Nanoprecipitates in Steels

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- **Office of Fossil Energy, Advanced Research Materials (ARM) Program**
- **SHaRE User Facility**

Ferritic ODS steels retain good creep strength at high temperatures because they contain a few vol% of nanoscale oxide particles

Fe-Cr-Al-Y-based (~22 wt% Cr, ~ 6 wt% Al)

- PM956 (Special Metals Corporation); PM2000 (Plansee):

  $YAlO_3$ particles, size ~10 nm

Fe-Cr-Ti-Y-based (~14 wt% Cr, ~ 0.5 wt% Ti

- PM957 (INCO Metals)
- 12YWT (Kim, Maziasz, 2003)
- 14YWT (Hoelzer, Miller, 2005)

  Complex Ti-Y-O nanoclusters, size ~ 4 nm

Mechanical alloying has been used since ~1970 (classic paper by Benjamin), BUT

- **High cost**
- **High energy consumption**
- **Reproducibility is an issue**
- **Inhomogeneity**
- **Porosity**
- **Joining difficult, although progress has been made (Wright, Kad, Hurley)**

MA956 and PM2000 have been discontinued:

- Limited market penetration due to high cost

Mechanical Alloying is not always needed for producing ultra-fine dispersoids – internal oxidation is also an option

- **Diffusion-controlled process resulting in the selective oxidation of a less noble solute**
- **Model systems:**
  - **Ag-Sn -> SnO_2**
  - **Ag-Al -> Al_2O_3**
  - **Cu-Si -> SiO_2**
  - **Cu-Al -> Al_2O_3**

GlidCop© copper is the only ODS material available in large quantities

GlidCop© copper is processed by

INTERNAL OXIDATION

of Cu-Al powder mixed with copper oxide powder

- Al_2O_3 particles 3-12 nm in size
- interparticle spacing 30-100 nm

Processing of ODS ferritic steels by internal oxidation of powders instead of mechanical alloying?

We are trying to ompeting with a process that has been studied and commercially used for ~40 years

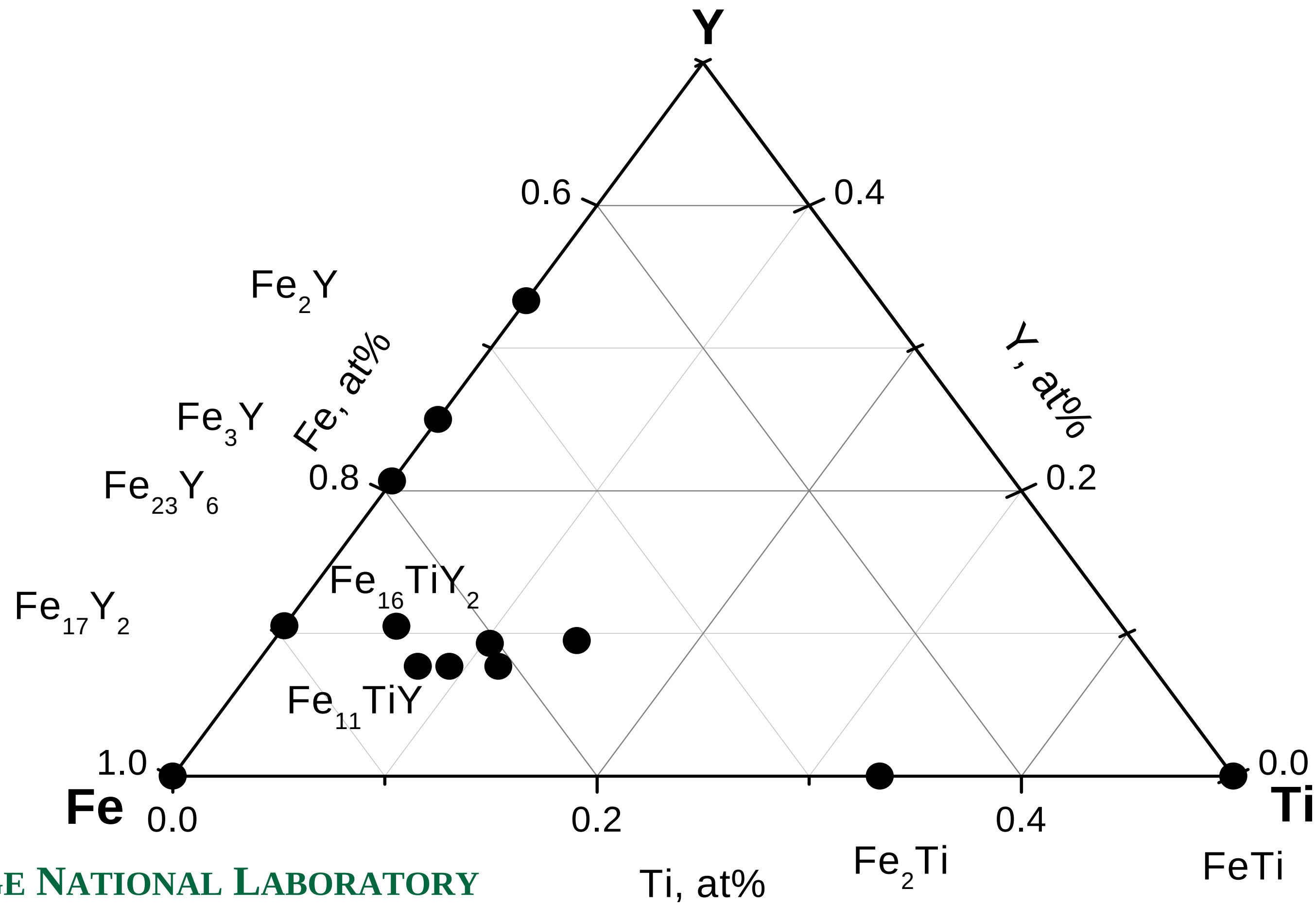
Ferritic ODS steels by internal oxidation: potential road blocks

- **Solubility of oxygen in bcc iron very low (a few ppm)**
  - **small concentration gradients, slow mass transport**
- **If several % of Al are needed, the Al can only be added after internal oxidation or else massive amounts of coarse alumina will form**

  -> diffusion of Al into internally oxidized Fe-Cr-Y powders?

Intermetallic Precursors

$Fe_{17}Y_2$, ~ $Fe_{16}Al_1Y_2$, ~$Fe_{11}TiY$



Solid Solution Precursor

Solubility limits in iron:

- **Y<0.6 at% at 1350^{o}C**
- **Ti = 10 at% at 1289^{o}C**
- **Al ~45 at% at 1310^{o}C**

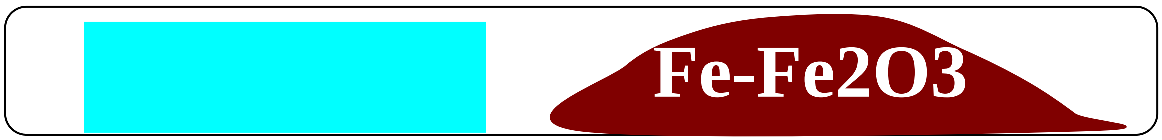
The low solubility of Y limits the oxide volume fraction that can be obtained

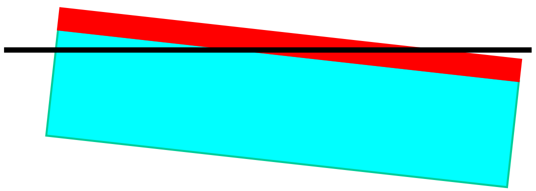
Experimental Procedure: processing of alloys

- **Arc-cast and homogenized alloys**
- **argon-atomized Fe-0.25 at% Y powder from Crucible Research**

Experimental Procedure: internal Oxidation

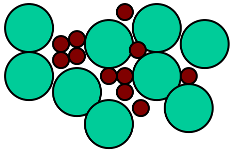
(a) encapsulate alloy coupon in evacuated quartz tube with non-contacting Fe-Fe_2O_3 powder mixture to generate suitable oxgyen partial pressure (Rhines pack)

