Advanced Alloys Systems for Fusion Applications

(other than the V-Cr-Ti system)

Summary of research programs by:

D.T. Hoelzer
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

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Critical Design Considerations for V-Based Alloys

- Low Activation
  - solution solution V-based alloys (such as V-4Cr-4Ti) are attractive
  - but, limits choices of alloying additions
- Interstitial impurities
  - high solubility limits impact mechanical and oxidation properties
- Corrosion and oxidation
  - compatibility with coolant
    - He....*requires protective scale*
    - Li-based molten metals....*requires insulating coating*
- High temperature strength
  - alloying to promote formation of stable second phase

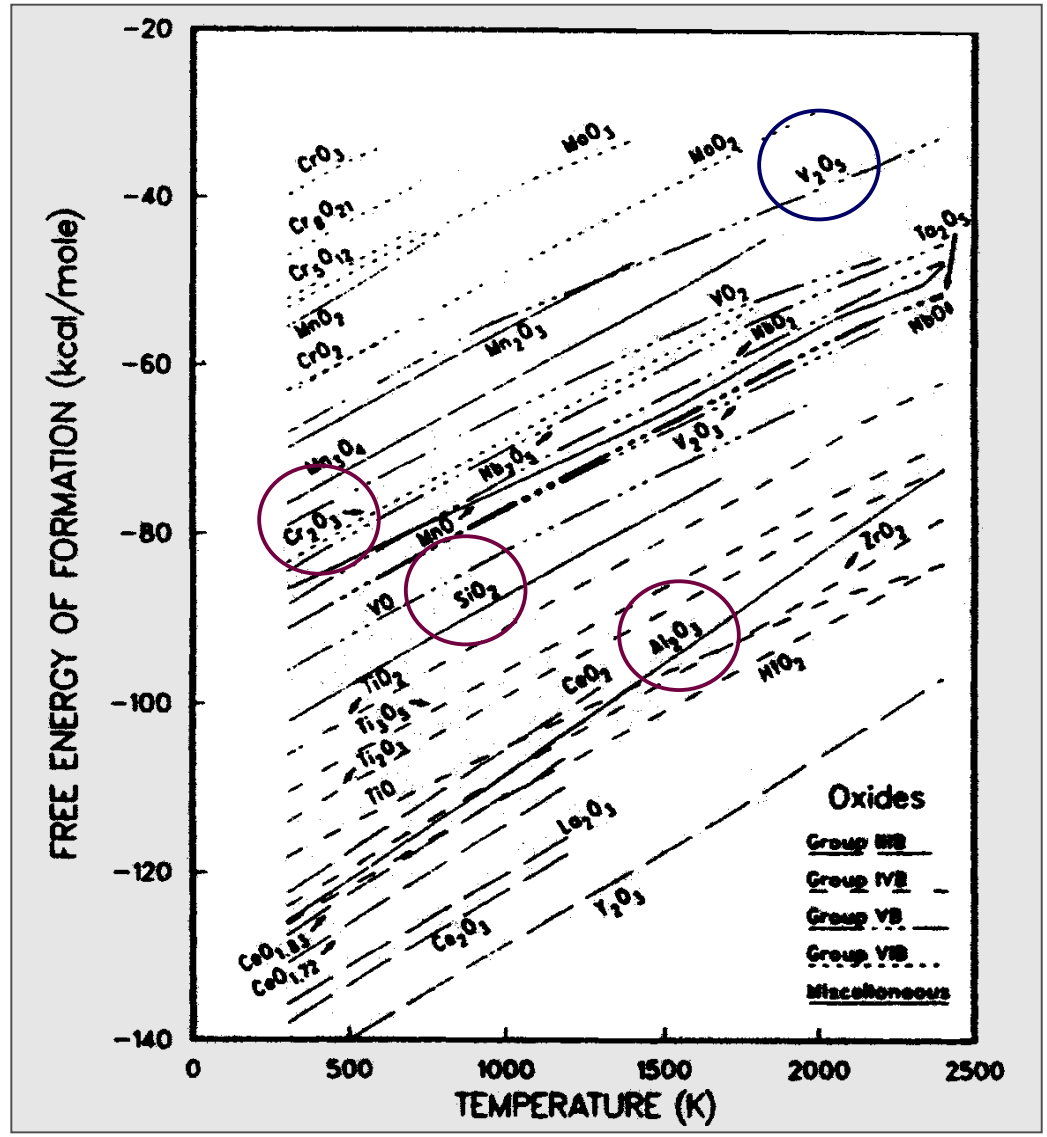
Strategies for Increasing the Upper Temperature Limits in V-Cr-Ti Alloys

- Management of the interstitial solute population by redistributing them in a uniformly dispersed phase
  - provide sites for enhancing point defect recombination and trapping of He bubbles
  - lowering the interstitial solute concentration to reduce the radiation hardening
  - develop a more uniform grain structure

- Approaches
  - controlled precipitation of Ti(OCN) by solutionization and isothermal aging treatments
  - addition of strong compound forming solutes, such as Si, Al, Y

Scale Formation on Vanadium Based Alloys

- Common oxides that form a protective external scale at high temperatures
  - Cr_2O_3
  - SiO_2
  - Al_2O_3
- Problem with vanadium
  - high solubility for O (and other interstitial solutes)
  - volatility of V_2O_5 phase
    - melting point ~690°C
    - V_5Si_3 and V-30%Al
- Prevention of V_2O_5 formation is paramount for high T use in ambient O pressures
  - *must lower the O solubility*



Overview

- Looking at the past

- Ongoing studies of advanced V-Cr-Ti alloys
  - Development of V-4Cr-4Ti containing Si, Al, Y
  - Development of V-Cr-Ti alloys with high Cr content
  - Advanced processing of V-4Cr-4Ti-Si,Al,Y alloys by levitation melting
  - Development of mechanically alloyed Y_2O_3-ODS V alloys

- Recent study looking beyond the V-Cr-Ti system
  - Multi-phase (intermetallic) V-Ti-Al alloys

History of Vanadium Alloy Development

- Early interest
  - radiation response
  - fundamental understanding of defect structures in bcc metals
- Programs focused on potential as fast breeder fuel cladding in 1960's
  - better high temperature mechanical properties than SS
  - resistant to elevated irradiation embrittlement effects
- Major alloy development programs
  - Argonne National Laboratory.....V-Ti and V-Cr-Ti
  - Westinghouse Electric Corporation.....multicomponent precipitation hardened alloys containing Zr and C (Vanstar)
  - European program (Karlsruhe).....table

