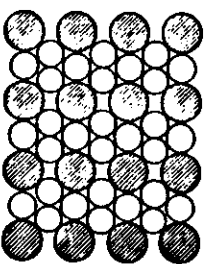
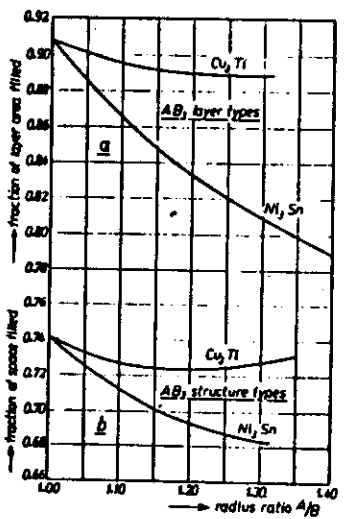
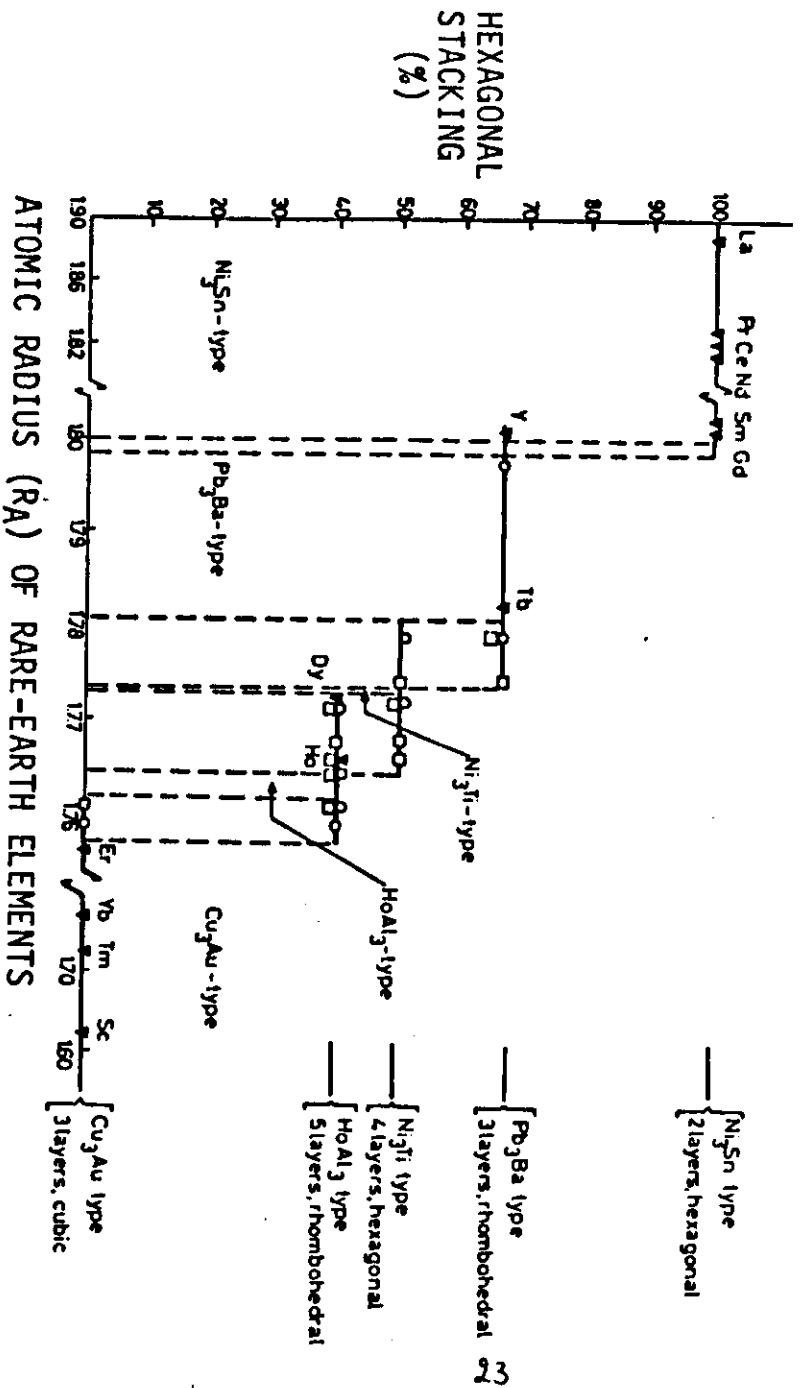
- AS R_A/R_B INCREASES IN AB_3 ALLOYS, THE STACKING SEQUENCE CHANGES FROM PURELY CUBIC THROUGH DIFFERENT ORDERED MIXTURE OF CUBIC TO HEXAGONAL LAYERS TO PURELY HEXAGONAL

- CLUSTERING OF SMALLER ATOMS IN THE LAYER LOWERS THE SYMMETRY OF SPACE GROUP FROM CUBIC TO HEXAGONAL, BUT ADMITS A BETTER PACKING WHEN THE LARGER A ATOMS OF BOTH ADJOINING LAYERS PROFIT FROM THE OPEN SPACES.



PCT OF HEXAGONAL STACKING DECREASES WITH THE DECREASE IN THE ATOMIC SIZE OF RARE-EARTH ELEMENTS (R_A) IN TRIALUMINIDES

▼ RAl_3 ; ○ (V,Er) Al_3 ; □ (Gd,Er) Al_3 ;



Cu_3Ti type layer

Fig. 3. Schematic drawing of a Cu_3Ti -type layer. Note the tendency for the larger atoms to approach each other.

Fig. 4. (a) The maximum packing density (two dimensional) as a function of radius ratio, calculated for layers of the Ni_3Sn and Cu_3Ti types. (b) Three-dimensional maximum packing density as a function of radius ratio, calculated for the Ni_3Sn and Cu_3Ti types.

AB_3

$A(B,C)_3$

2. ELECTRON CONCENTRATION EFFECT (PAUL BECK'S RULE)

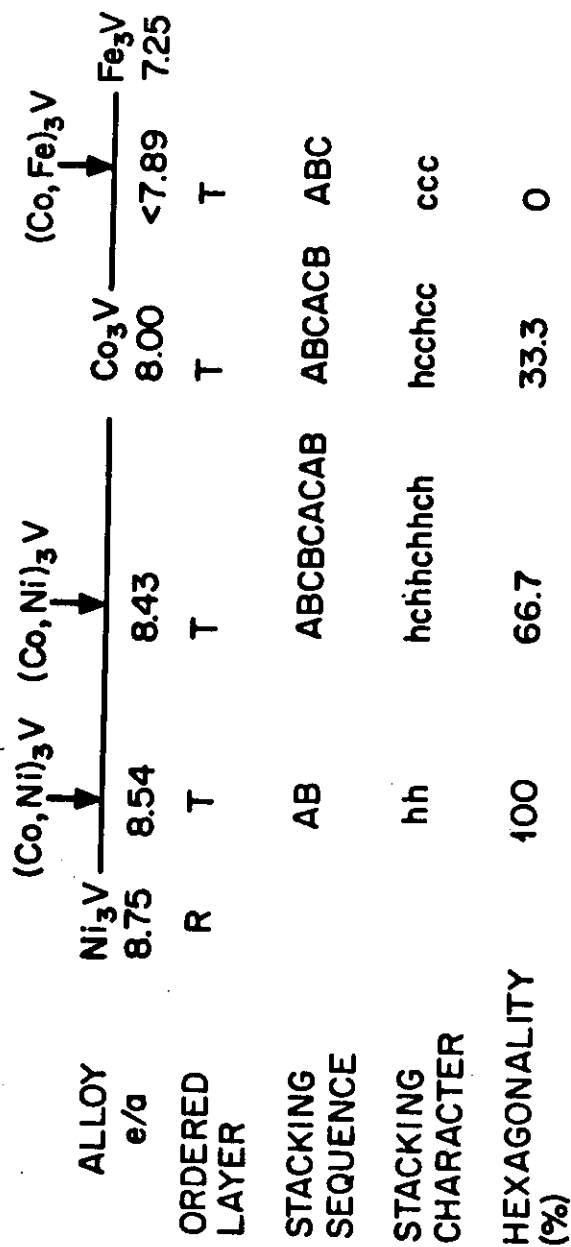
- ELECTRON CONCENTRATION INFLUENCE ON STRUCTURE HAS BEEN ATTRIBUTED TO THE FILLING OF BRILLOUIN ZONES.

- e/a IS DEFINED AS NUMBER OF ELECTRONS OUTSIDE THE INERT GAS SHELLS.