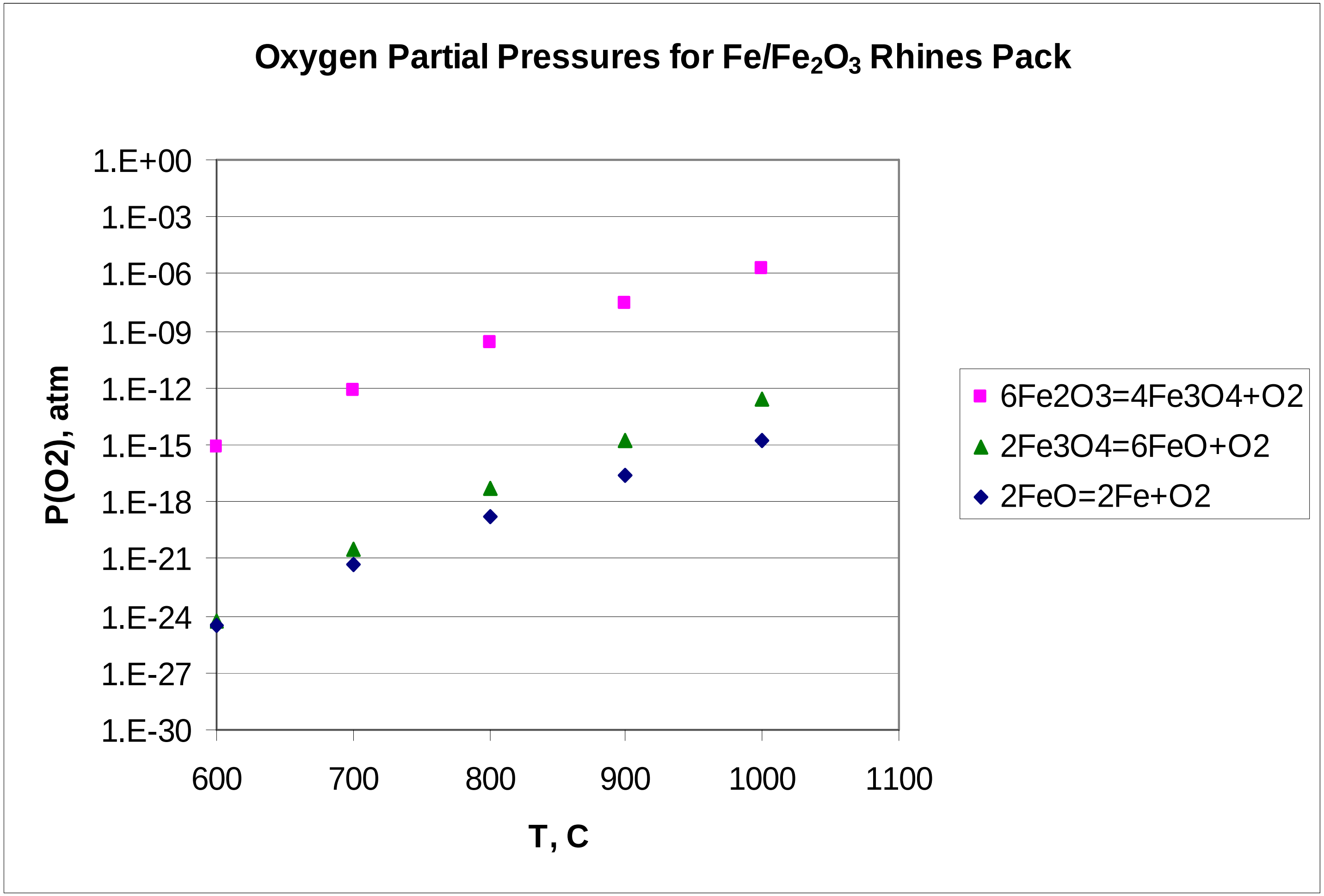




(b) mix alloy powder with Fe_2O_3 and anneal in vacuum:

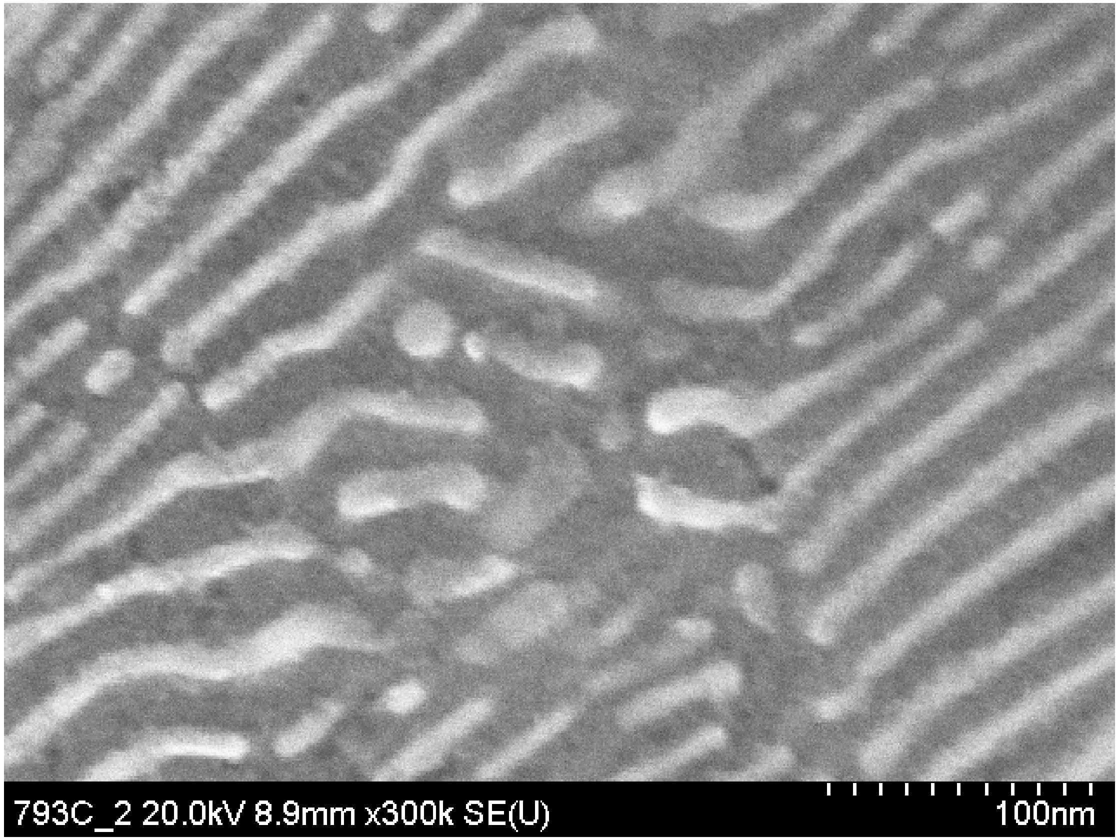
Displacement reaction $Fe_2O_3 + 2Y \rightarrow 2Fe + Y_2O_3$




Oxygen Partial Pressures for Fe/Fe2O3 Rhines Pack
1.E+00
1.E-03
1.E-06
1.E-09
1.E-12
1.E-15
1.E-18
1.E-21
1.E-24
1.E-27
1.E-30
P(O2), atm
600
700
800
900
1000
1100
T, C
6Fe2O3=4Fe3O4+O2
2Fe3O4=6FeO+O2
2FeO=2Fe+O2

Internal Oxidation of $Fe_{17}Y_2$ Intermetallic Coupon

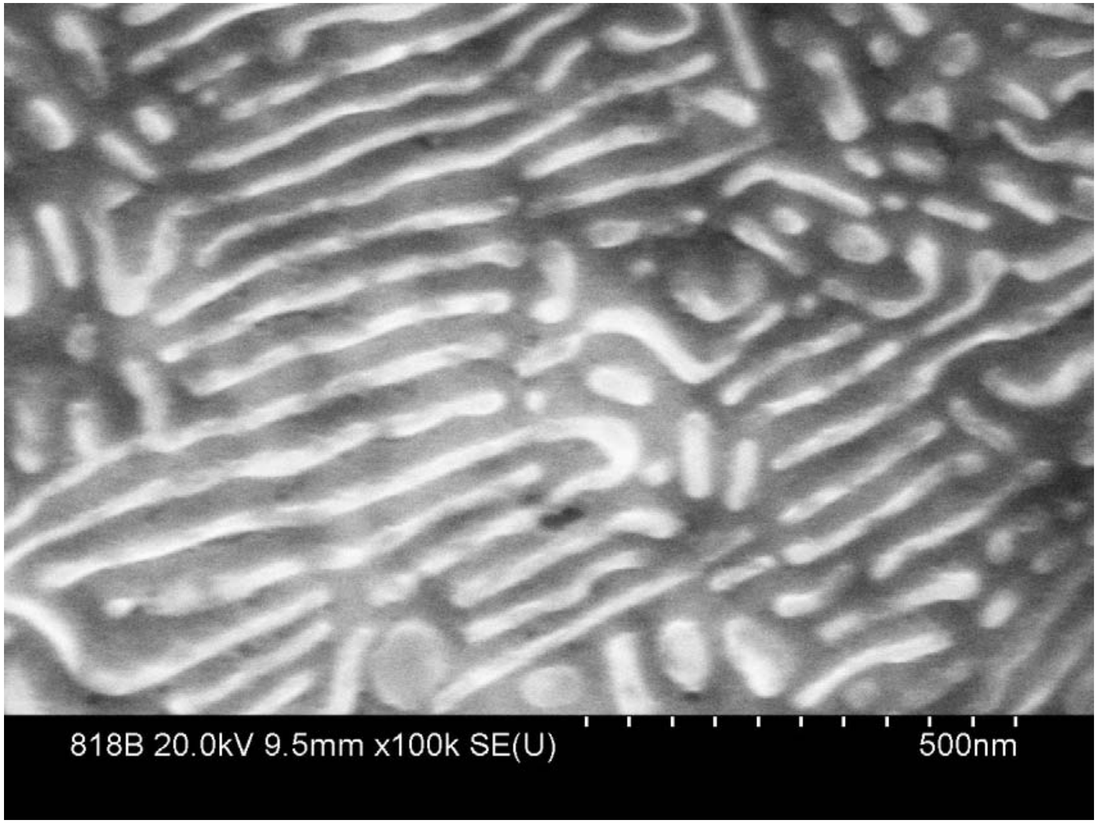
$Fe_{17}Y_2$ annealed with Fe-Fe_2O_3 Rhines pack for 3 days at 700°C: 10 nm Y_2O_3 lamellae!