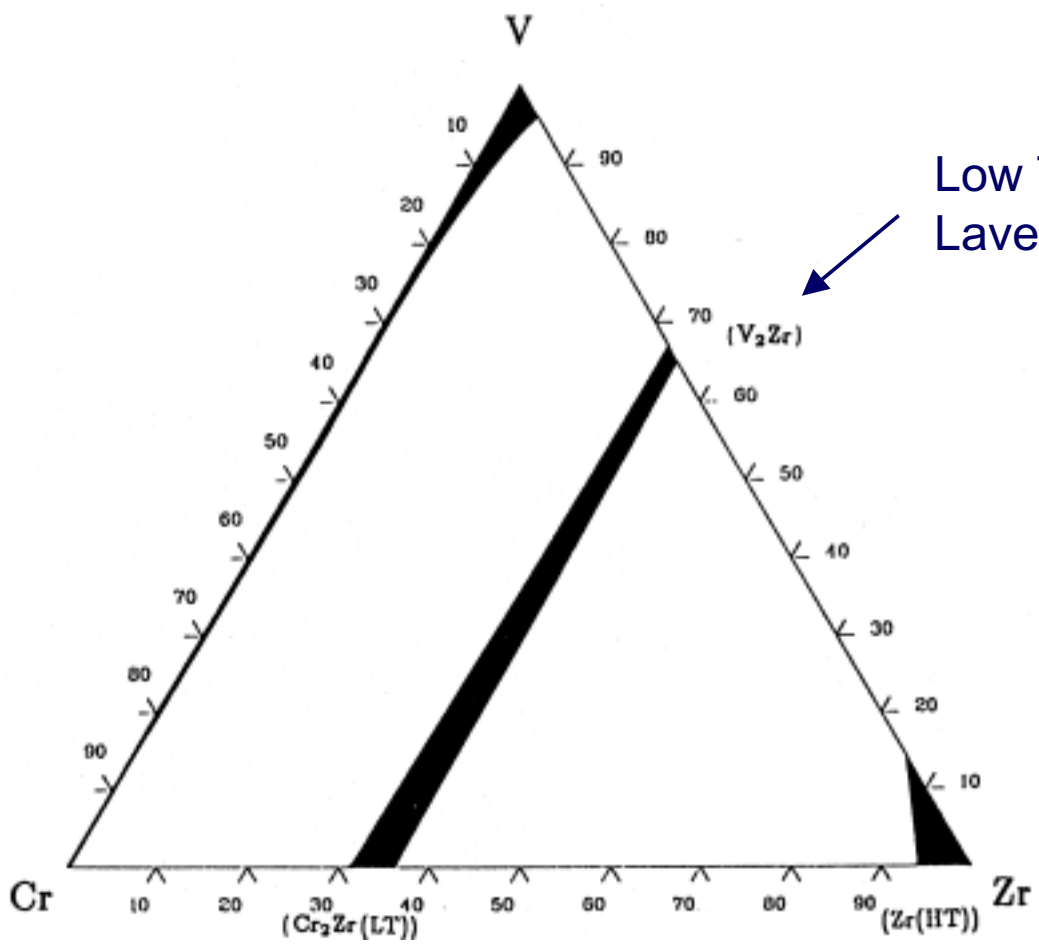
Investigation of Vanadium Alloys in Europe for Breeder Reactor Fuel Cladding during the 1960's

Programs in U.S. and Europe

Alloy	Objective
V ***(pure)***	
V-Ti ***(3-20% Ti)***	**Improve tensile strength, better fabricability**
V-Ti-Nb ***(1-20% Ti, 10-20% Nb)***	**Matrix strengthening**
V-Zr-Cr ***(1.7-3% Zr, 1.6-15% Cr)***	**Improve corrosion resistance**
V-Zr-Nb ***(3% Zr, 15% Cr)***	**Improve corrosion resistance**
V-Ti-Cr ***(0-5% Ti, 2-13% Cr)***	**Improve corrosion resistance**
V-Ti-Nb-Cr ***(1-5% Ti, 5-10% Nb, 5-10% Cr)***	**Improve corrosion resistance, matrix strengthening**
V-Ti-Si ***(3% Ti, 1-1.5% Si)***	**High strength alloy (to 850°C)**
V-Ti-Nb-Si ***(3% Ti, 1% Si, 5-15% Nb)***	**High strength alloy**
V-Ti-Ge ***(3% Ti, 1-4% Ge)***	**Substitution of Si**

(compilation by F.W. Wiffen)

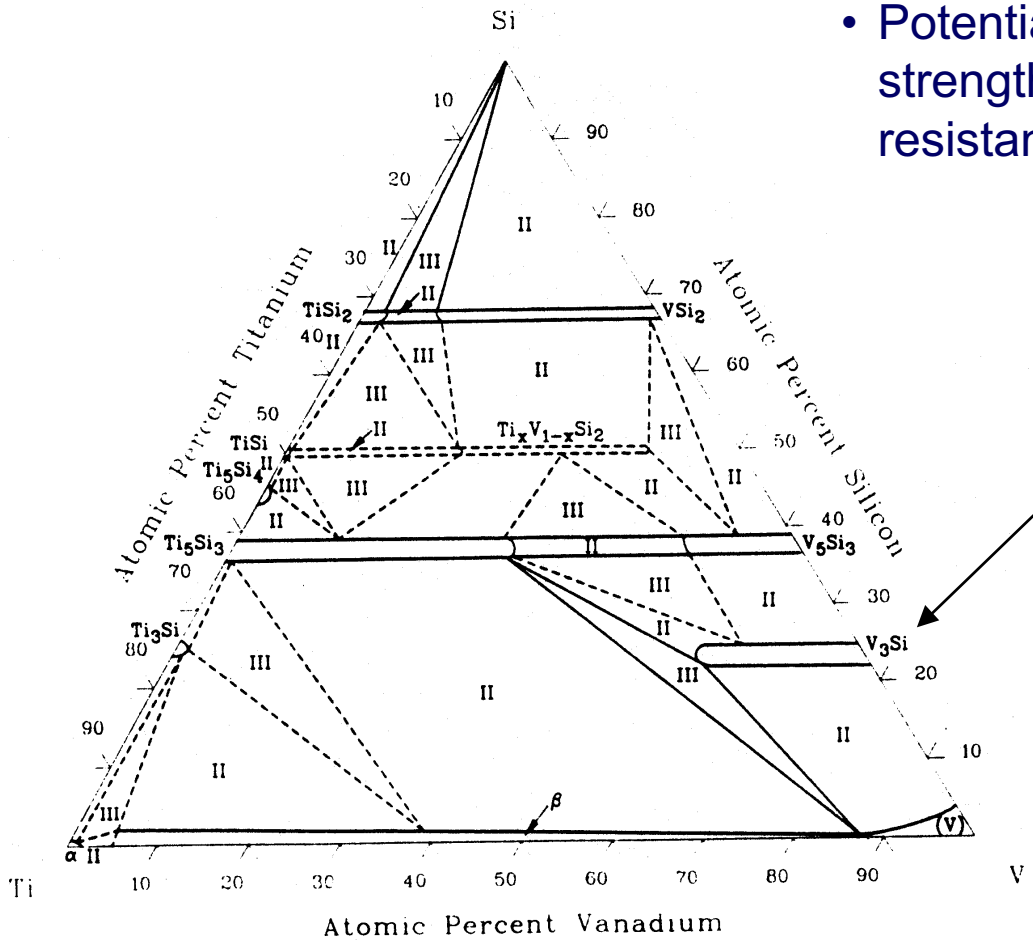
1150°C Isotherm of Ternary V-Cr-Zr System



Low T_c superconducting Laves phase

(V.N. Eremenko, et.al, Russian Metallurgy, 1970)