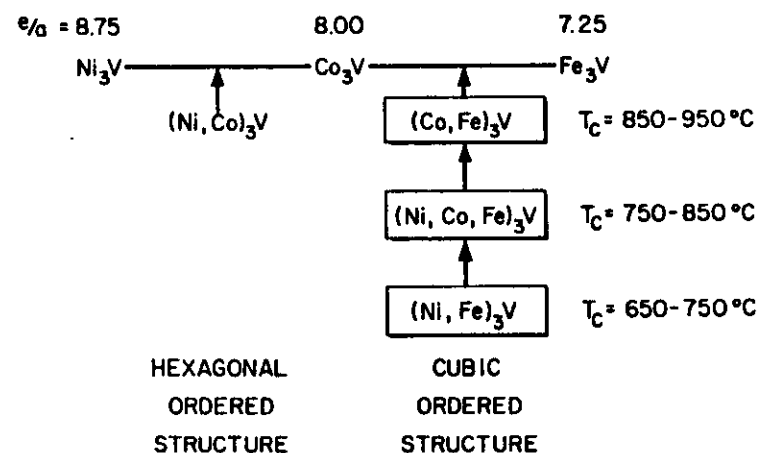
ELEMENT V	e/a 5
Mn	7
Fe	8
Co	9
Ni	10

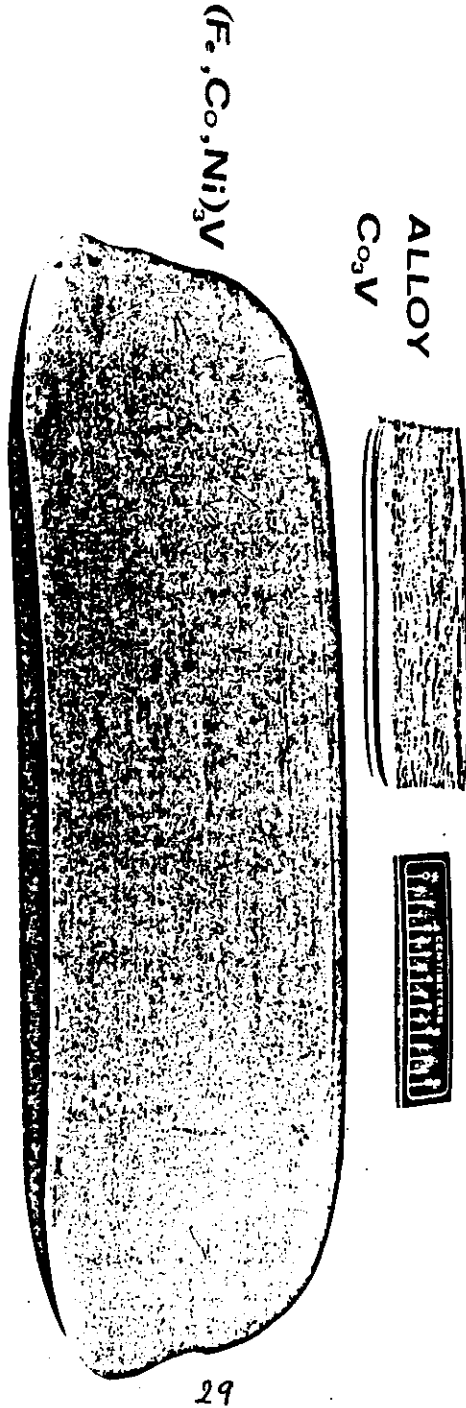
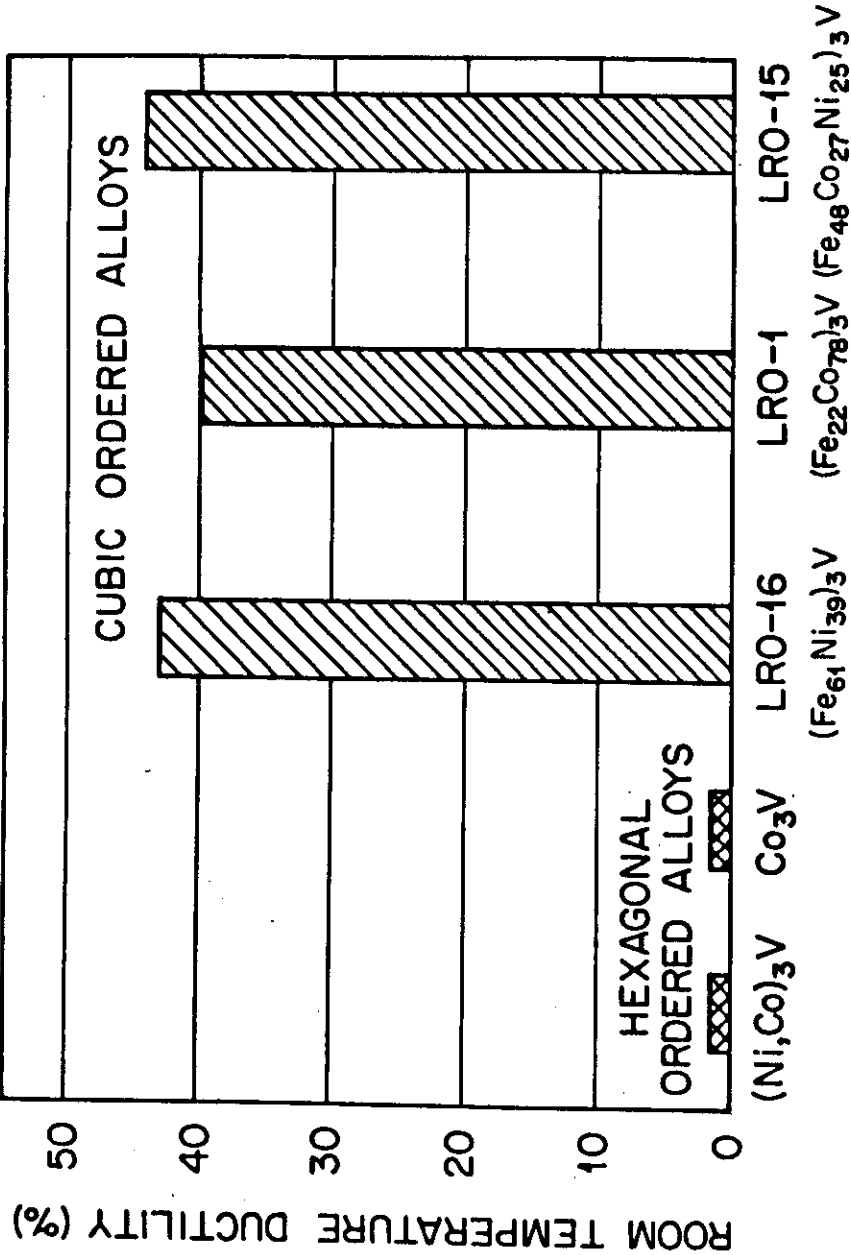
- AS e/a DECREASES, THE STACKING SEQUENCE CHANGES FROM PURE HEXAGONAL THROUGH DIFFERENT ORDERED MIXTURE OF HEXAGONAL TO CUBIC LAYERS TO PURELY CUBIC.

	VNi_3	VCo_3	VFe_3
STRUCTURE	ORDERED TETRAGONAL	ORDERED HEXAGONAL	DISORDERED bcc
ORDERED LAYER	R-TYPE	T-TYPE	
e/a	8.75	8.00	7.25

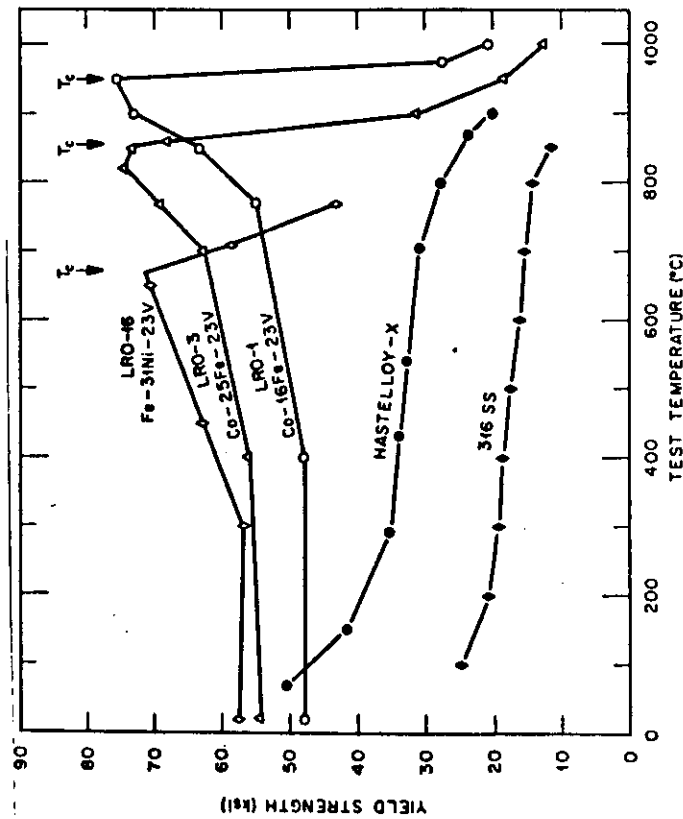


WE HAVE DEVELOPED DUCTILE LRO ALLOYS
IN THE $(\text{Ni, Co, Fe})_3\text{V}$ ALLOY SYSTEM THROUGH
CONTROL OF ELECTRON DENSITY AND ORDERED STRUCTURE