Internal Oxidation
of $Fe_{17}Al_1Y_2$ Intermetallic Coupon

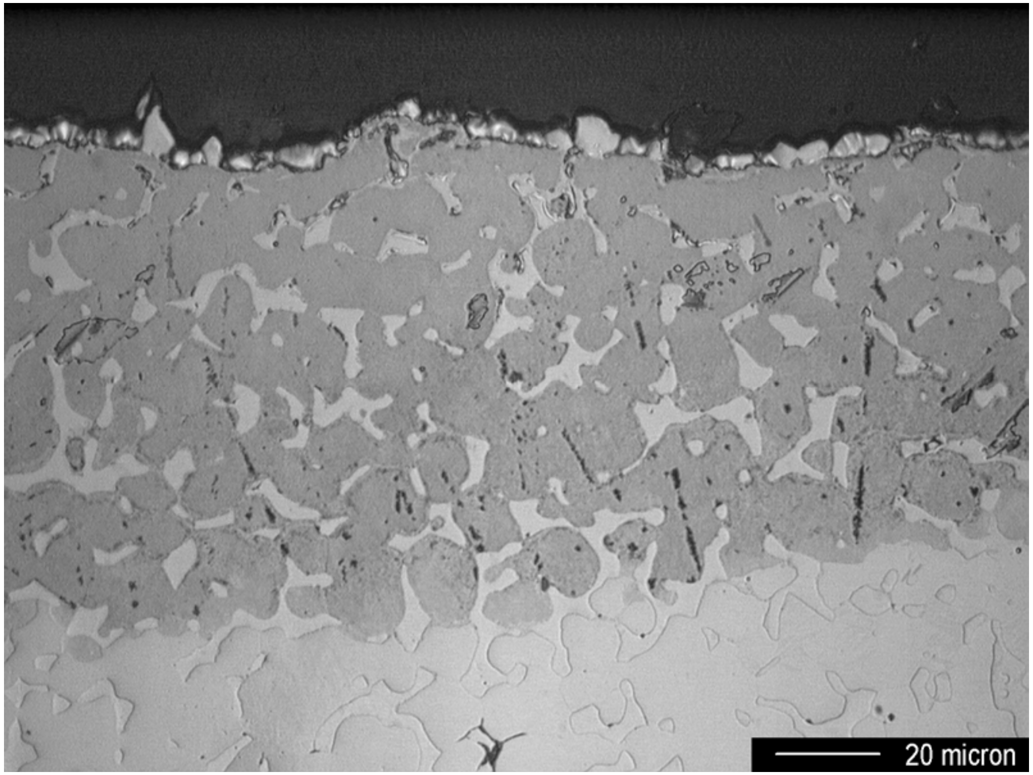
$Fe_{17}Al_1Y_2$ Intermetallic coupon

Fe/Fe_2O_3 Rhines Pack, 3 days-700^oC

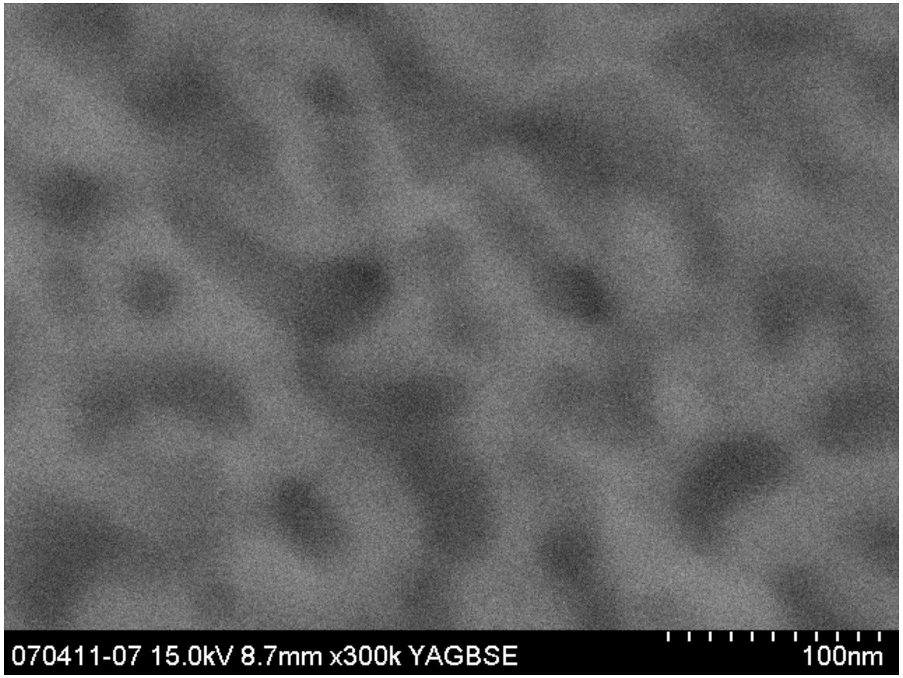


Internal Oxidation of Fe-Ti-Y Intermetallic Coupon

Fe-6.5Ti-6.5Y coupon, at%
Fe-Fe_2O_3 Rhines pack, 3d/700^oC
Penetration Depth ~60 micron

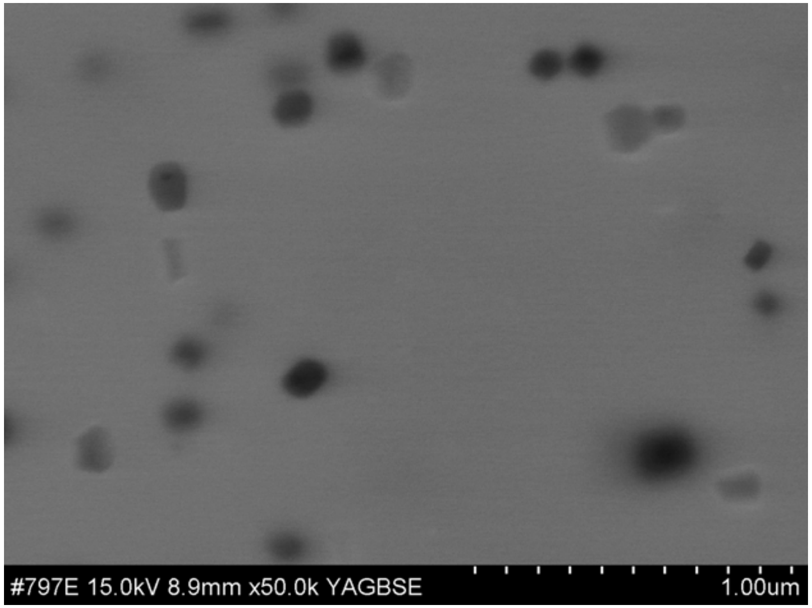


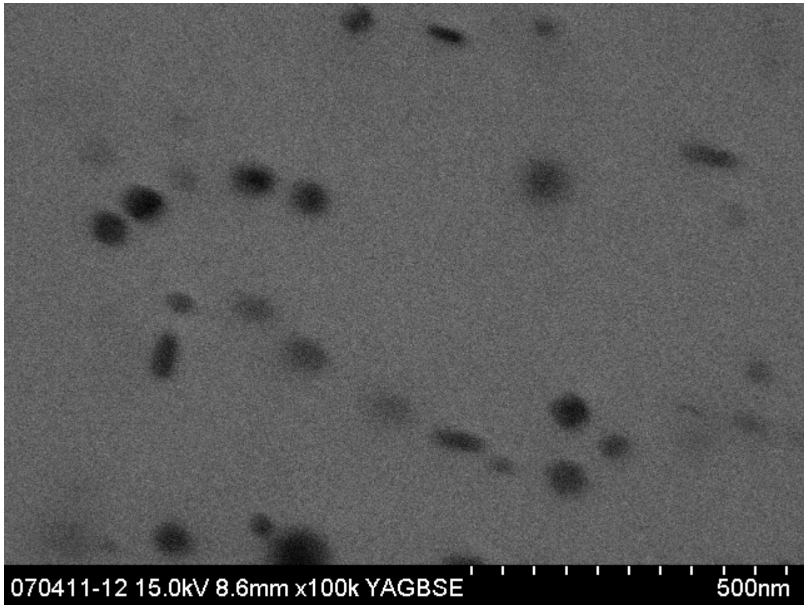
Fe-6.5Ti-6.5Y coupon, Fe-Fe_2O_3 Rhines pack, 3 days at 700˚C
20 nm particles: $Y_2Ti_2O_7$ and Fe_2TiO_4