800°C Isotherm of Ternary V-Ti-Si System



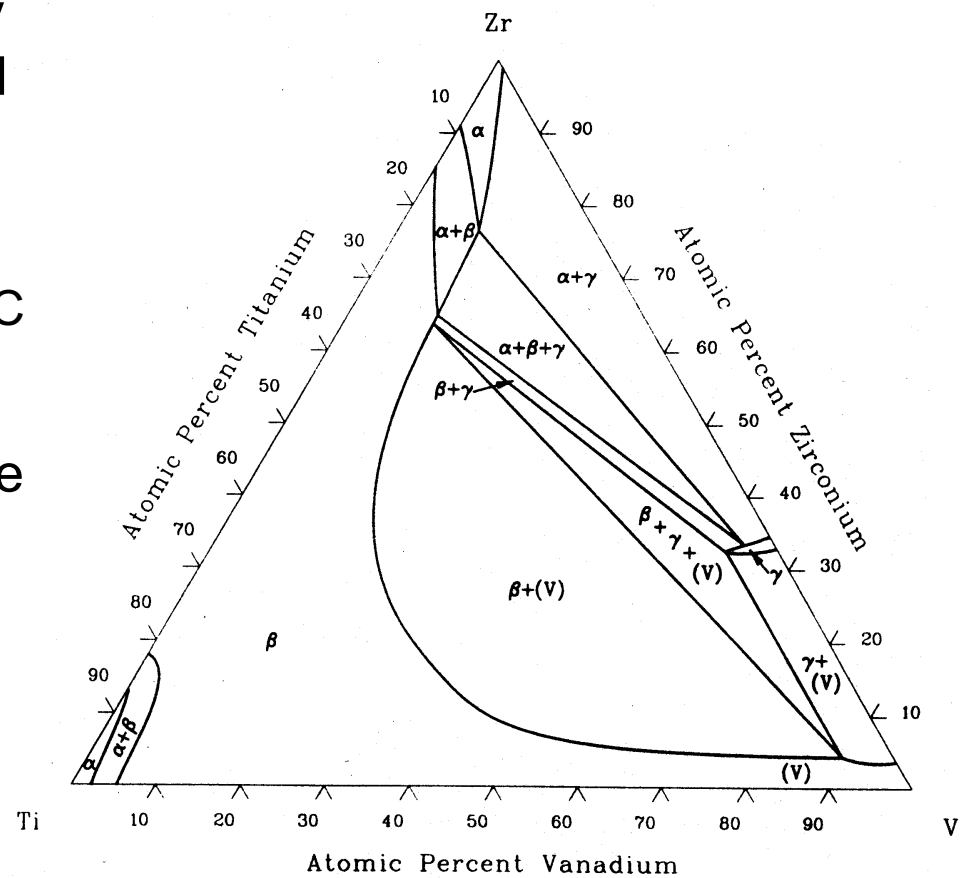
- Potential for precipitation strengthening and oxidation resistance along V-Si binary

A15 compound V_3Si is low Tc superconducting phase

(Y. V. Efimov et. al, Izv. Akad. Nauk SSSR, Neorg. Mater.1, 1965)

Development of Carbide Strengthened V-Ti-C and V-Ti-Zr-C Alloys

- Subject Invention: D.N. Braski and P.J. Maziasz, 1988
- Precipitation strengthened by {100} disc and blocky shaped MC-type carbides
- Alloys:
  - V-(1.5-3)Ti-(.15-.3)Zr-(.05-.1)C
  - V-(1.5-3)Ti-(.05-.25)C
- Implanted with ~300 appm He
  - He trapped at MC-disc interface



(A. Nowikov and H.G. Baer, Z. Metallkd., 1958)

Development of V-4Cr-4Ti-Si,Al,Y Alloys

Presented by:

M. Satou

Development of V-Cr-Ti alloys with high Cr content

Presented by:

K. Abe

Advanced processing of V-4Cr-4Ti-Si,Al,Y alloys by Levitation Melting

Review

Review: Fabrication of V-4Cr-4Ti-Si, Al, Y Alloys using Levitation Melting

- From 5th IEA & JUPITER Joint WS Vanadium Alloys Fusion Applications

T. Chuto[1], A. Hasegawa[1], K.Abe[1], T. Nagasaka[2], T. Muroga[2], S. Tomiyama[3], and M. Sakata[4]

1 Dept. Quantum Science and Energy Engineering, Graduate School of Engin., Tohoku University
2 National Institute for Fusion Science
3 Daido Bunseki Research Inc.
4 Daido Steel Co. Ltd.

- Objective: To establish the fabrication method of large ingots (25kg) by reducing interstitial O, C, N using Levitation Melting

- Highlights of the results:
  - Y added to reduce O content to <100 wppm
  - slag off Y oxide
  - achieved with Y>0.2 (wt.%)
  - but, large inclusions formed along grain boundaries with Y>0.3 wt.%

Development of Mechanically Alloyed Y_2O_3-ODS V-alloys

Contributed by:

H. Kurishita

Review: Powder Metallurgical Vanadium Alloy Development

- From 5th IEA & JUPITER Joint WS Vanadium Alloys Fusion Applications

H. Kurishita[1], T. Kuwabara[2], and M. Hasegawa[1]
1 The Oarai Branch, IMR, Tohoku University, Oarai, Ibaraki, Japan
2 Graduate Student, Tohoku Univ., Present Address: Sumitomo Electric Industries Ltd, Osaka, Japan

- Objective: To improve the resistance to irradiation embrittlement and the strength at high temperatures by producing finely dispersed, thermally stable particles in vanadium alloys by the mechanical alloying (MA) method
  - sinks for irradiation produced defects
  - obstacles impeding dislocation motion
- Difficult to develop vanadium alloys by MA because of high solubility and chemical activity for interstitial impurities
- Highlights of the results
  - V and Y powders mixed in Ar atmosphere, mechanically alloyed, and HIPed
  - Significant improvement in high temperature strength while maintaining low temperature ductility was achieved in V-(3-8%)W-(1.4-1.8)Y alloys

Current Status of Vanadium Alloy Development by Mechanical Alloying

H. Kurishita[1], T. Kuwabara[2], M. Hasegawa[1], H. Matsui[1]

[1]The Oarai Branch, IMR, Tohoku University, Oarai, Ibaraki, Japan

[2]Graduate Student, Tohoku University, Present Address:Sumitomo Electric Industries Ltd, Osaka, Japan

1) **Processing issues and recent progress**
2) **Effect of composition and microstructure on high temperature properties**

Processing Issues and Recent Progress

1. To develop ductile V-Cr (Cr > 25 wt%) alloys that have never been fabricated because of difficulty in plastic working needed to destroy the cast structure

   - Successfully developed V-28Cr-2.3Y and V-52Cr-1.8Y alloys with good tensile properties without any plastic working after HIP:

     V-28Cr-2.3Y (1473K anneal) : V-0.7vol%Y_2O_3-0.5vol%YN-1.3Y
     σ_y= 590MPa
     σ_U = 670MPa
     ε_t = 25%
     ε_u = 14%
     RA = 58%

     V-52Cr-1.8Y (1673K anneal) : V-0.7vol%Y_2O_3-0.3vol%YN-1.0Y
     σ_y = 610MPa
     σ_U = 790MPa
     ε_t = 19%
     ε_u = 16%
     RA = 31%

   - Effect of cold rolling for V-28Cr-2.3Y :

     70% cold rolling increases RA from 58 to 64%

Processing Issues and Recent Progress (Cont'd)

2. To achieve negligible contents of radioactive Co coming from contamination with pots and balls made of WC/Co used for mechanical alloying (MA) process:
   - Achieved Co content of less than 10 wppm which is the detectable limit of chemical analysis.
   - Tensile specimens of the alloy are being irradiated in HFIR.