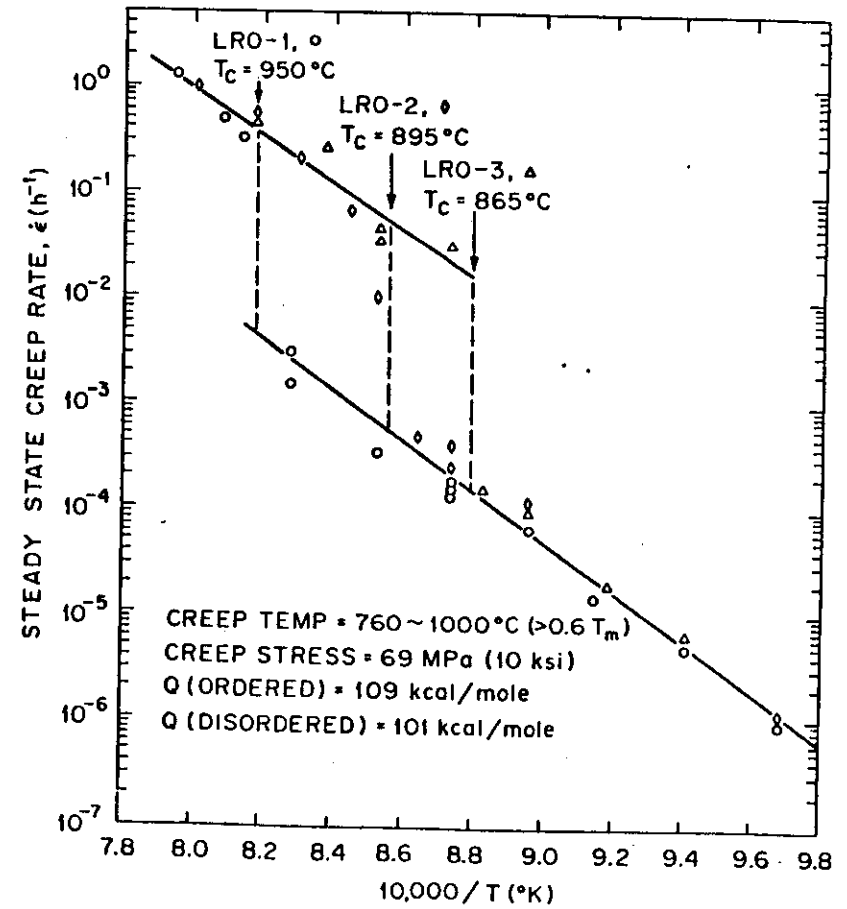




LRO ALLOYS SHOW UNUSUAL MECHANICAL PROPERTIES-THEIR STRENGTH
INCREASES RATHER THAN DECREASES WITH TEST TEMPERATURE

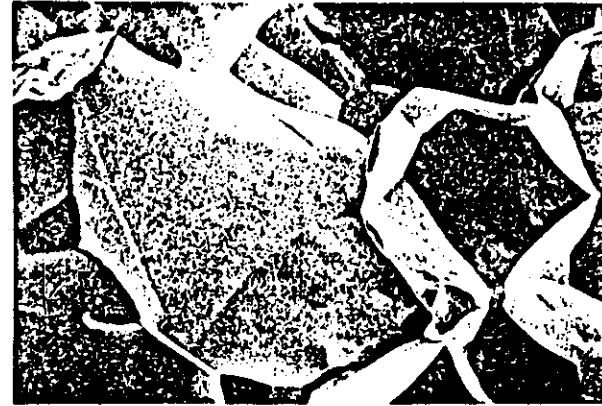


LRO ALLOYS SHOW A DISCONTINUOUS CHANGE IN CREEP RATE ($\dot{\epsilon}$) AROUND
FORMATION OF LRO LOWERS $\dot{\epsilon}$ BY 2 ORDERS OF MAGNITUDE

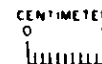
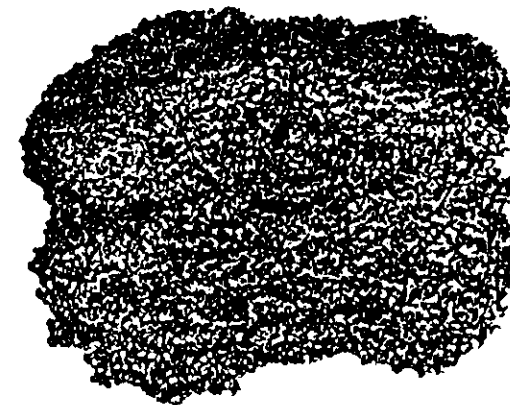


**POLYCRYSTALLINE Ni_3Al SHOWS POOR DUCTILITY
AND BRITTLE GRAIN-BOUNDARY FRACTURE**

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



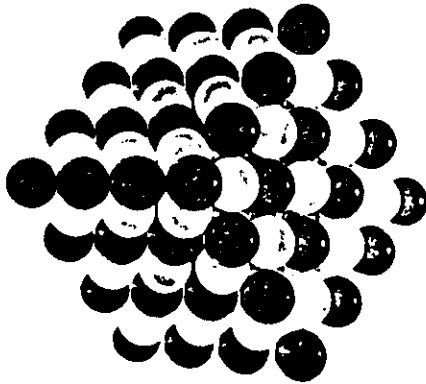
BRITTLE GRAIN BOUNDARY FRACTURE AT ROOM TEMPERATURE



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

GENERAL PROPERTIES OF Ni_3Al

- L1_2 ORDERED CRYSTAL STRUCTURE



○ : Ni ATOMS ● : Al ATOMS

- INCREASE IN YIELD STRESS WITH INCREASING TEMPERATURE
- EXCELLENT OXIDATION RESISTANCE
- SINGLE CRYSTALS OF Ni_3Al ARE DUCTILE
- POLYCRYSTALLINE Ni_3Al IS EXTREMELY BRITTLE

THE GRAIN-BOUNDARY FRACTURE IN Ni_3X CAN BE CORRELATED
WITH THE DIFFERENCE IN VALENCY, ELECTRONEGATIVITY
AND ATOM SIZE BETWEEN Ni AND X ATOMS

ALLOY	VALENCY(A) DIFFERENCE	ELECTRONEGATIVITY(B) DIFFERENCE	SIZE(C) RATIO	FRACTURE BEHAVIOR(D)	
	(ΔZ)	(PAULING'S)	$\frac{r_{Ni-X}}{r_{Ni-Ni}}$	UNDOPED	B-DOPED
Ni_3Fe	0.2		1.02	D	-
Ni_3Mn	0.9	-0.36	1.01	D	-
Ni_3Al	3.0	-0.30	1.135	B	D
Ni_3Ga	3.0	-0.10	1.083	B	D
Ni_3Si	4.0	-0.01	1.089	B	D
Ni_3Ge	4.0	+0.10	1.132	B	B

(A) TAKASUGI ET AL.

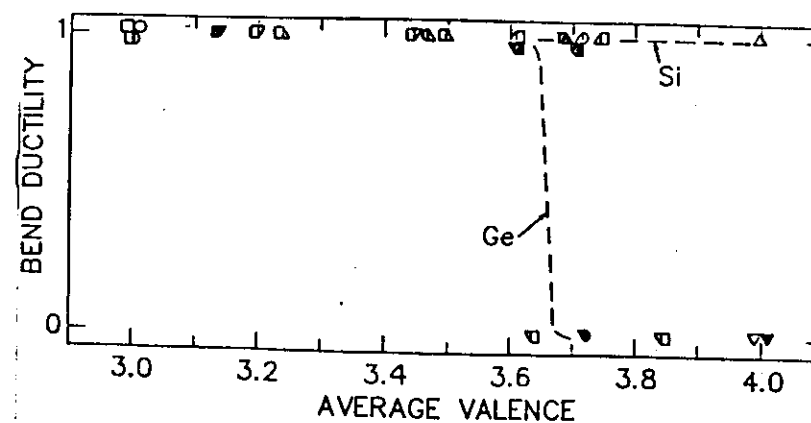
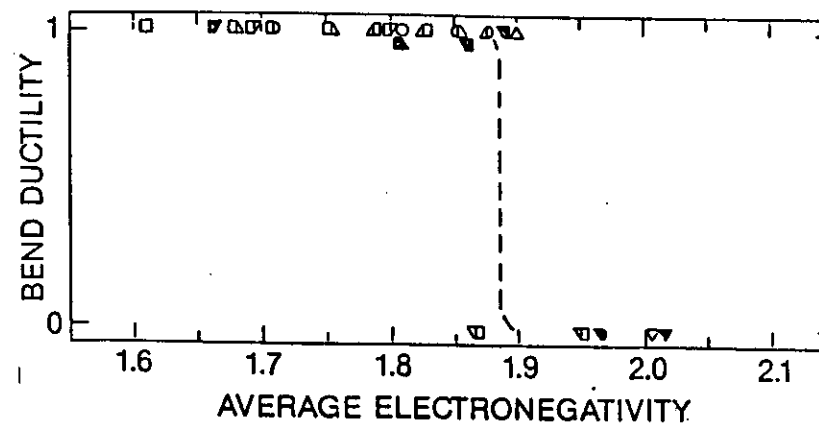
(B) TAUB ET AL.

(C) FARKAS ET AL.