Internal Oxidation of Fe-0.8Ti-0.4Y (at%) Solid Solution Coupon

Fe-0.8Ti-0.4Y (at%) coupon
annealed with Fe-Fe_2O_3 Rhines pack



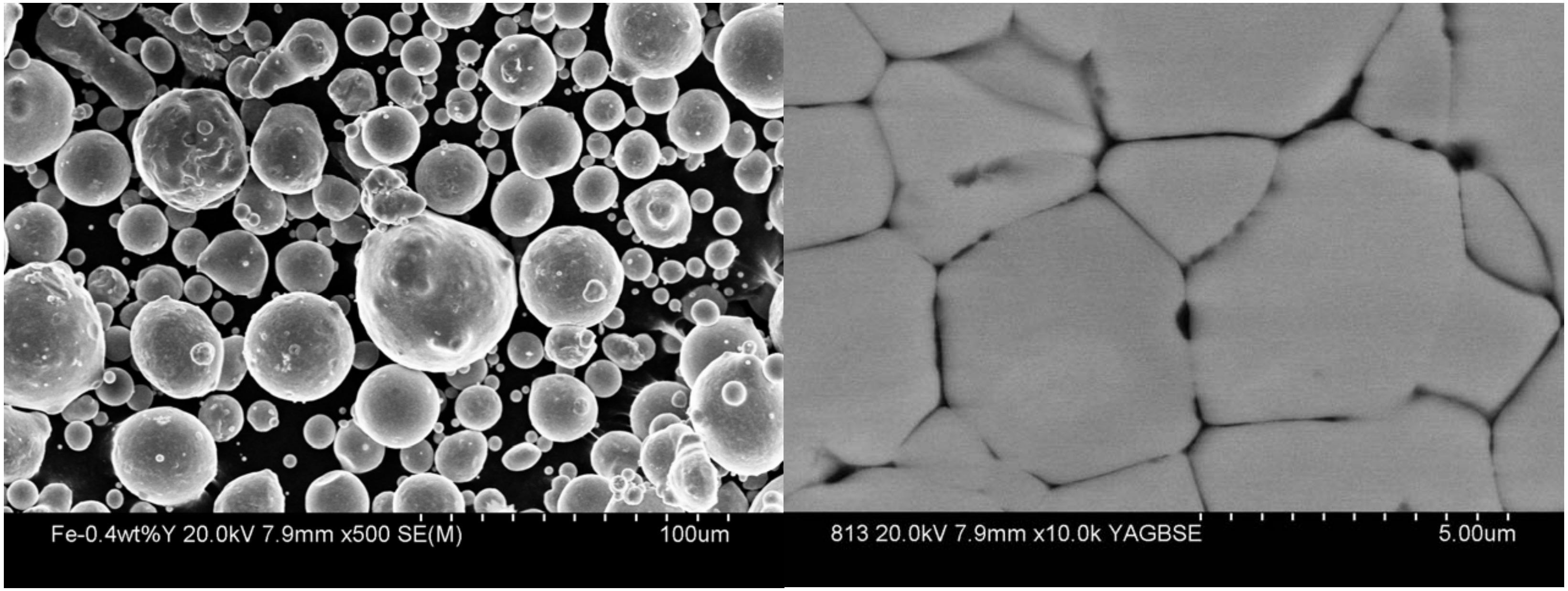


4 days – 800^{o}C
~100 nm

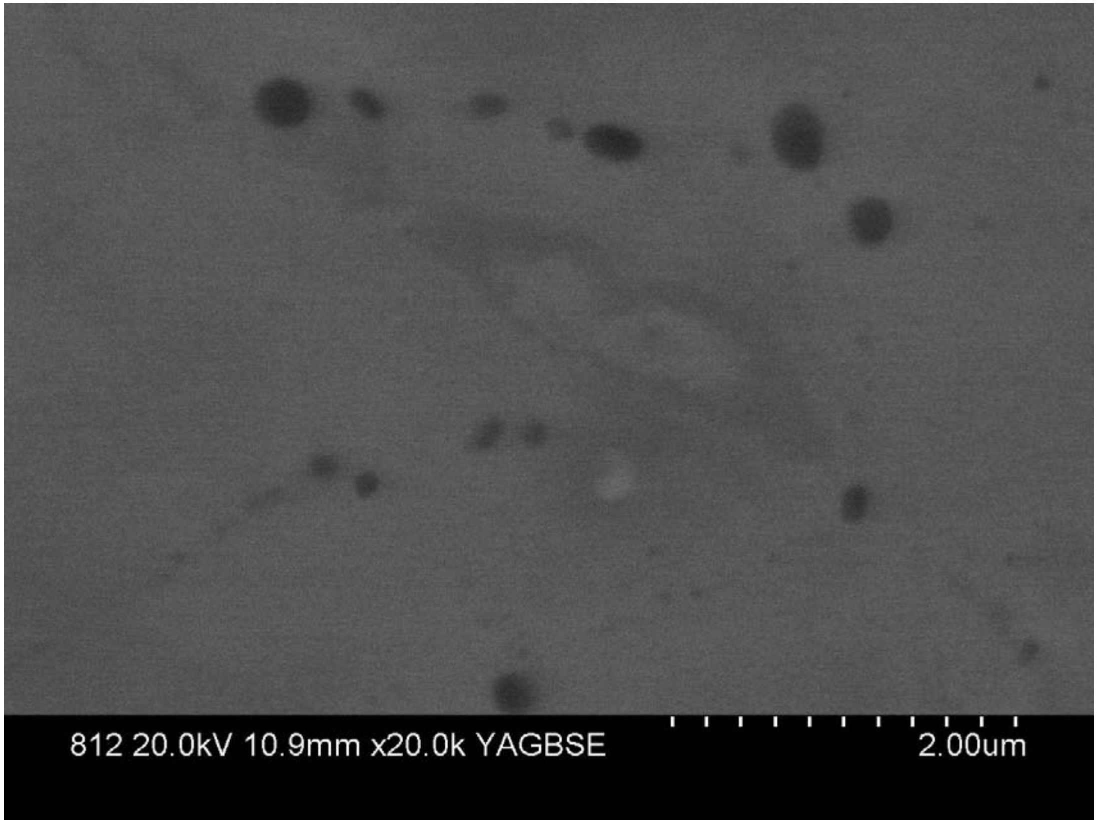
4 days – 700^{o}C
~50 nm

Internal Oxidation and Consolidation of Fe-0.25 at%Y Powder

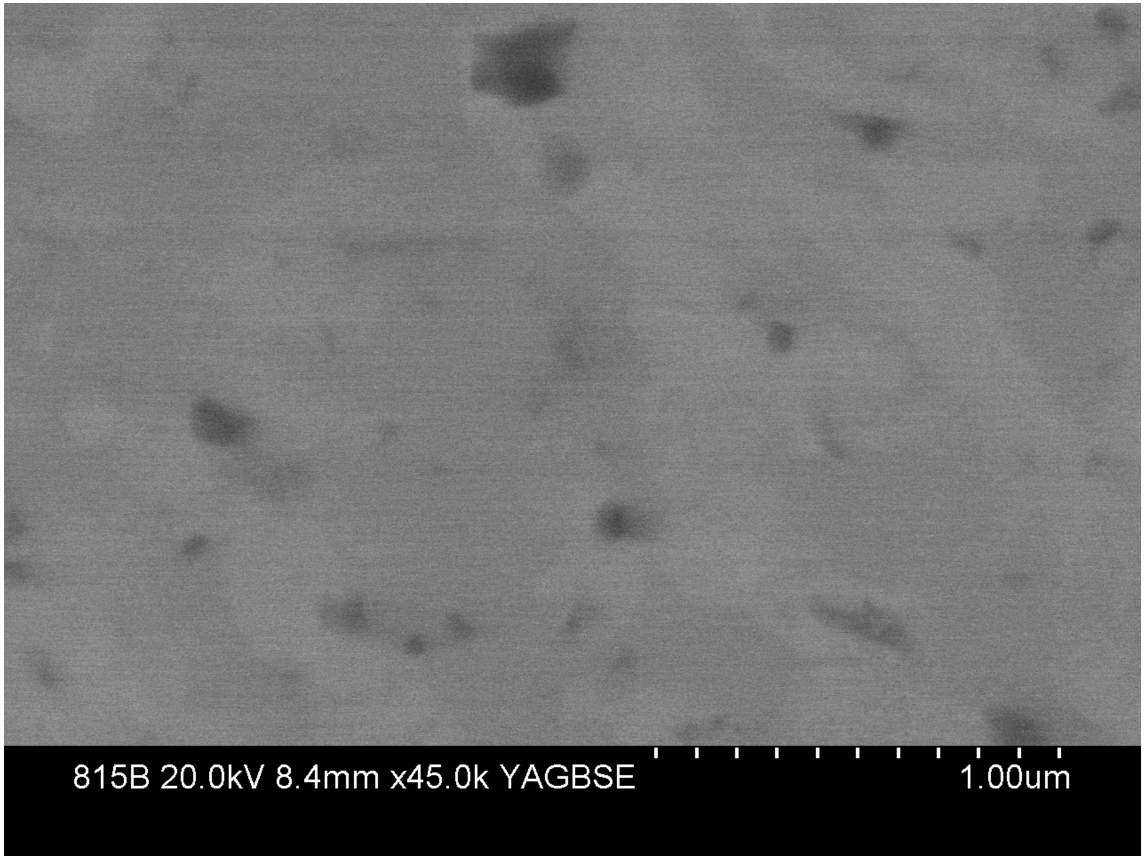
Argon-atomized Fe-0.25 at% Y powder (Crucible Research)