3. To determine optimum dispersion of thermally stable particles (Y_2O_3, YN) for improvement in the resistance to radiation embrittlement, without appreciable loss of ductility in the unirradiated condition.
   - Very fine particles less than 5 nm in diameter and higher volume fraction of 2-3 % : Now in progress

Effect of Composition and Microstructure on High Temperature Properties

Recent experimental results on high-temperature microstructure stability and high-temperature strength for V-1.7%Y, V-28%Cr-2.3%Y and V-52%Cr-1.8%Y with fine grains and finely dispersed particles of Y_2O_3 and YN show that:

- **Annealing at 1273-1673 K (0.60-0.78Tm) changes the grain size from 0.27 to 4.6 μm and particle size from 6 to 75 nm.**
- **Increase in solute Cr slightly improves the microstructure stability and strength at high temperatures.**
- **Increase in volume fraction of dispersed particles significantly improves the microstructure stability and strength at high temperatures.**
- **Uncombined Y particles may cause significant embrittlement at high temperatures.**
- **There appears no simple relationship between grain size and yield strength at 1073-1273K.**

Multi-Phase (Intermetallic) V-Ti-Al Approach

Presented by:

D.T. Hoelzer

Note: this is a review of previous work since no further progress has occurred since mid-2000

Motivation for Exploring Multi-Phase V-Ti-Al Alloys

- Based on intermetallic γ - TiAl (ordered $L1_0$)phase:
  - disordered β - V solid solution (bcc) matrix
  - ordered β (B2 - CsCl) matrix
- Microstructural control
- Combination of attractive properties
  - Low temperature ductility and fracture toughness (β)
  - Thermal stress factor (β, γ)
  - Low activation (β - no Al)
  - High temperature strength (B2, γ)
  - High temperature creep (γ)
  - Oxidation resistance (γ - alumina former)
    - external protective scale consisting mostly of Al_2O_3 formed above 800°C in a He + 20vol.%O_2 atmosphere (*M.Groβ, V. Kolarik, and A. Rahmel, Oxidation of Metals, 1997)*

Thermal/Physical Properties of γ-TiAl

Temperature (°C)	Thermal Conductivity[1] (W/cm°C)	Thermal Expansion Coefficient[2] ($°C^{-1}$)	Ultimate Tensile Stress (MPa)	Elastic Modulus[3] (GPa)	Thermal Stress Factor (M/m)
200	0.68200	3.134E-05	600	163	5368
300	0.74460	3.260E-05			
400	0.82790	3.387E-05			
500	0.80620	3.514E-05			
600	0.82060	3.641E-05	550	152	5464
700	0.82570	3.768E-05			
800	0.79830	3.894E-05	500	144	4769
900	0.78410	4.021E-05			
1000	0.67510	4.148E-05			

- [1] Unpublished results of G.E. Fuchs, University of Florida
- [2] Y. He et al., (1997)
- [3] S.C. Huang and J.C. Chesnutt, (1994)

Experimental Procedure

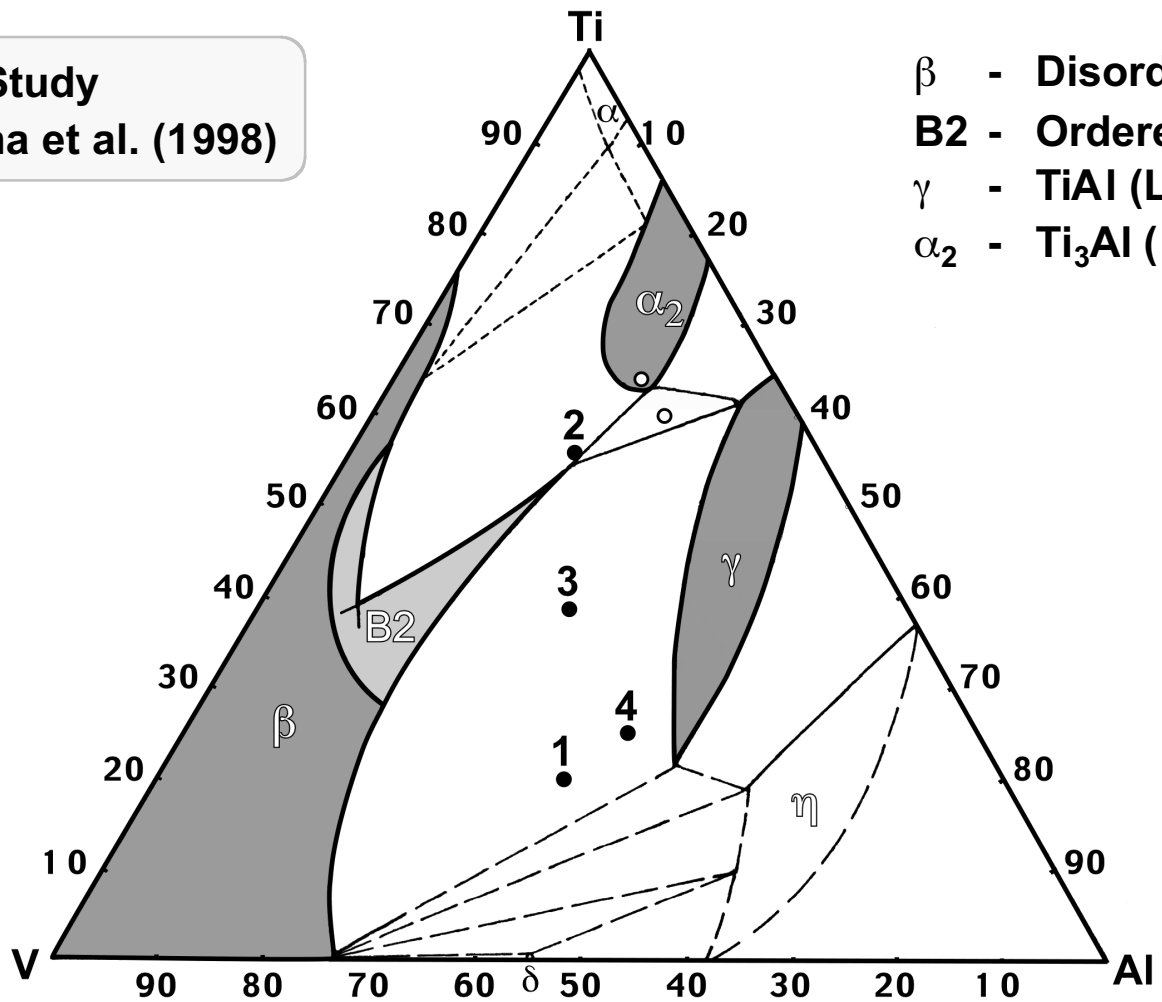
- Material : Alloys made from 99.99% base metals
- Alloy Compositions :

Alloy	Composition (wt.%)			Composition (at.%)		
	V	Ti	Al	V	Ti	Al
1	41.6	20.1	38.3	30.7	15.8	53.5
2	23.5	55.8	20.7	19.3	48.6	32.1
3	32.1	38.8	29.1	25	32.2	42.8
4	33.5	24.8	41.7	24.2	19.0	56.8

- Processing :
  - Arc melted in ~150 to 200 gram cylindrical shaped buttons
  - Flowing argon (pre-evacuated chamber)
  - 6 re-melts to ensure chemical mixing

Selection of Alloy Compositions Based on 600°C Isotherm of V-Ti-Al System

- • Current Study
- ○ Hishinuma et al. (1998)