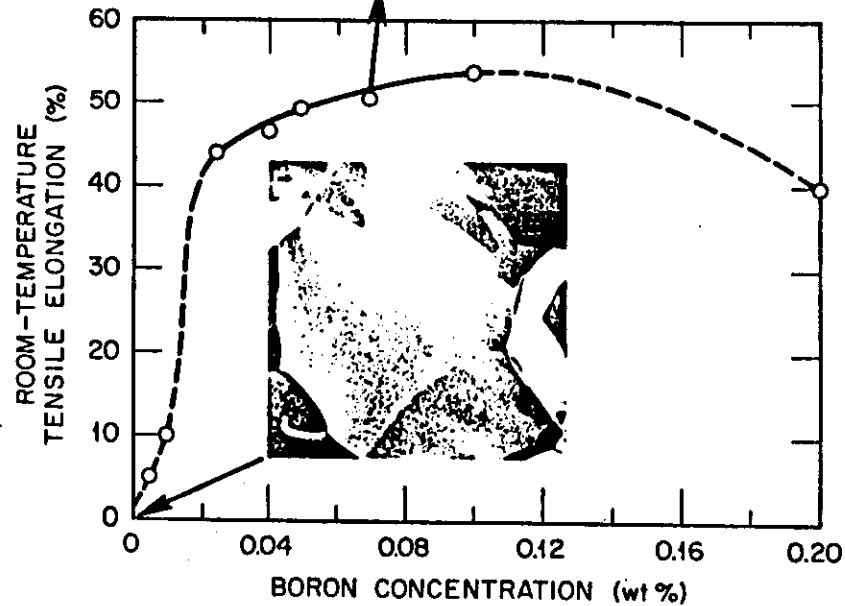
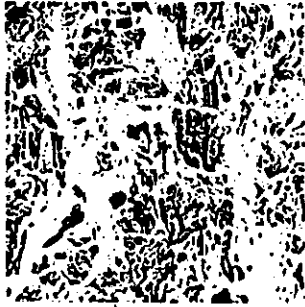
(D) TAUB ET AL.

D = DUCTILE, B = BRITTLE

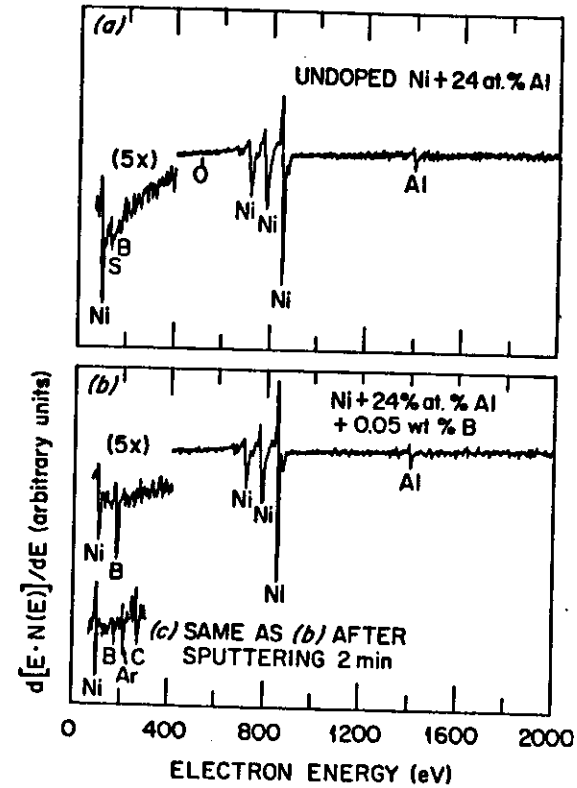
THE AVERAGE ELECTRONEGATIVITY APPEARS TO CONTROL THE BEND DUCTILITY
OF B-DOPED Ni_3X ALLOYS (WHERE $X = Al, Ga, Si, \text{ AND/OR } Ge$)



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

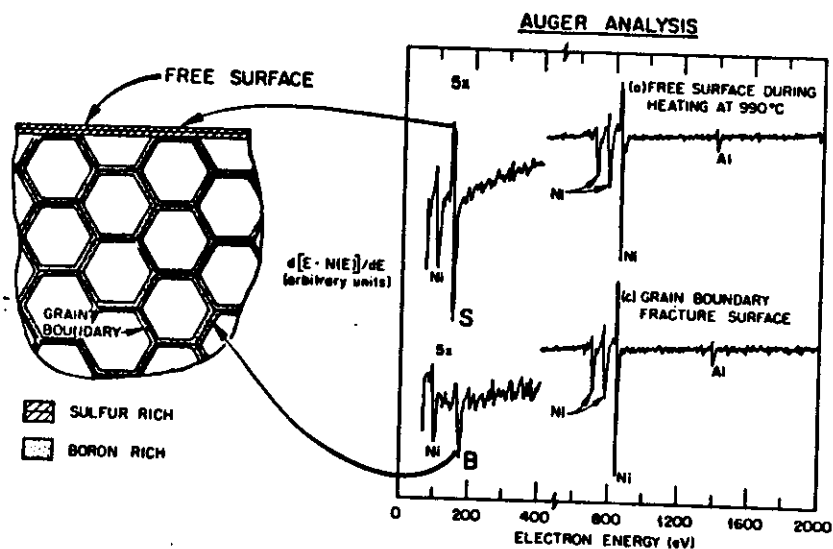


**BORON SEGREGATES STRONGLY TO GRAIN
BOUNDARIES IN 24 AT. % AL ALLOYS**



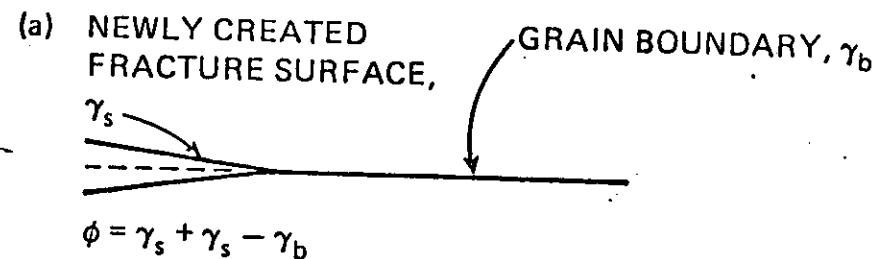
BORON EXHIBITS AN UNIQUE SEGREGATION BEHAVIOR - STRONG SEGREGATION TO GRAIN BOUNDARIES BUT NOT TO FREE SURFACES

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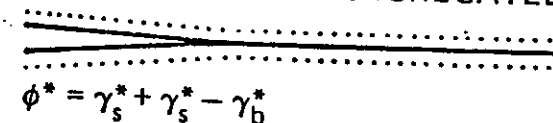


- IN CONTRAST, SULFUR, AN EMBRITTLING ELEMENT, SEGREGATES MUCH MORE STRONGLY TO FREE SURFACES THAN TO GRAIN BOUNDARIES.

EFFECTS OF SOLUTE SEGREGATION ON GRAIN-BOUNDARY COHESIVE ENERGY (ϕ)



- (b) GRAIN BOUNDARY SEGREGATED WITH SOLUTES



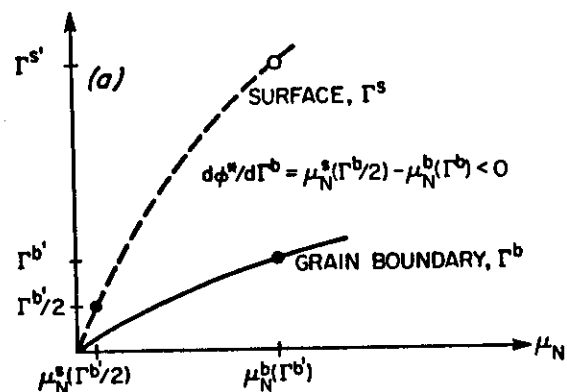
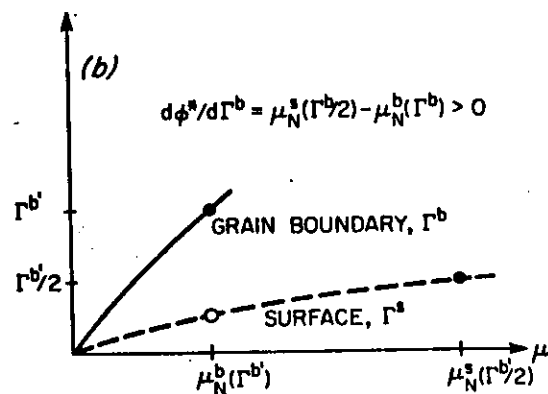
EMBRITTLING ELEMENTS (SUCH AS S)

$$\phi^*(\downarrow) = \gamma_s^*(\downarrow) + \gamma_s^*(\downarrow) - \gamma_b^*(\downarrow)$$

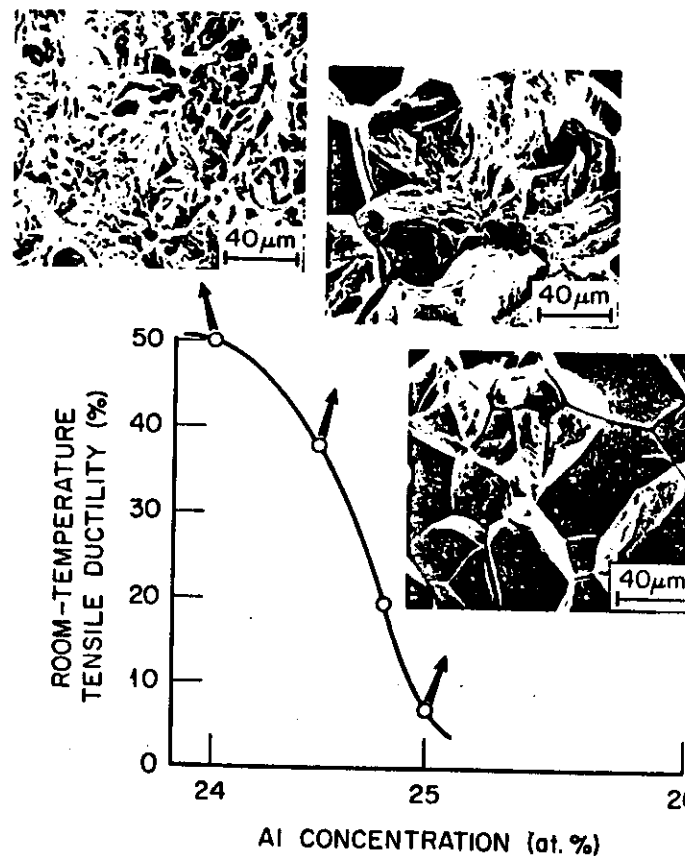
STRENGTHENING ELEMENTS (SUCH AS B)

$$\phi^*(\uparrow) = \gamma_s^*(\uparrow) + \gamma_s^*(\uparrow) - \gamma_b^*(\uparrow)$$