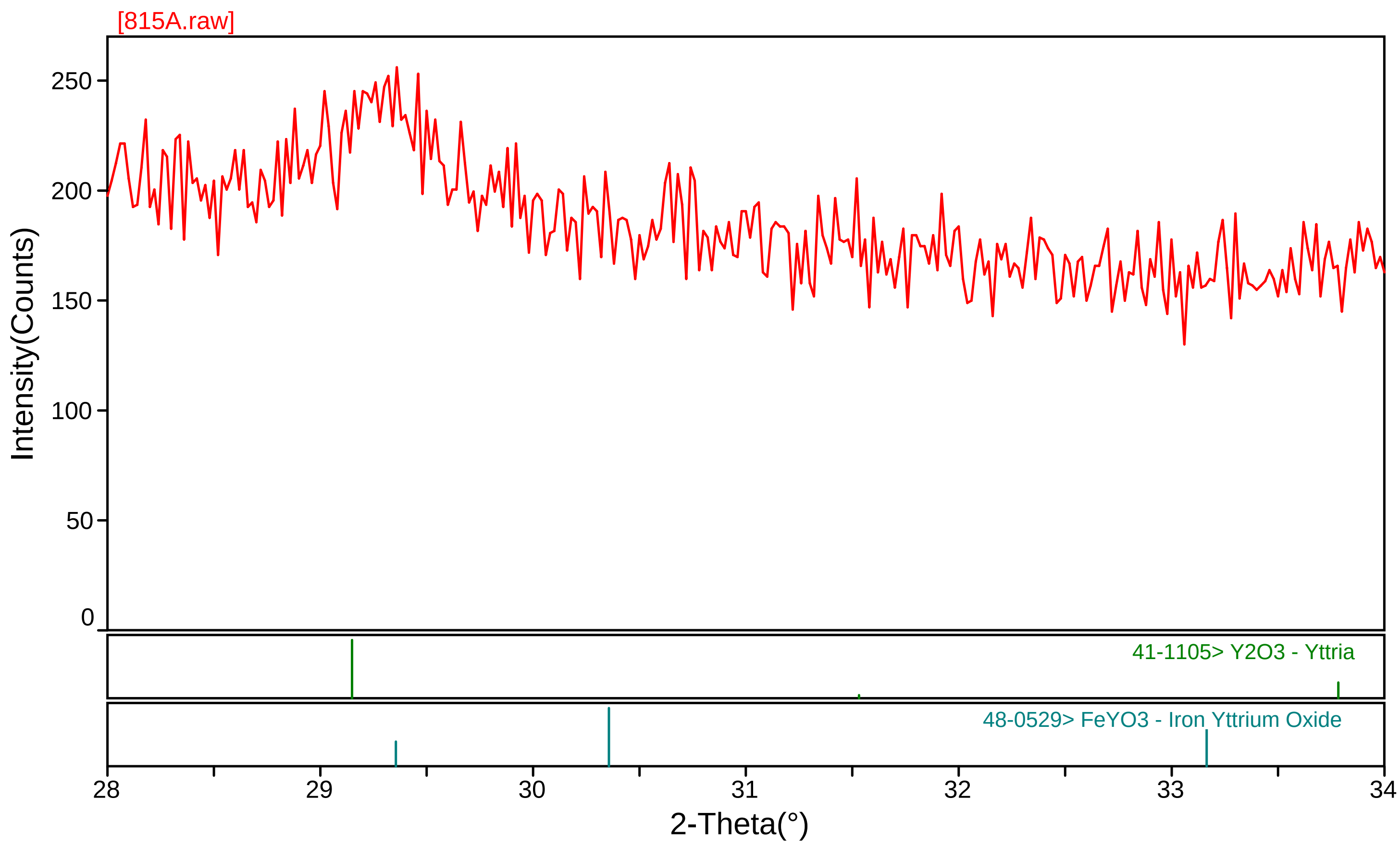
Fe-0.25Y, at%, atomized powder
Fe-Fe_2O_3 Rhines pack, 3d-1000C



Fe-0.25 at% Y, annealed with Fe_2O_3 pwdr 1day-1000C-Vac (covered crucible)



Fe-0.25 at% Y, annealed with Fe_2O_3 in vacuum for 1 day at 1000ºC: Powder xrd indicates Y_2O_3



Consolidation of Fe-0.25 at% Y powder with and without internal oxidation

Canning of Fe-Y powders with and without Fe_2O_3 addition

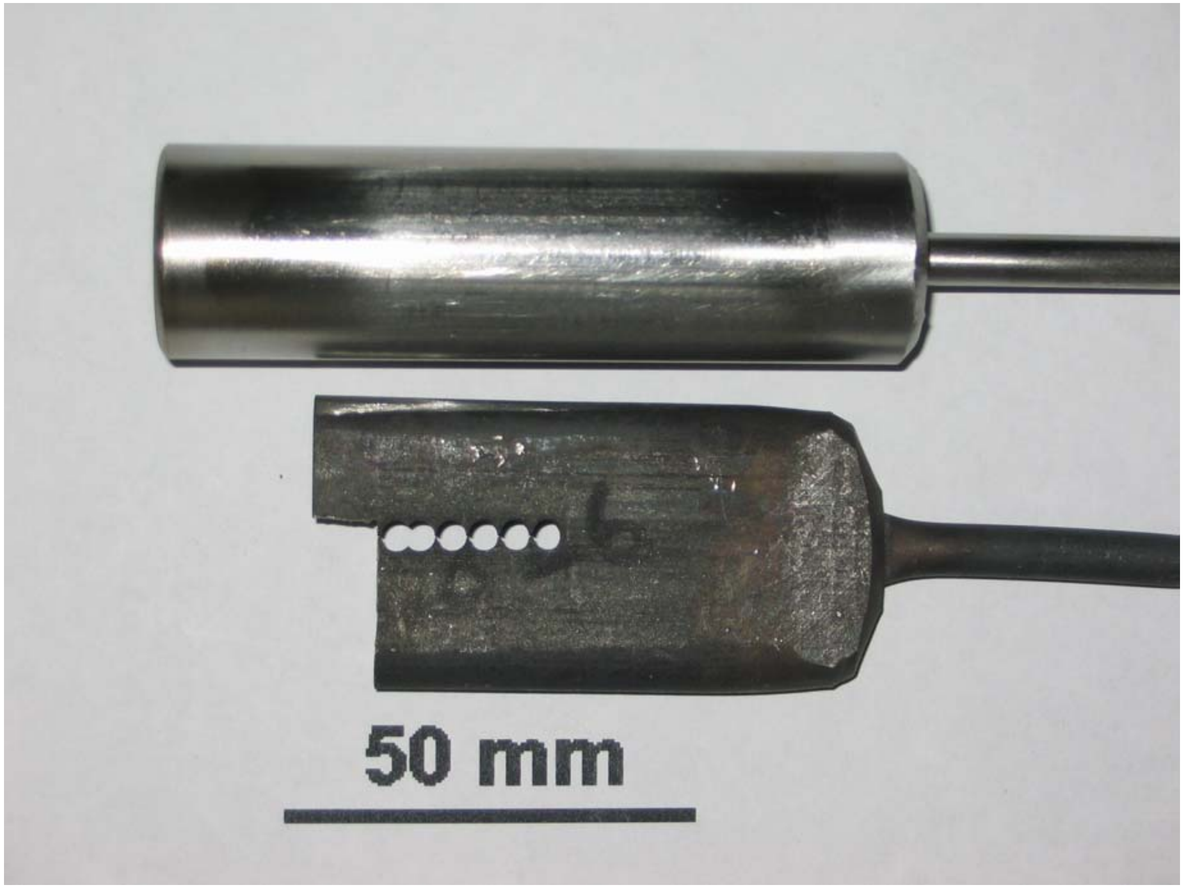
Anneal 3d-800^{o}C (internal oxidation)