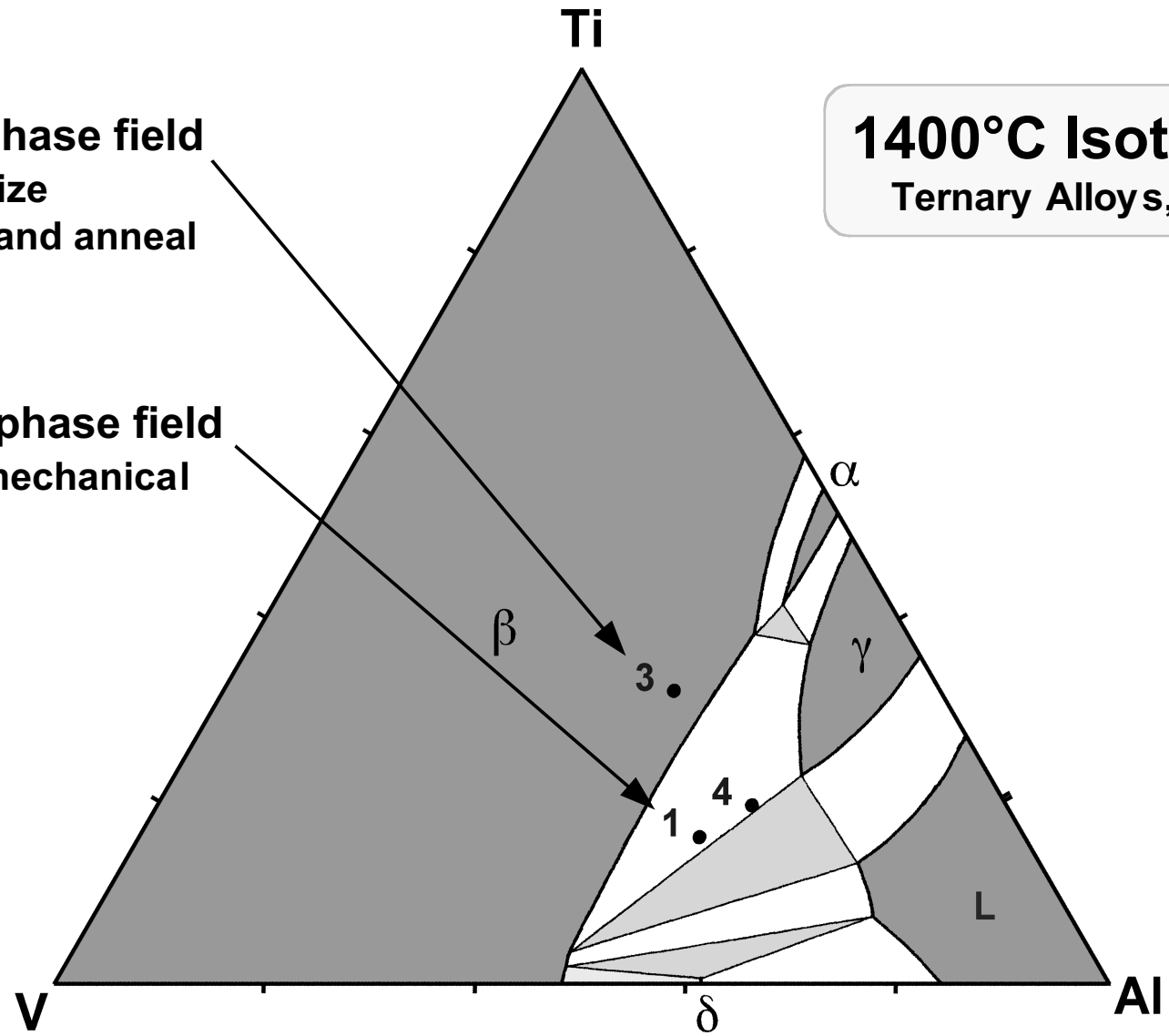
- β - Disordered bcc
- B2 - Ordered bcc
- γ - TiAl ($L1_0$)
- α_2 - Ti_3Al (DO_{19})

Ahmed and Fowler, 1994

Control of Two Phase Microstructures using High Temperature Phase Equilibria

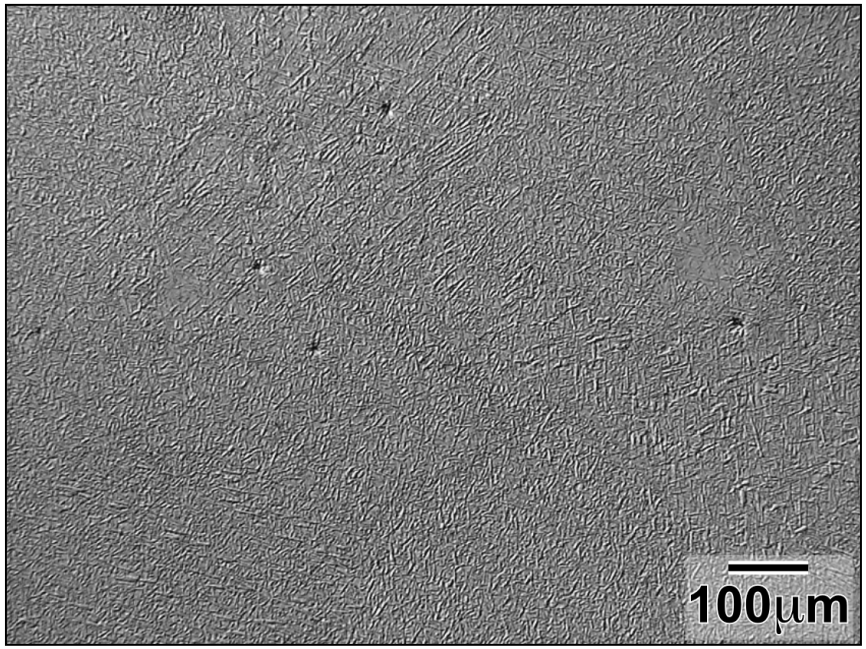
β single phase field
- **solutionize**
- **quench and anneal**

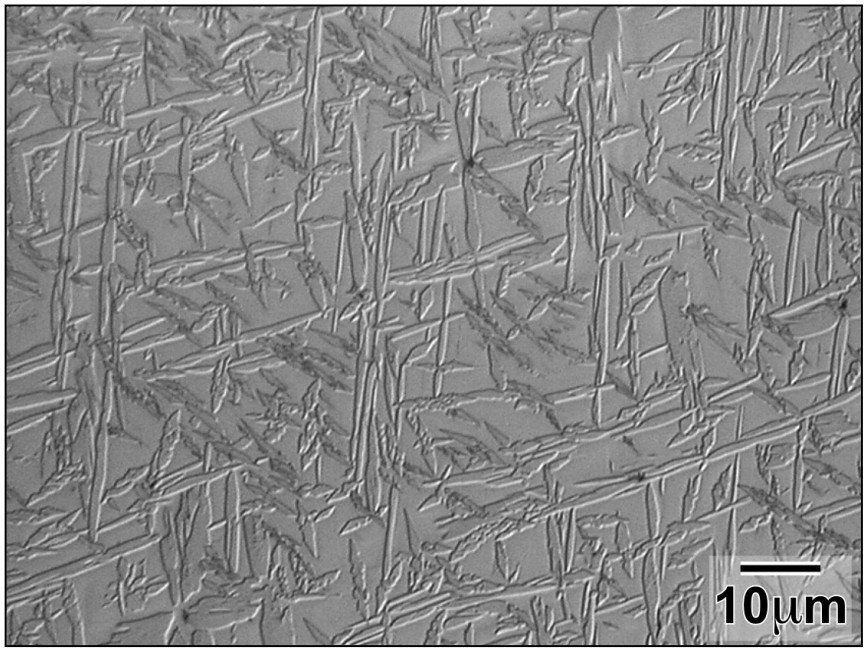
β + γ two-phase field
- **thermomechanical**
- **lamellar**