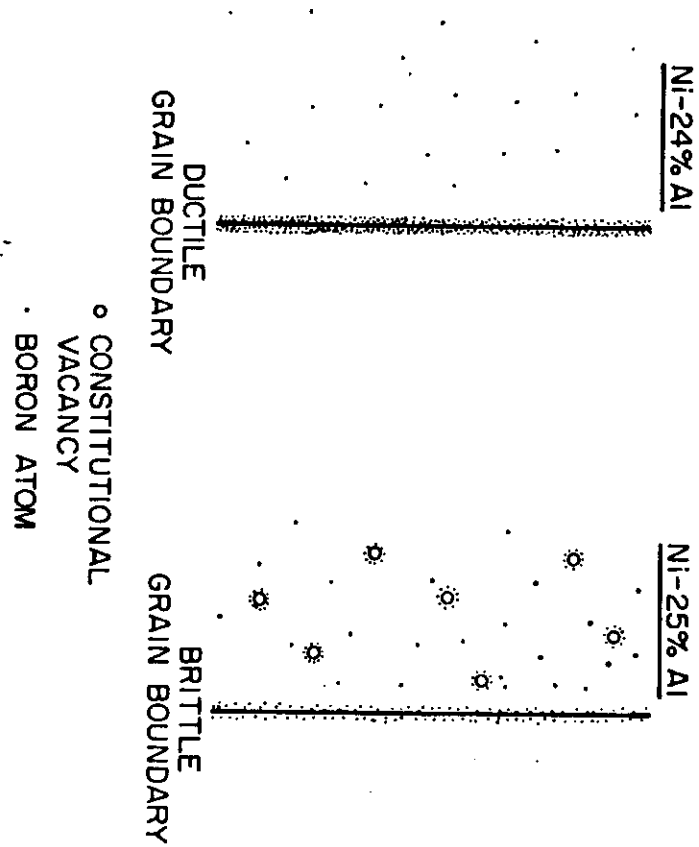
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SURFACE SEGREGATION (Γ^s) > GRAIN BOUNDARY SEGREGATION (Γ^b)SURFACE SEGREGATION (Γ^s) << GRAIN BOUNDARY SEGREGATION (Γ^b)

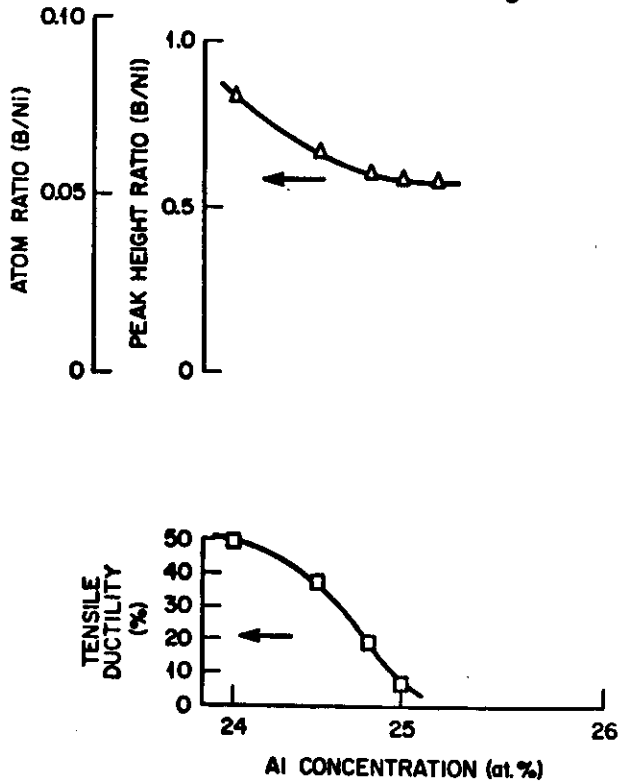
INCREASING Al CONTENT FROM 24 TO 25%
SHARPLY DECREASES TENSILE DUCTILITY AND PROMOTES
GRAIN-BOUNDARY FRACTURE IN Ni_3Al ALLOYS
DOPED WITH 0.2% BORON

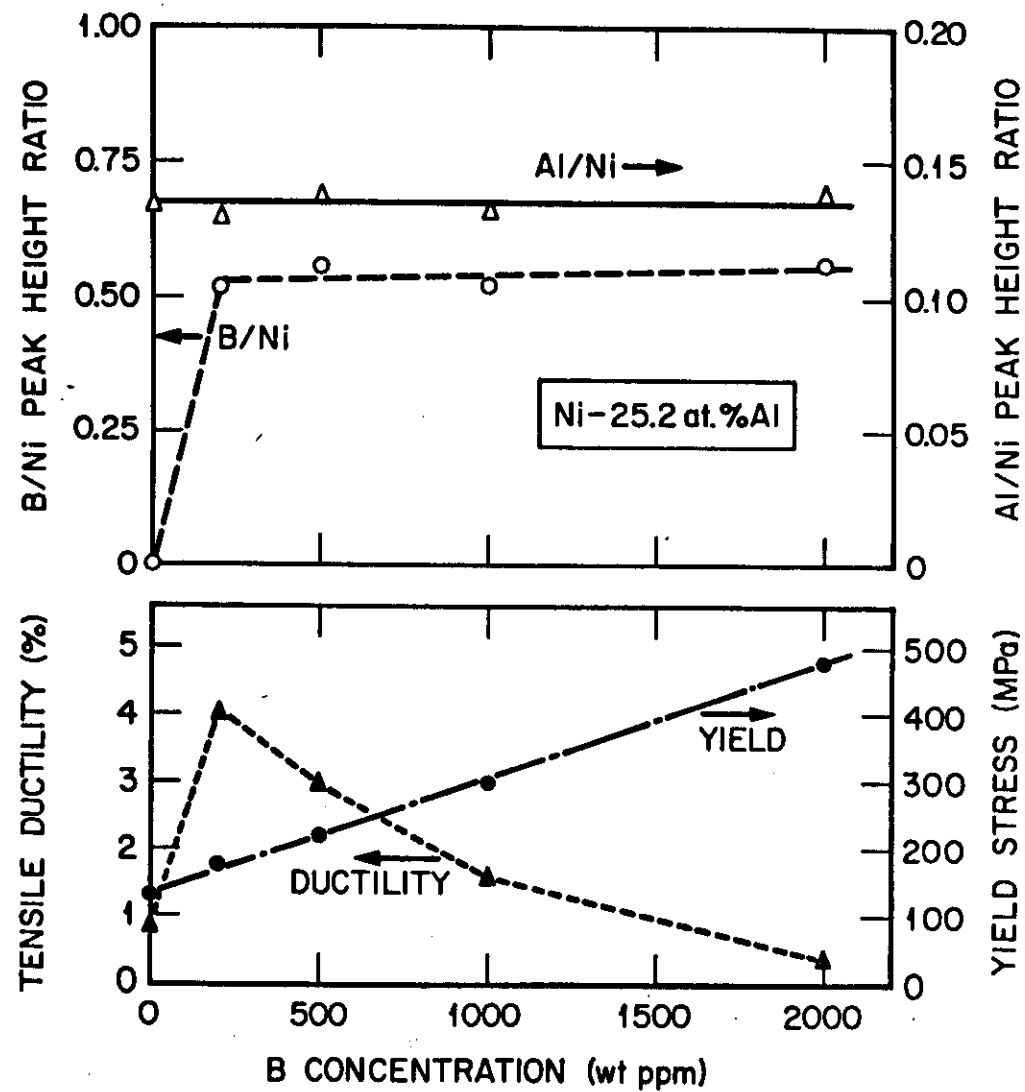
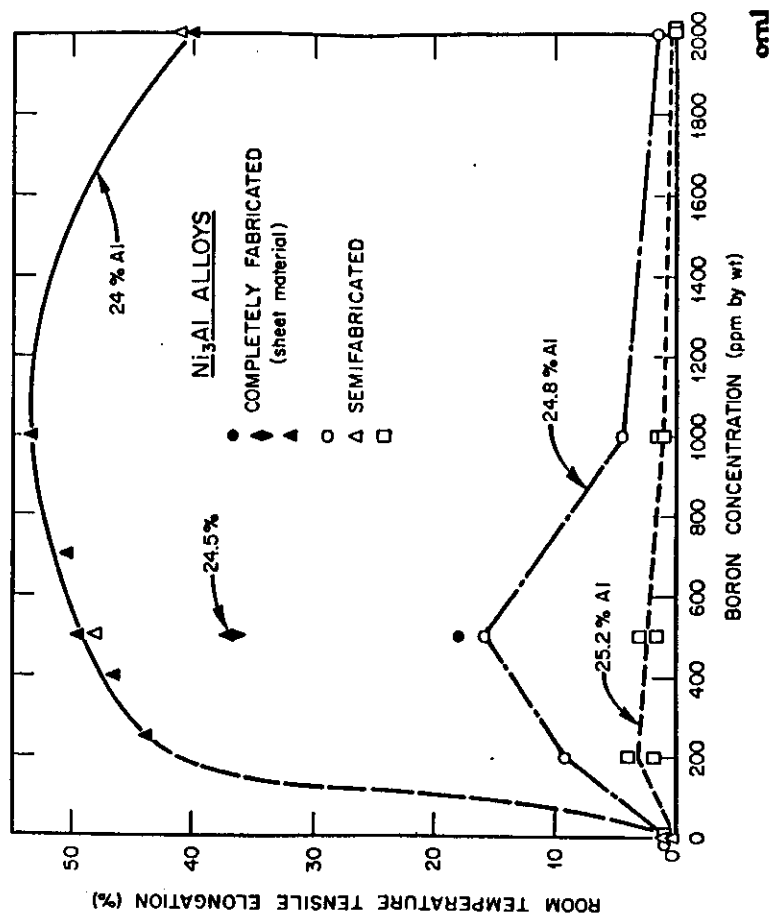