Hot forge at 800^{o}C

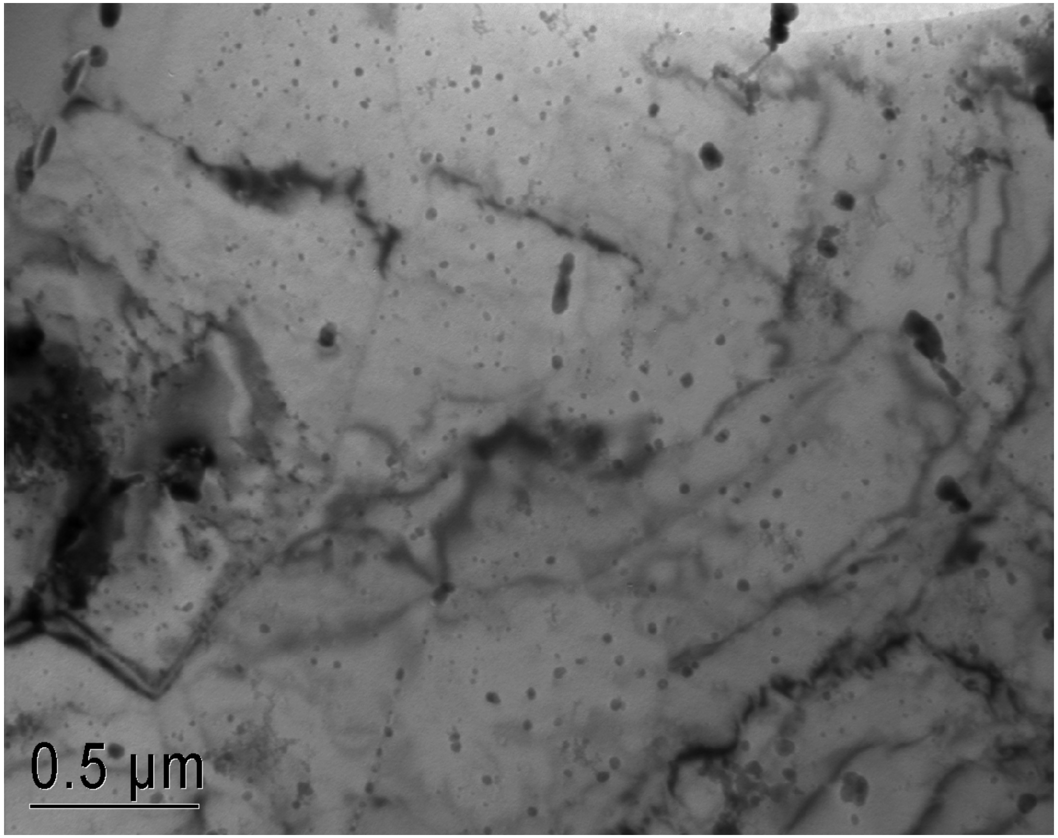
Anneal for 1hr at 1000^{o}C

Measure strength at room temperature and 800^{o}C

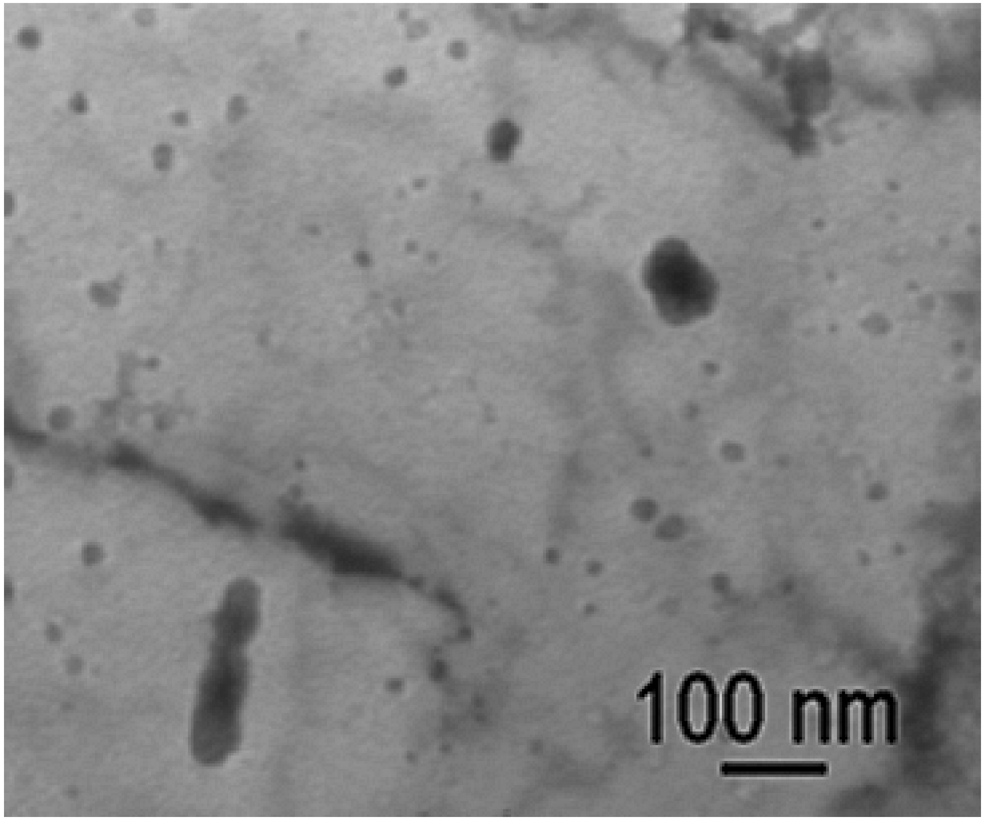
Hot forging from height of ~25 mm to ~10 mm



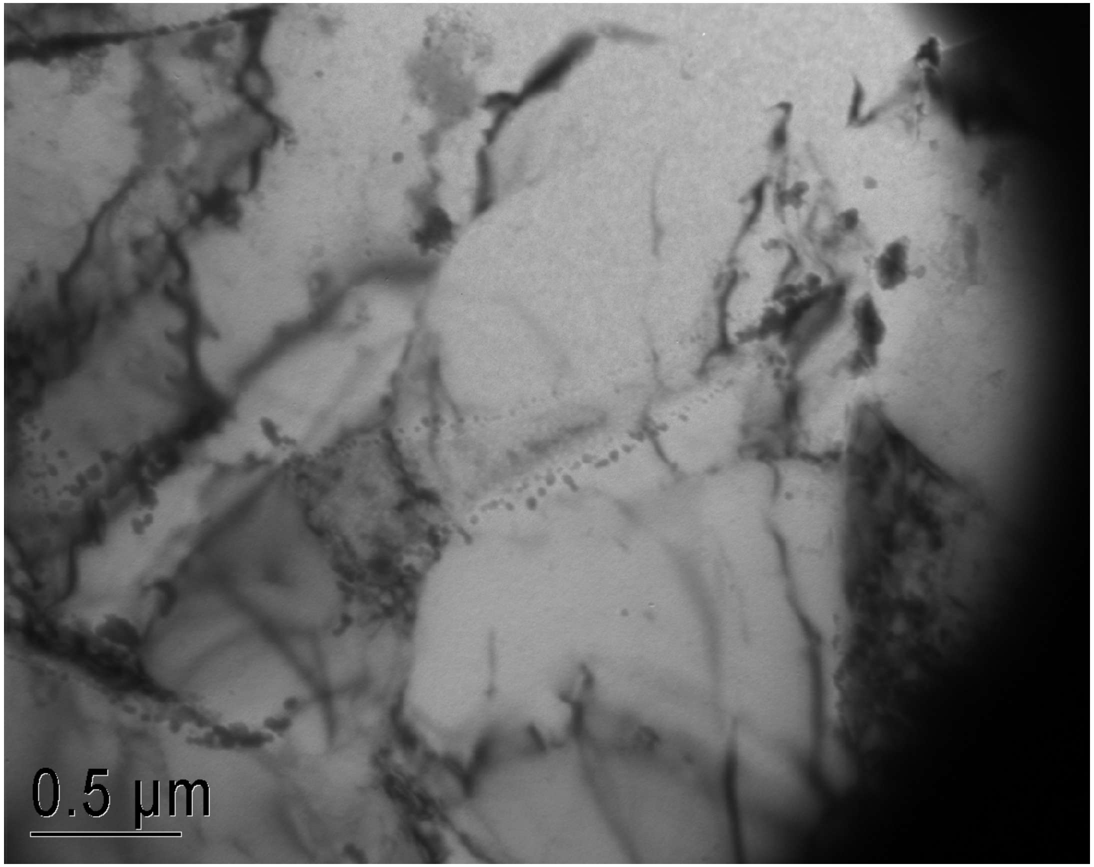
TEM of internally oxidized Fe-0.25 at%Y hot-forged, annealed 1hr-800^{o}C-Vac



TEM of internally oxidized Fe-0.25 at%Y hot-forged and annealed 1hr-800^{o}C-Vac



TEM of internally oxidized Fe-0.25 at%Y
hot-forged, annealed 1hr-800ºC-Vac
inhomogeneous particle distribution



Fe-0.25 at% Y, forged, 1hr-1000°C-Vac

Internal oxidation results in strengthening

	0.2% YS RT (MPa)	true stress at 5% 800°C, 1E-5/s (MPa)
Without Y_2O_3	***153***	***41***
With Y_2O_3	***209***	***49***