1400°C Isotherm
Ternary Alloys, 1993

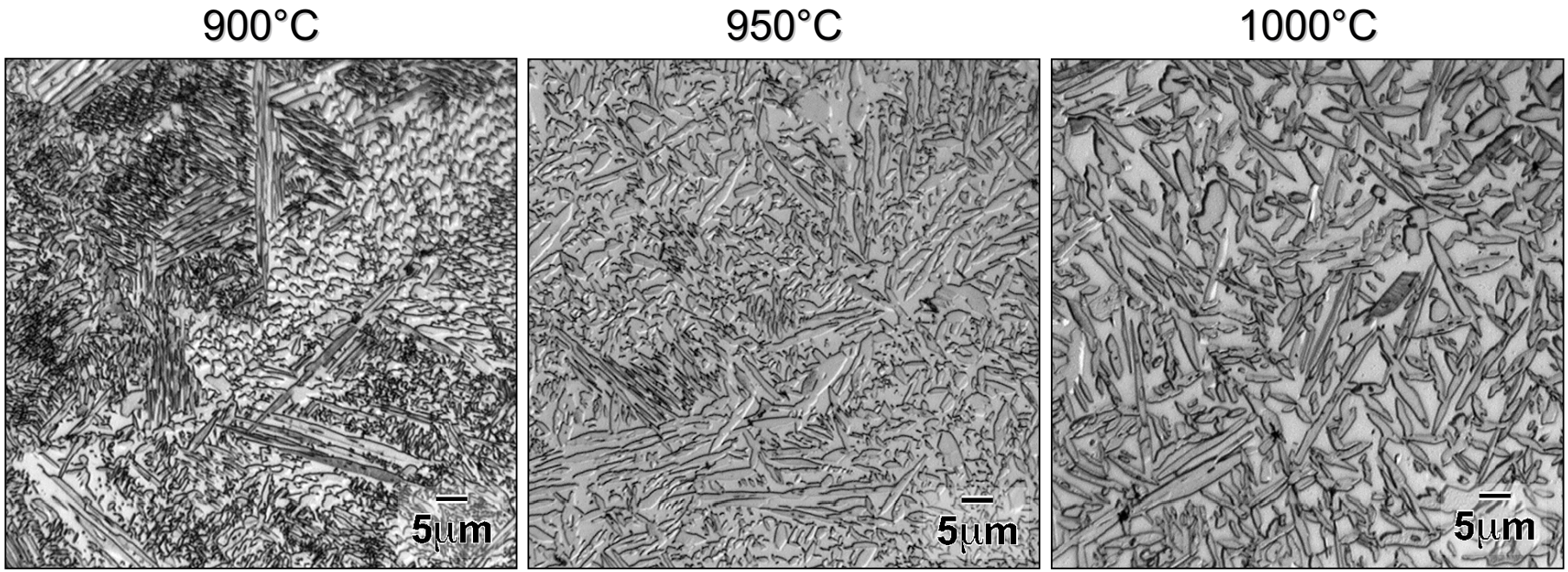
Cast Microstructure of Alloy 3 (V-32Ti-43Al)





- Solidification of primary disordered β phase, which orders to the B2 (CsCl) phase during cooling
- The γ-(TiAl) phase forms from the B2 phase

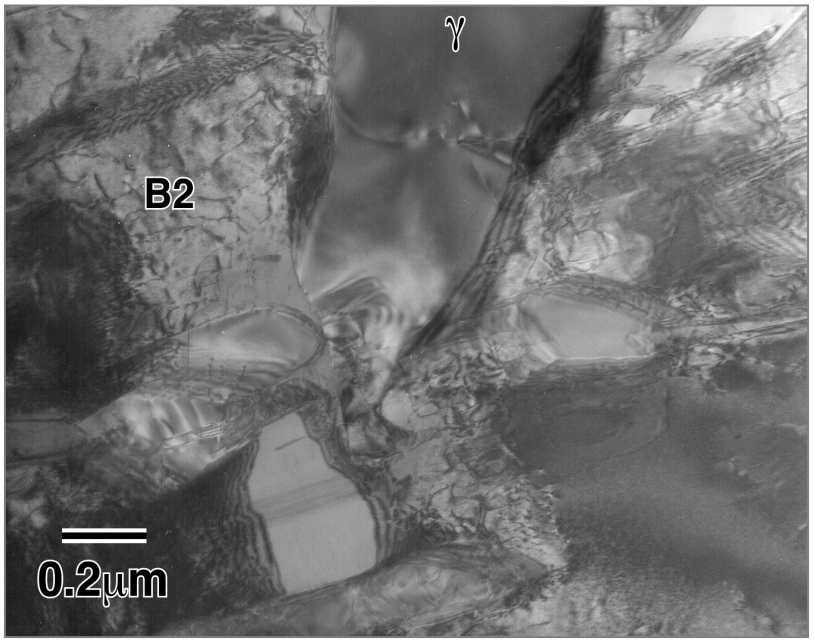
Development of Equilibrium Microstructures in Alloy 3



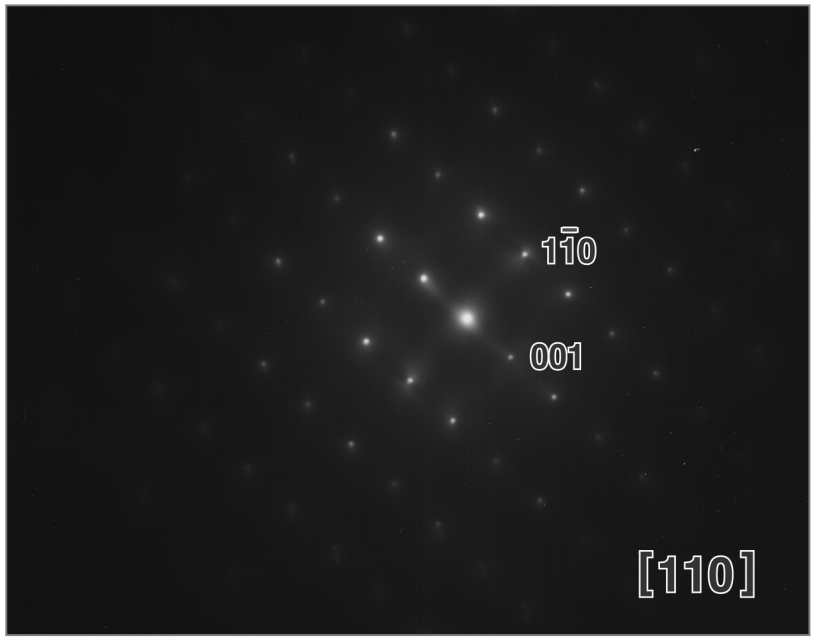
- Two-phase B2 + γ microstructure stable up to 1000°C
  - determining the high temperature β solvus temperature is required
- Volume fraction of γ plates increased during annealing
- Increase in microstructural scale at higher annealing temperatures