THE INTERACTION OF CONSTITUTIONAL VACANCIES WITH BORON IS THOUGHT TO REDUCE BORON ENRICHMENT AT GRAIN BOUNDARIES IN Ni_3Al WITH $\geq 25\%\text{Al}$



INCREASING Al CONTENT FROM 24% TO 25.2% DECREASES TENSILE DUCTILITY AND B LEVELS AT GRAIN BOUNDARIES IN Ni_3Al + 0.05wt % B



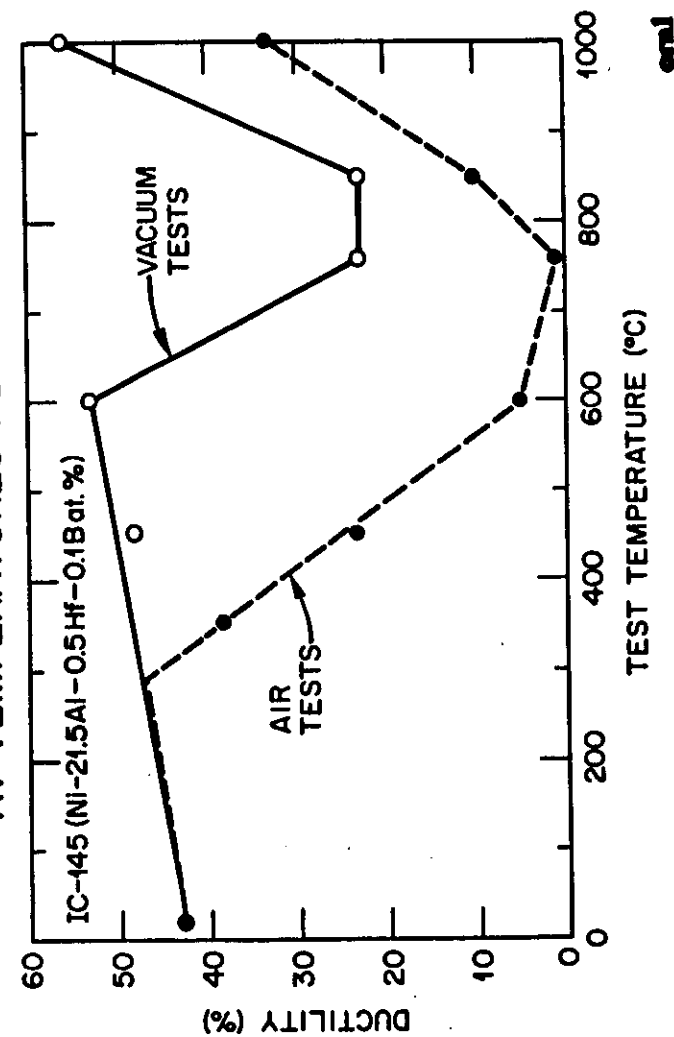


THE ALLOY STOICHIOMETRY EFFECT IS A COMBINATION OF

- (1) LOWERING BORON SEGREGATION TO GRAIN BOUNDARIES
AS THE BULK AL LEVEL INCREASES FROM 24 TO
24.5%
- (2) INCREASING THE AL LEVEL AT GRAIN BOUNDARIES
AS THE BULK AL INCREASES FROM BELOW TO ABOVE
25%
- (3) TREMENDOUS HARDENING EFFECT OF BORON IN
>25% AL ALLOYS

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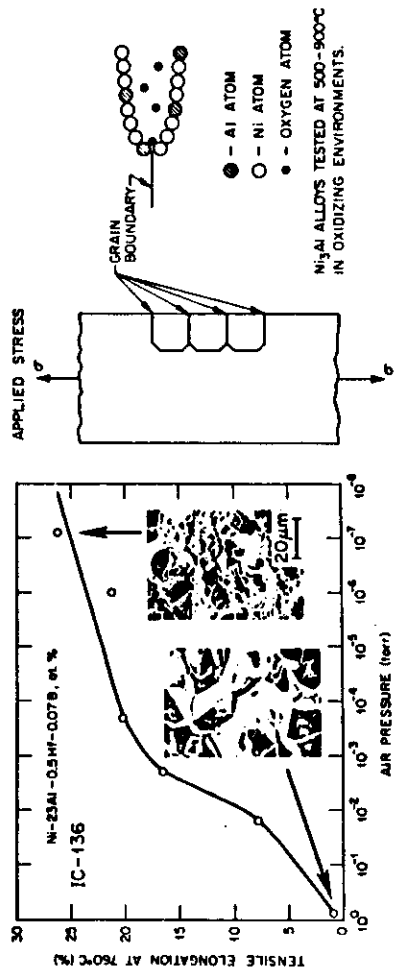
**NICKEL ALUMINIDES SHOW LOWER DUCTILITY
WHEN TESTED IN AIR THAN IN VACUUM
AT TEMPERATURES ABOVE 300 °C**



MECHANISM OF DYNAMIC EMBRITTLEMENT IN Ni_3Al ALLOYS

TECHNICAL ACCOMPLISHMENT:

- SMALL PARTIAL PRESSURES OF OXYGEN IN TEST ENVIRONMENTS WERE FOUND TO BE THE CAUSE FOR ELEVATED-TEMPERATURE EMBRITTLEMENT IN Ni_3Al ALLOYS.
- VACUUM TESTING OF PREOXIDIZED SPECIMENS FAIL TO SHOW ANY EMBRITTLEMENT, INDICATING A DYNAMIC PHENOMENON INVOLVING HIGH LOCALIZED STRESSES, ELEVATED TEMPERATURE, AND GASEOUS OXYGEN.



SIGNIFICANCE:

- THE DYNAMIC EMBRITTLEMENT COULD RESTRICT THE APPLICATION OF Ni_3Al IN OXIDIZING ENVIRONMENTS.
- IDENTIFICATION OF THE MECHANISM RESPONSIBLE FOR THE EMBRITTLEMENT SUGGESTS METALLURGICAL SOLUTIONS TO THE PROBLEM, SUCH AS CONTROL OF GRAIN-ORIENTED AND ALLOY ADDITIONS.

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THE EMBRITTLEMENT AT 300-900°C IS DUE TO A
DYNAMIC EFFECT

- PREOXIDATION DOES NOT EMBRITTLE THE ALUMINIDE SAMPLES TESTED IN VACUUM AT ELEVATED TEMPERATURES.
- ALLOY SAMPLES FRACTURED BRITTELY AT 600 AND 760°C REMAIN DUCTILE AND SHOW DUCTILE FAILURE WHEN BEND-TESTED AT ROOM TEMPERATURE.
- ALLOY SAMPLES LOST ELEVATED-TEMPERATURE DUCTILITY ALMOST INSTANTANEOUSLY WHEN OXYGEN WAS INTRODUCED TO VACUUM SYSTEMS.
- THE DUCTILITY DEPENDS STRONGLY ON PARTIAL PRESSURE OF O_2 AT ELEVATED TEMPERATURES.

EFFECTIVE SOLUTIONS TO THE DYNAMIC EMBRITTLEMENT PROBLEM

- CONTROL OF GRAIN SHAPE
 - REDUCE NORMAL STRESSES ACROSS GRAIN BOUNDARIES.
- ADDITION OF MODERATE AMOUNTS OF Cr (6-10%)
 - CHROMIUM ADDITIONS PROMOTE A RAPID FORMATION OF PROTECTIVE Cr OXIDE FILMS THAT SHUT OFF GASEOUS OXYGEN FROM GRAIN BOUNDARIES AND BASE METALS.