Composition critical for obtaining fine, stable oxide particles:

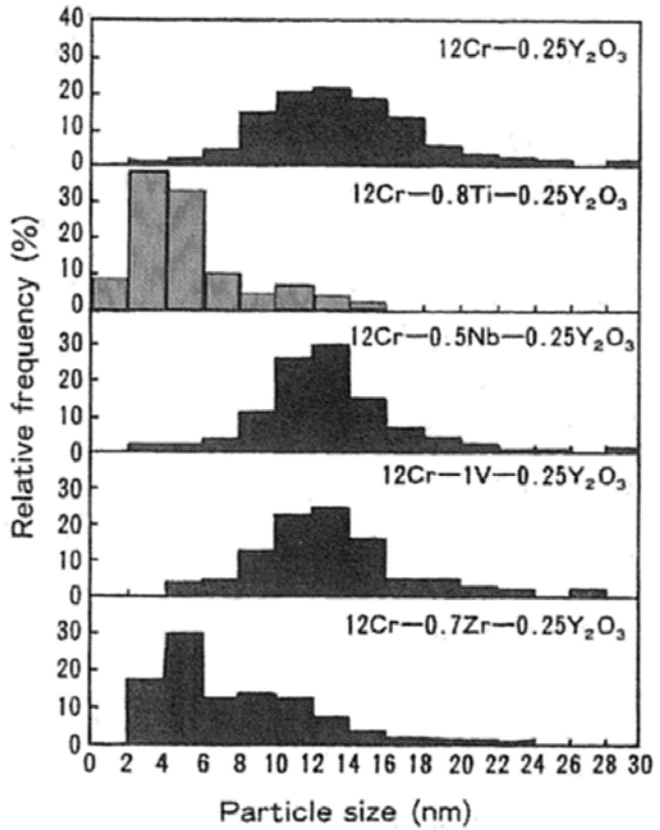


Fig. 1. Size distribution of oxide particles determined by TEM in 12Cr-ODS ferritic steels in various elements addition: Ti, Nb, V and Zr [13].

Ukai&Fujiwara Mechanical Alloying (2002):

Finding the right composition: Need rapid screening tests

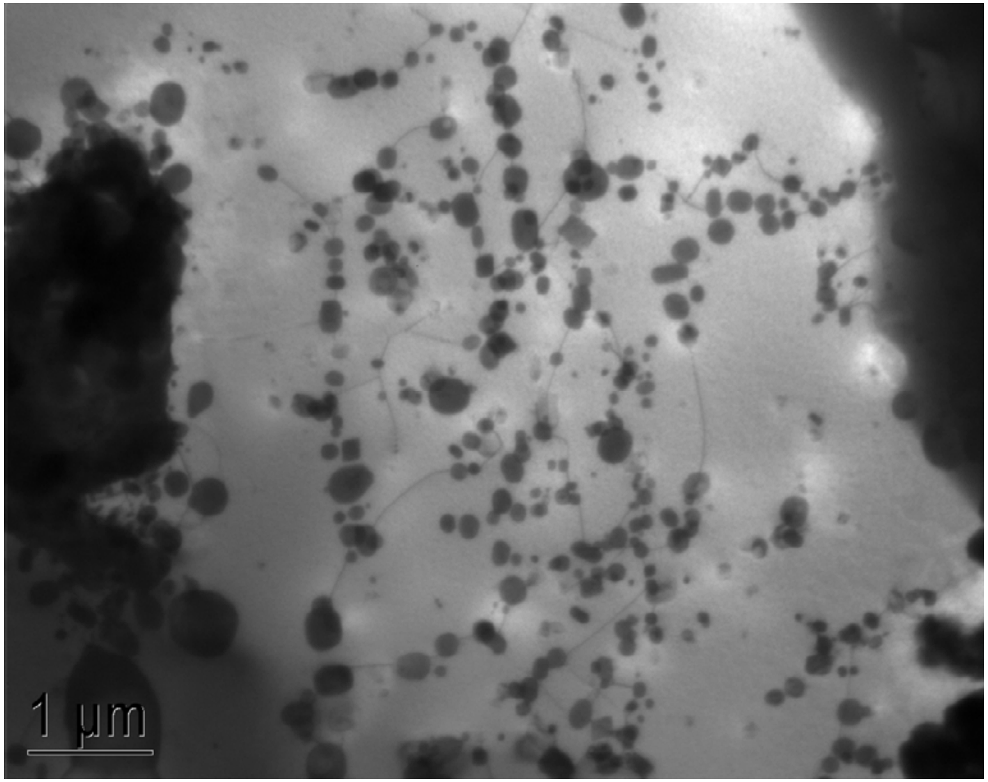
(a)

- cold rolling of castings into foils
- internal oxidation
- Conventional preparation of TEM specimens

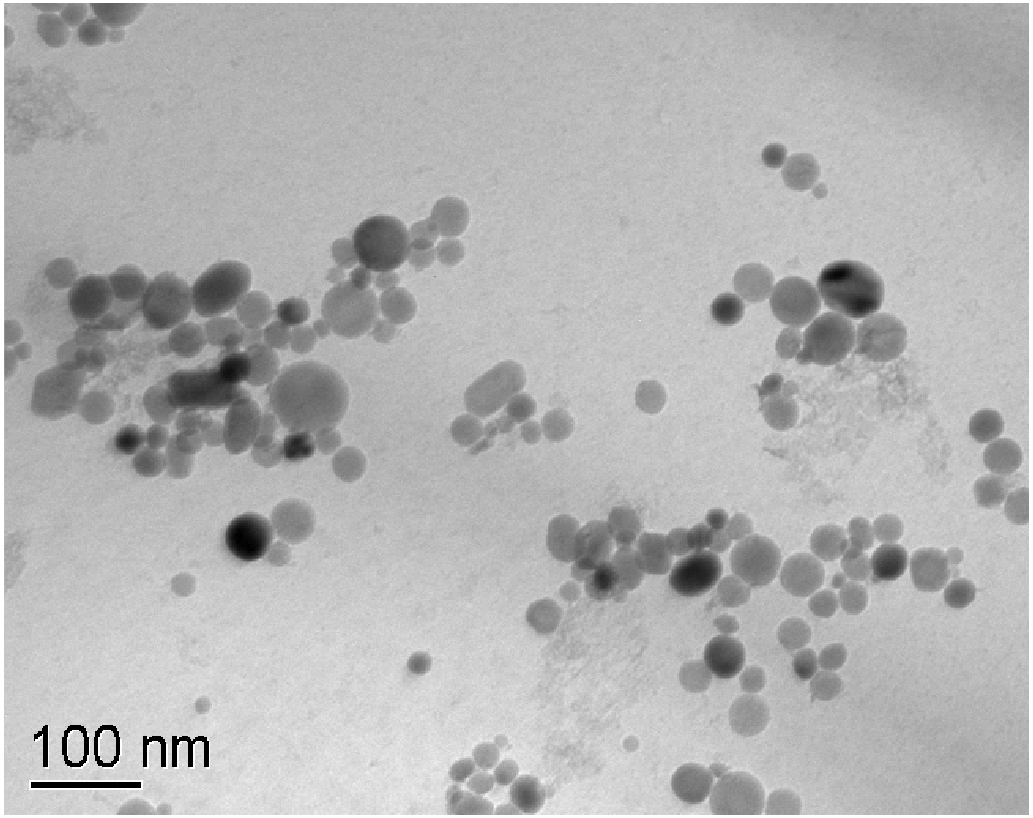
(b)

- Internal oxidation of coupons
- FIB preparation of TEM specimens (small mass is a plus for ferromagnetic material)

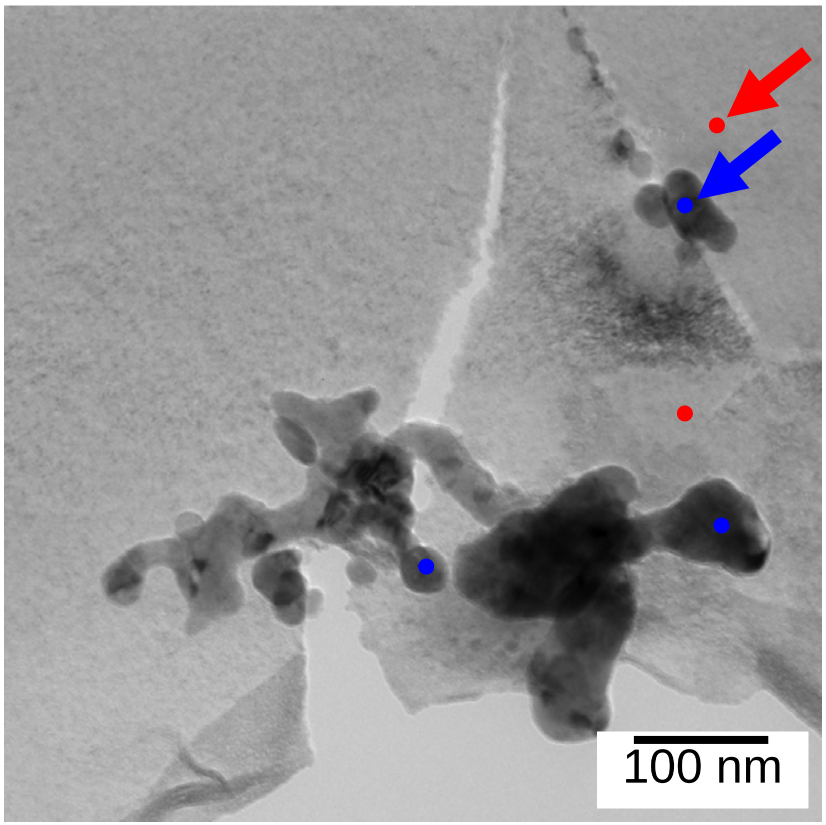
Fe-0.8Ti-0.4Y, at%, cold-rolled to ~40 micron, internal oxidation with Fe/Fe_2O_3 Rhines pack for 4 days at 800^{o}C, TEM