Formation of the γ-TiAl ($L1_0$) Phase from the B2 Matrix

Bright Field TEM

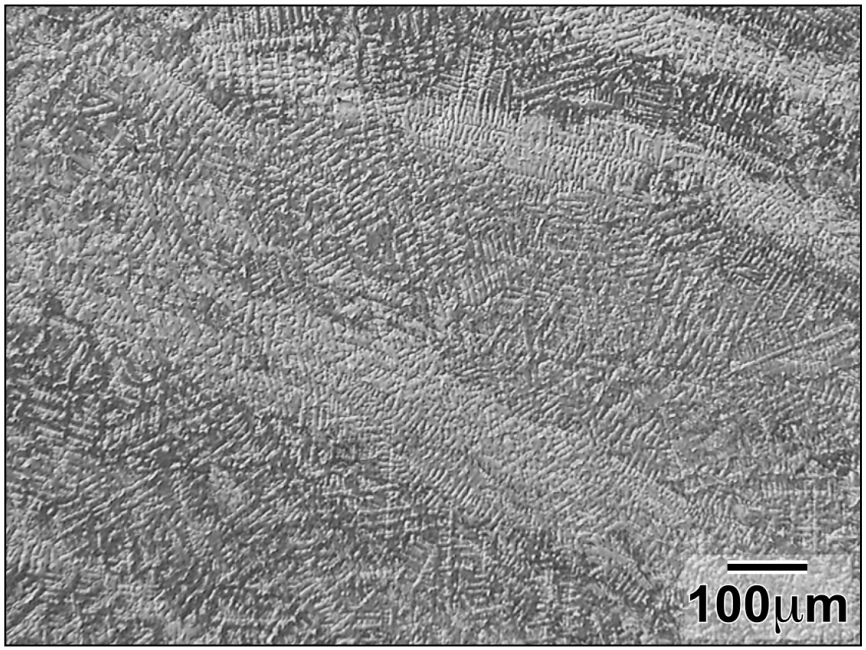


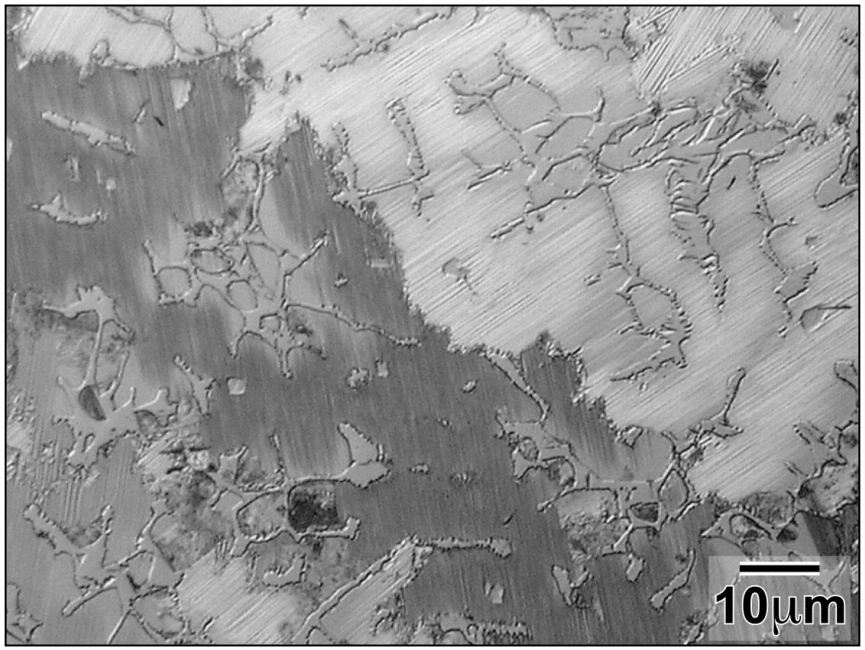
SAED Pattern



- Diffusional-based transformation
- Lath morphology
- SAED pattern of the $[110]_\gamma$ zone axis

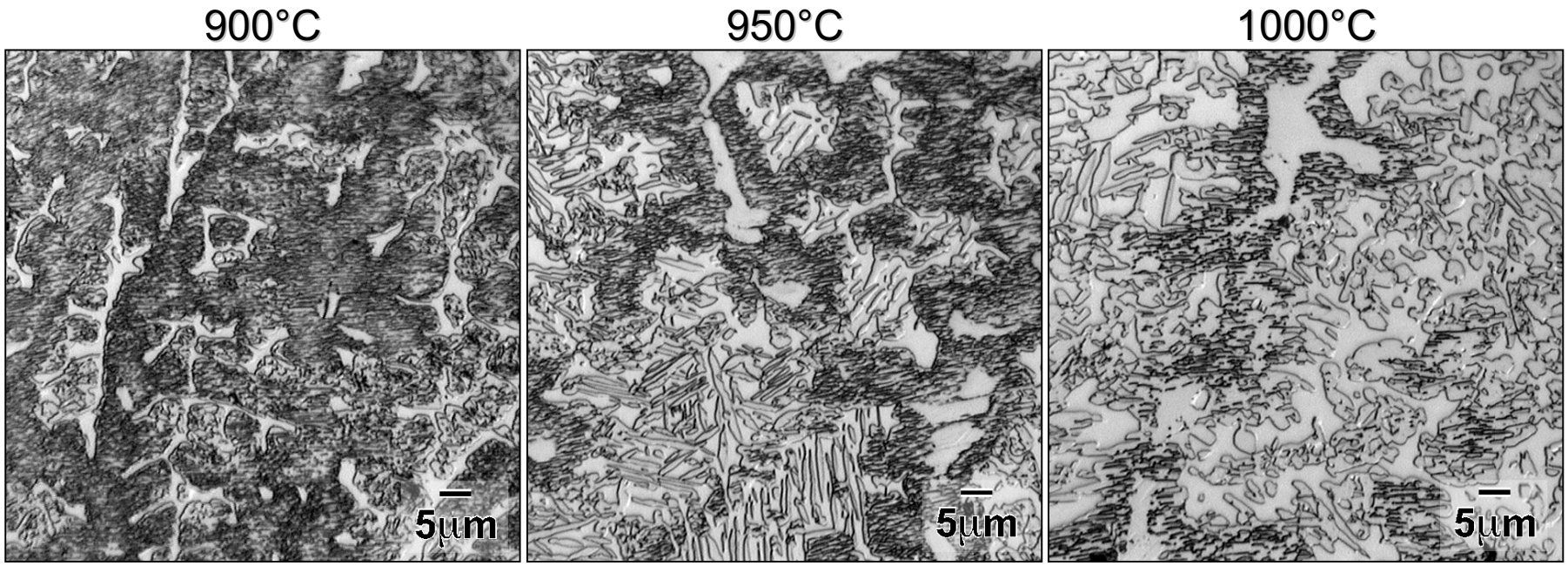
Cast Microstructure of Alloy 1 (V-16Ti-54Al)