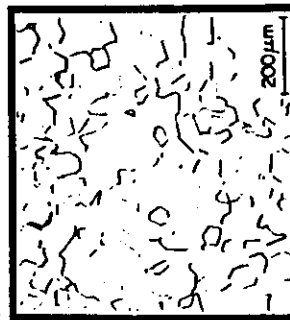
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ELIMINATION OF ENVIRONMENTAL EMBRITTLEMENT IN Ni₃Al ALLOYS BY CONTROL OF GRAIN SHAPE

TECHNICAL ACCOMPLISHMENT:

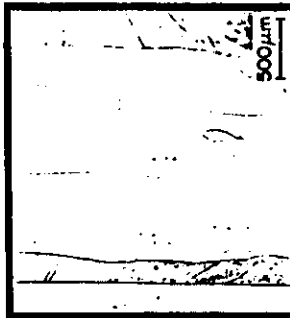
- SMALL PARTIAL PRESSURES OF OXYGEN IN TEST ENVIRONMENTS CAUSE DYNAMIC EMBRITTLEMENT IN Ni₃Al ALLOYS AT ELEVATED TEMPERATURES.
- THE EMBRITTLEMENT CAN BE ELIMINATED IN ALLOYS WITH COLUMNAR GRAIN STRUCTURES PRODUCED BY LEVITATION ZONE-REFINE METHODS.

EQUIAXED-GRAIN STRUCTURE



TENSILE TEST
AT 600°C IN AIR $\epsilon = 0.5\%$
INTERGRANULAR
FRACTURE

COLUMNAR GRAIN STRUCTURE



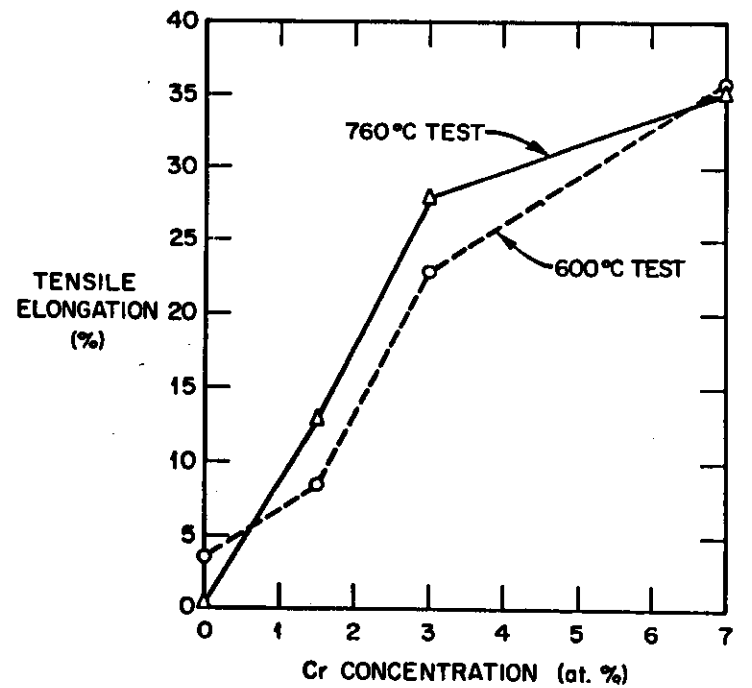
$\epsilon = 33\%$
TRANSGRANULAR
FRACTURE

SIGNIFICANCE:

- THE ENVIRONMENTAL EMBRITTLEMENT IN Ni₃Al ALLOYS CAN BE ALLEVIATED SIMPLY BY CONTROL OF GRAIN SHAPE.
- MOST SIGNIFICANTLY, THIS RESEARCH HAS DEMONSTRATED A NEW DIMENSION IN DESIGN OF METALS AND ALLOYS WITH GRAIN-BOUNDARY PROBLEMS.

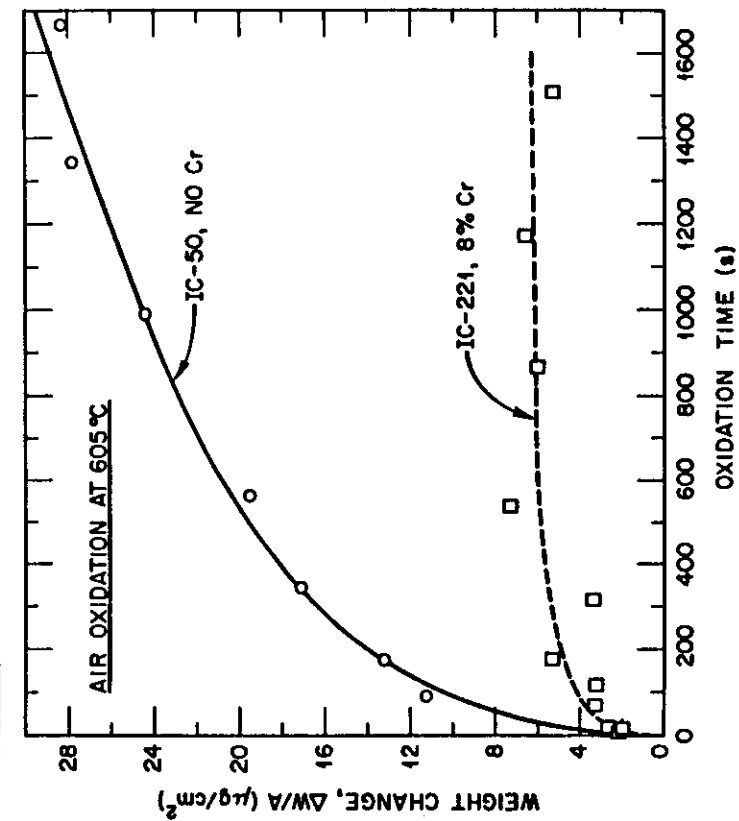
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CHROMIUM ADDITIONS SUBSTANTIALLY IMPROVE
TENSILE DUCTILITY OF Ni-Fe ALUMINIDES
(15.5 at. % Fe) AT 600 AND 760 °C IN AIR



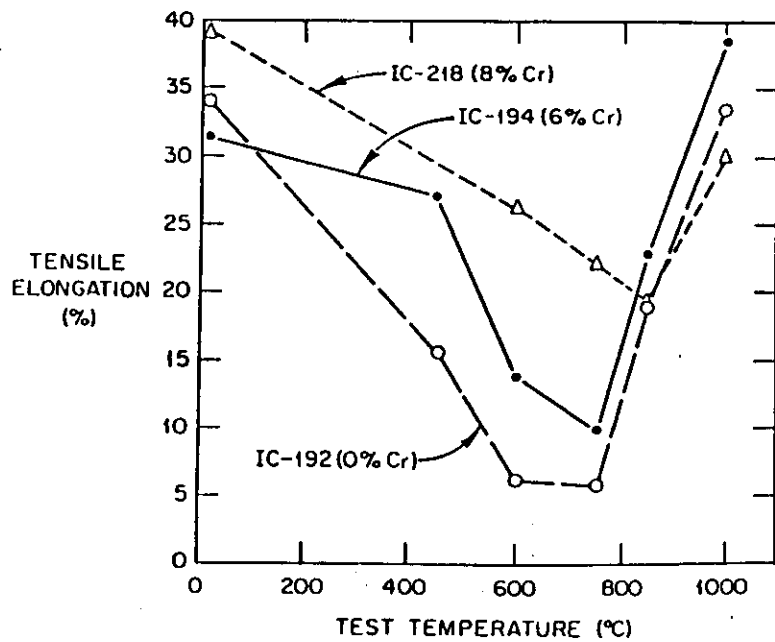
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CHROMIUM ADDITIONS PROMOTE A RAPID FORMATION OF
PROTECTIVE OXIDE FILMS ON SURFACES OF Ni₃Al ALLOYS



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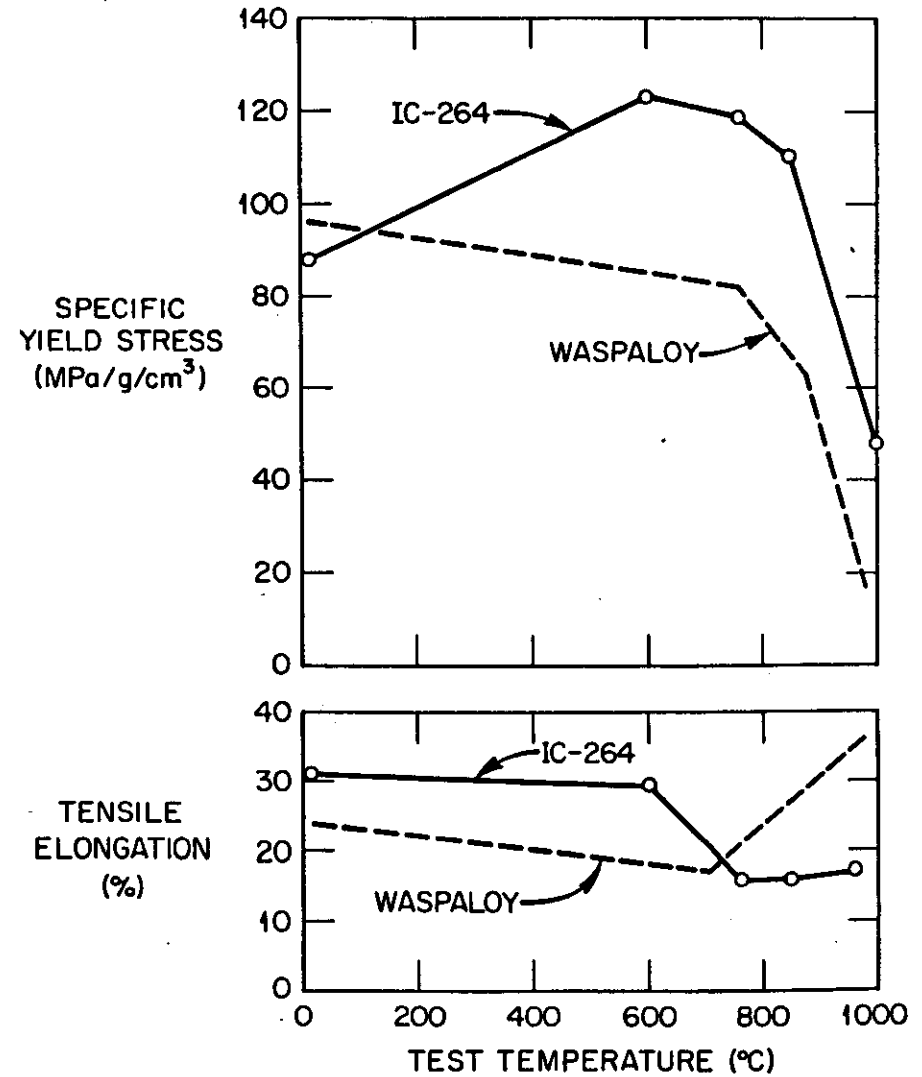
ALLOYING WITH 8at.%Cr SUBSTANTIALLY
REDUCES DYNAMIC EMBRITTLEMENT
IN OXIDIZING ENVIRONMENTS



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NICKEL ALUMINIDE (IC-264) HAS
SUPERIOR TENSILE PROPERTIES
AT ELEVATED TEMPERATURES



ornl

EFFECT OF COLD WORK (20-22%) ON TENSILE
PROPERTIES OF Ni_3Al ALLOYS

ALLOY (AT. %)	TEST TEMPERATURE (C°)	STRENGTH (ksi)		DUCTILITY (%)
		YIELD	TENSILE	
$\text{Ni}_3\text{Al} + 13 \text{ Fe}$	RT	231	249	4.0
$\text{Ni}_3\text{Al} + 1 \text{ Hf}$	RT	221	254	2.0
$\text{Ni}_3\text{Al} + 1 \text{ Hf}$	600	166	212	12.0
$\text{Ni}_3\text{Al} + 1 \text{ Hf}$	760	143	163	8.7

RECENT DEVELOPMENT OF ORDERED INTERMETALLIC
ALLOYS HAS FOCUSED ON
ALUMINIDES AND SILICIDES

ALLOY	T_M (C°)	DENSITY (G/CM ³)	CRYSTAL STRUCTURE
Ni_3Al	1400	7.5	L1_2
NiAl	1640	5.9	B2
FeAl	1250/1400	5.6	B2
Fe_3Al	1540	6.7	DO_3
Ti_3	1600	4.2	DO_{19}
TiAl	1460	3.9	L1_0
TiAl_3	1350	3.2	DO_{22}
Ni_3Si	1143	7.3	L1_2
MoSi_2	2020	5.0	C11_B
Ti_5Si_3	2130	3.7	D8_8

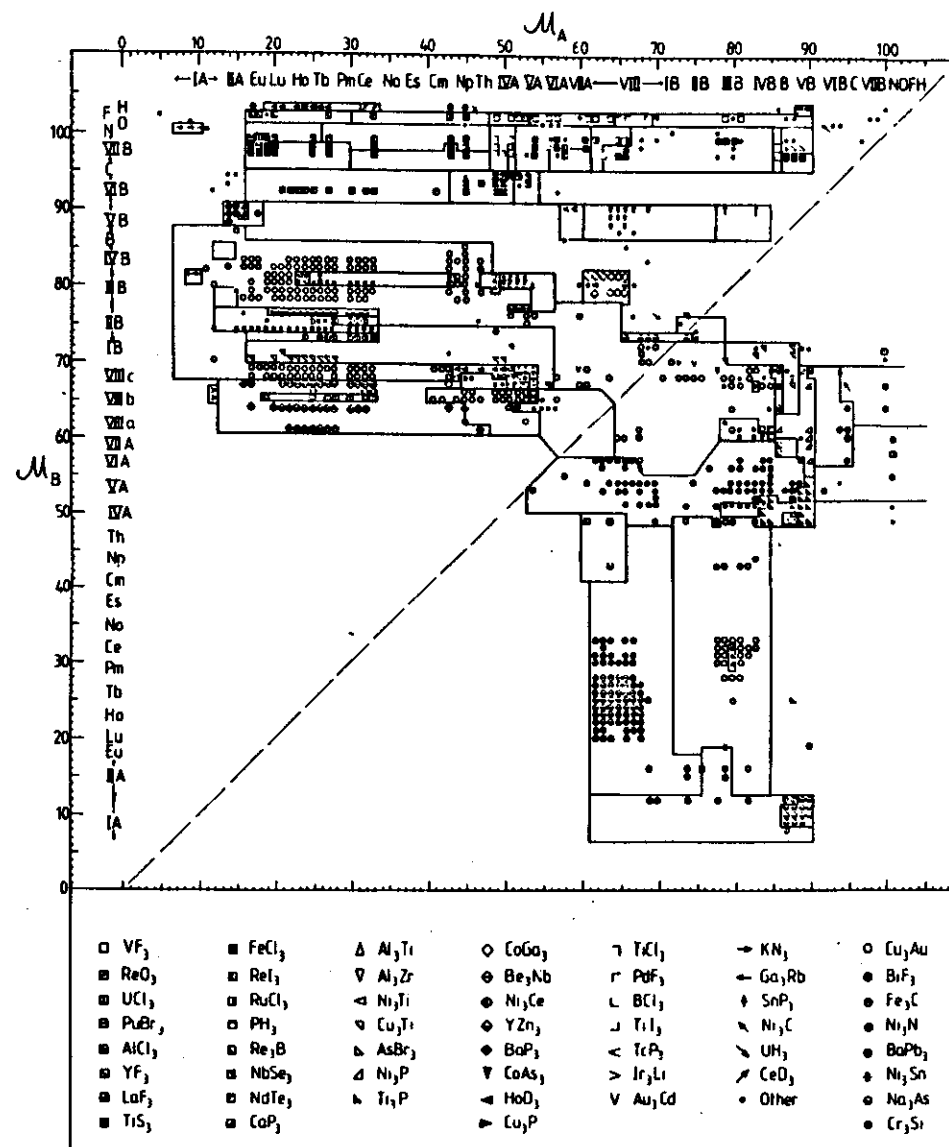
STRUCTURAL MAPS DEVELOPED BY
PROF. DAVE PETTIFOR

- PETTIFOR HAS ATTEMPTED TO USE ONE NUMBER, MENDELEEV NUMBER, TO REPRESENT ALL EFFECTS FROM ATOM SIZE, ELECTRONEGATIVITY AND VALENCE ELECTRON
- THE STRING RUNNING THROUGH A MODIFIED PERIODIC TABLE PUTS ALL THE ELEMENTS IN SEQUENTIAL ORDER, GIVEN BY THE MENDELEEV NUMBER

0 IA																		IIIB IIIB IVB VB VIB VIIB										103 H
1 He	2 Li																	77 Be	78 B	79 C	80 N	81 O	82 P					
3 Ne	4 Na	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIb	VIIIc	IB	73 Mg	74 Al	75 Si	76 P	77 S	78 Cl											
5 Ar	6 K	9 Ca	10 Sc	51 Ti	52 V	53 Cr	54 Mn	55 Fe	56 Co	57 Ni	58 Cu	79 Zn	80 Ga	81 Ge	82 As	83 Se	84 Br											
8 Kr	9 Rb	11 Sr	20 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I											
5 Xe	6 Cs	12 Ba	17	50 Hf	51 Ta	52 W	53 Re	54 Os	55 Ir	56 Pt	57 Au	58 Hg	59 Tl	60 Pb	61 Bi	62 Po	63 At											
8 Rn-Fr	9 Ra	54 Hf		55 Ta	56 W	57 Re	58 Os	59 Ir	60 Pt	61 Au	62 Hg	63 Tl	64 Pb	65 Bi	66 Po	67 At												
		17 Yb		18 Eu		33 La	34 Ce	35 Pr	36 Nd	37 Pm	38 Sm (Eu)	39 Gd	40 Tb	41 Dy	42 Ho	43 Er	44 Tm (Yb)	45 Lu										
				46 Ac	47 Th	48 Pa	49 U	50 Np	51 Pu	52 Am	53 Cm	54 Bk	55 Cf	56 Es	57 Fm	58 Md	59 No	60 Lr										

The string running through this modified periodic table puts all the elements in sequential order, given by the Mendeleev number

THE AB₃ MAP



SUMMARY

1. SIGNIFICANT PROGRESS HAS BEEN MADE IN IMPROVING THE DUCTILITY AND FRACTURE BEHAVIOR OF ORDERED INTERMETALLIC ALLOYS.
2. BORON IS EFFECTIVE IN SUPPRESSING BRITTLE GRAIN-BOUNDARY FRACTURE AND INCREASING THE DUCTILITY OF Ni_3X ALLOYS ($\text{X} = \text{Al}, \text{Si}$ AND Ga) WITH HYPO-STOICHIOMETRIC COMPOSITIONS.
3. DUCTILITY IN $\text{Ni}_3\text{V-Co}_3\text{V-Fe}_3\text{V}$ ALLOYS CAN BE DRAMATICALLY IMPROVED BY CONTROL OF ELECTRON CONCENTRATION AND ORDERED CRYSTAL STRUCTURES.
4. ALUMINIDES HAVE POTENTIAL TO BE DEVELOPED AS NEW HIGH-TEMPERATURE STRUCTURAL MATERIALS.