- Primary phase dendrites and interdendritic secondary phase

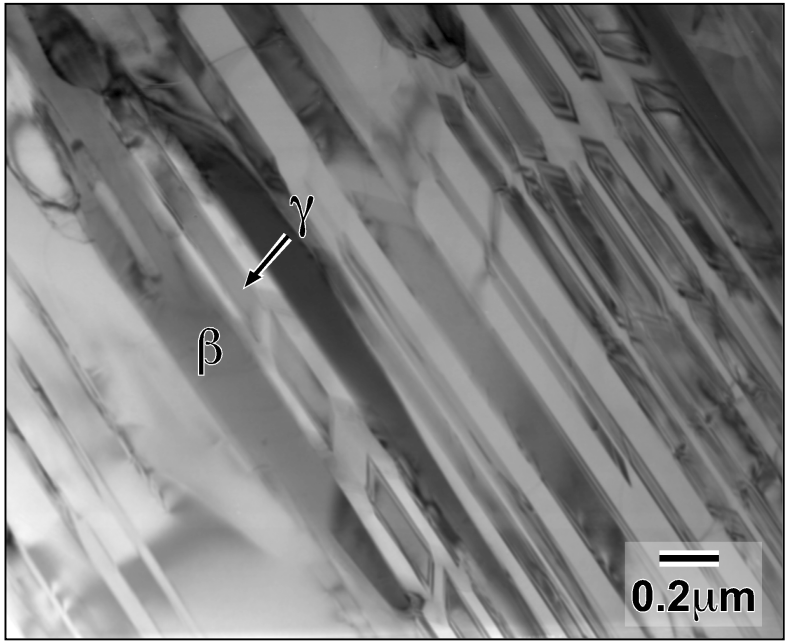
Development of Equilibrium Microstructures in Alloy 1



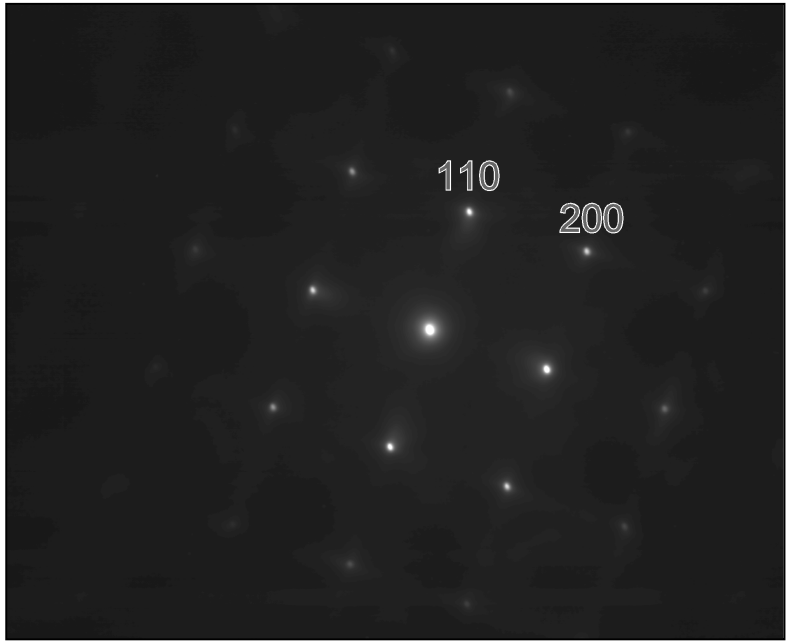
- Prior cast microstructures is retained during heat treatment
  - thermal-mechanical processing required for microstructural homogenization
- Microstructural scale increase at higher annealing temperatures
- Phase change occurred in prior lamellar ($\alpha_2 + \gamma$) dendrites

Formation of Lamellar β + γ Microstructure in Alloy 1 Following Annealing at 1000°C

Bright Field TEM

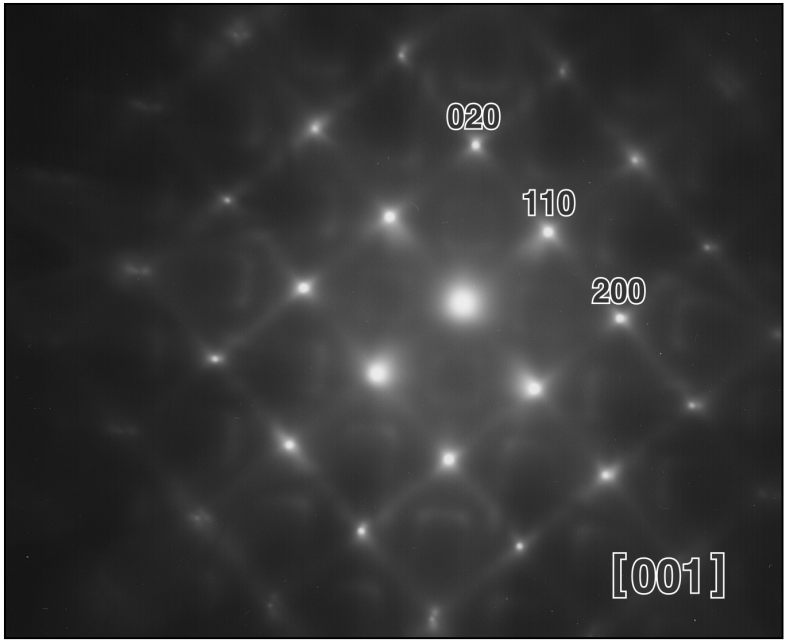


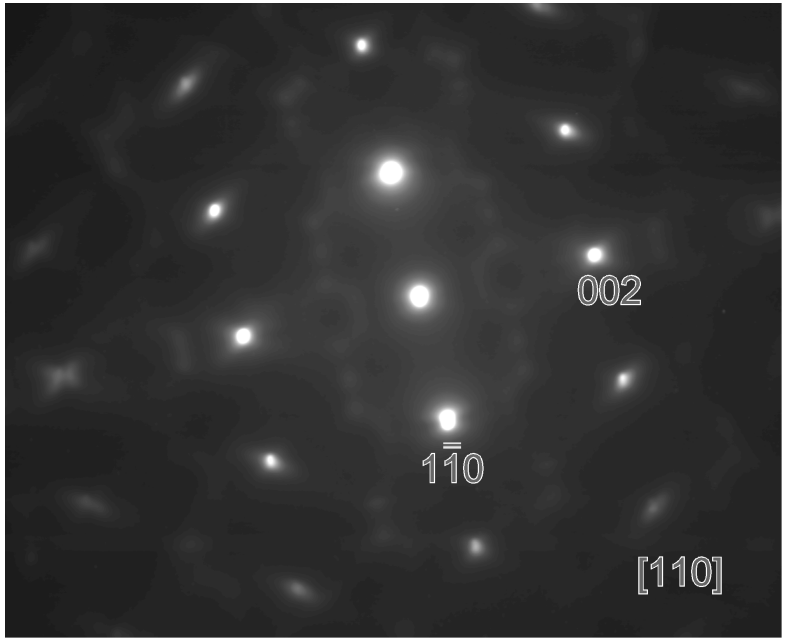
SAED Pattern of $[001]_\beta$ Zone Axis



- Significance of forming the lamellar β + γ microstructure:
  - high heterophase interfacial area
  - retention of high temperature creep properties
  - potential improvement in low temperature fracture toughness

The bcc β Phase Retains a Disordered Crystal Structure





- No <100> superlattice reflections from B2 ordering
- No diffuse scattering associated with the ω-phase
- The disordered β crystal structure and multi-phase approach could lead to improvements in the typically poor fracture toughness properties of intermetallic based alloys

Summary and Future Work

- Two alloy compositions will be investigated further:
  - Alloy 1 (31V-16Ti-54Al) - disordered β and γ -TiAl phases
  - Alloy 3 (25V-32Ti-43Al) - ordered β (B2) and γ-TiAl phases

- The results indicate that microstructural control can be achieved in the two alloys using physical metallurgy principles
  - Alloy 1 - thermal-mechanical processing to refine and homogenize the cast microstructure
  - Alloy 3 - solutionize in single β phase field, quench, and anneal

- Establish proof-of-principle with properties testing
  - oxidation resistance in He-atmosphere
  - low temperature fracture toughness