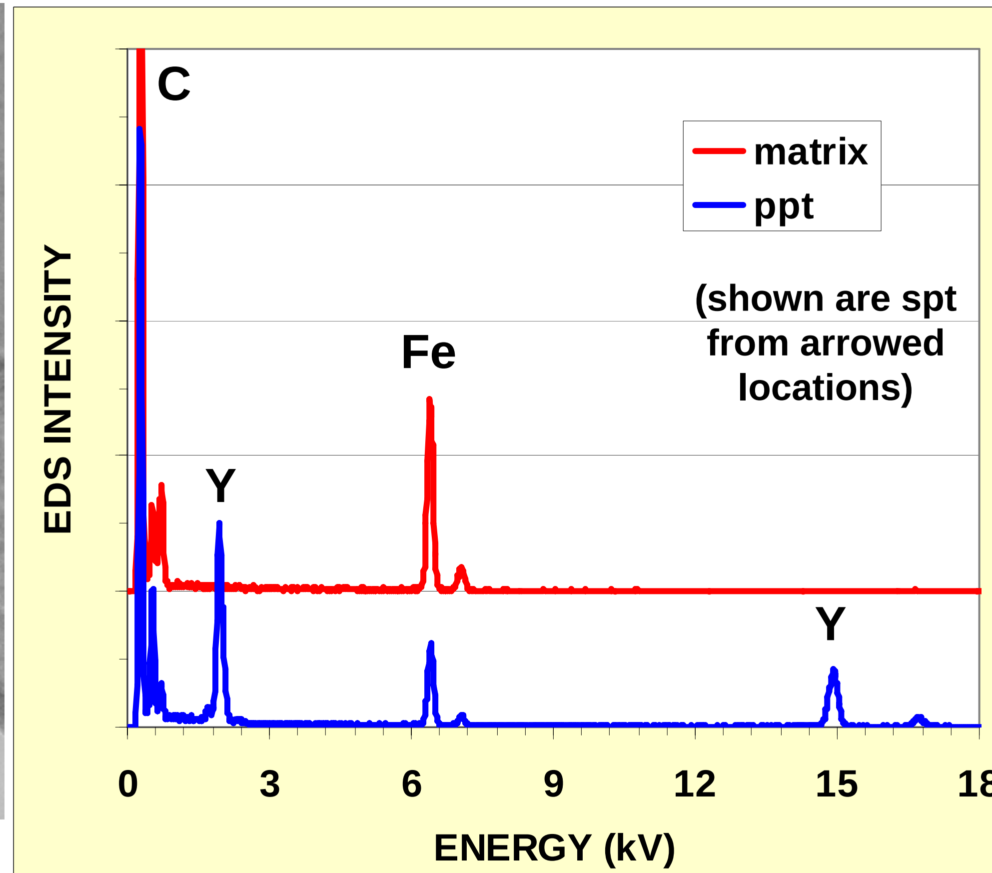


Internally oxidized 40 micron foil of Fe-0.8Ti-0.4Y (at%) foil, TEM



Fe-0.8Ti-0.4Y (at.%), cold rolled to ~40 μm, internal oxidation with Fe/Fe_2O_3 Rhines pack for 4 days at 800^{o}C (TEM by Neal Evans)





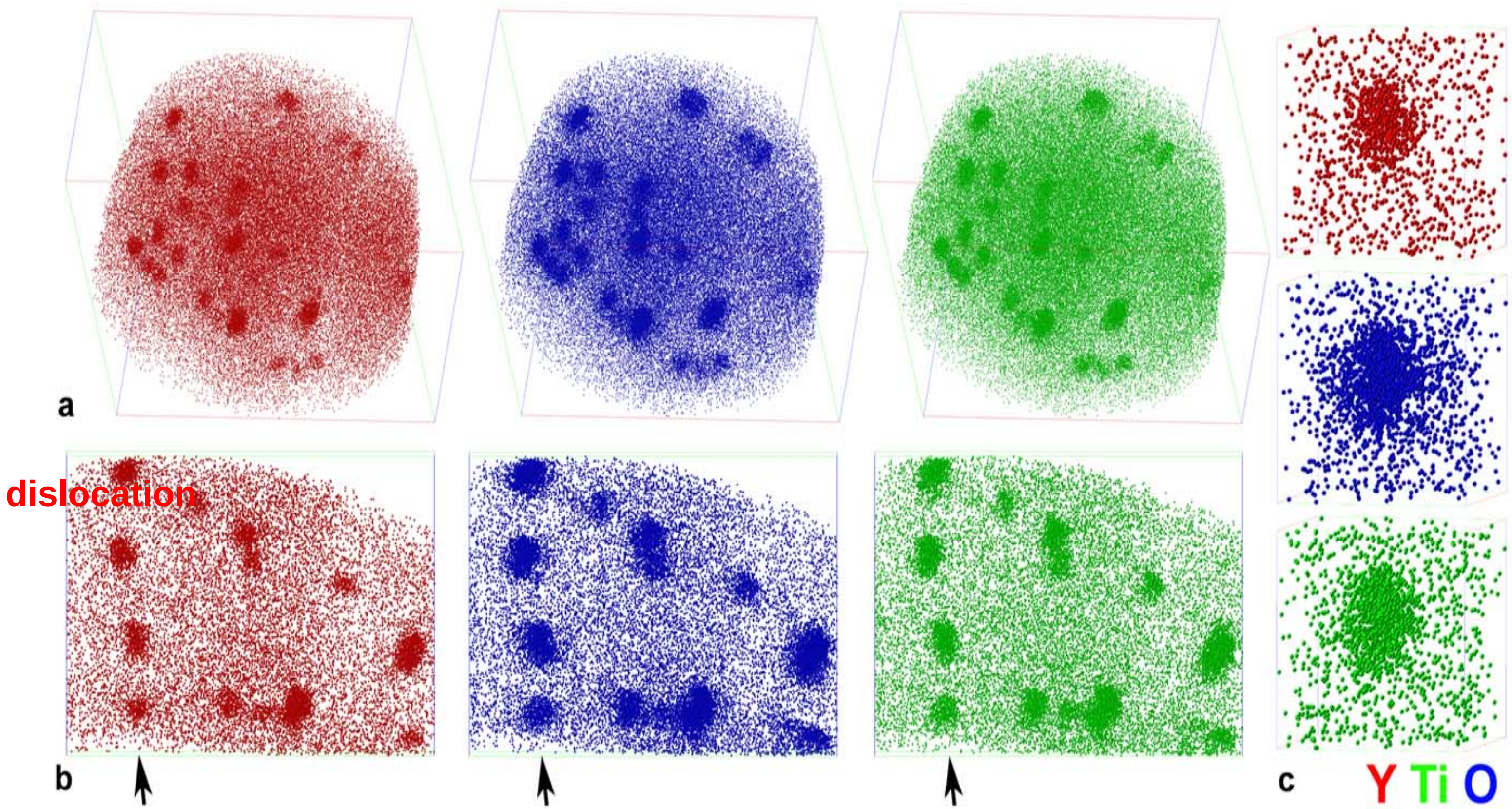
Summary and Conclusions

- Internal oxidation has potential to be competitive with mechanical alloying
- Internal oxidation of Fe-Ti-Y and Fe-Al-Y intermetallics results in high volume fractions of small (~10-20 nm) oxide particles or lamellae
- Internal oxidation of solid solutions produces fine oxide particles
- Internal oxidation of Fe-0.25 at% Y powder followed by consolidation results in modest strengthening
- The exact composition of the precursor material is likely to be important
- The next step is a methodical TEM investigation with emphasis on the role of the precursor composition on the size and stability of the ODS particles

Haynes NS-163

- Cobalt-base superalloy
- Co-28Cr-9Ni-21Fe-1.25Ti-1Nb, wt%
- processing into sheet
- Nitridation to form TiN and NbN dispersoids
- Excellent creep strength at high temperatures
  - 982°C, 56 MPa: rupture life > 250 hours

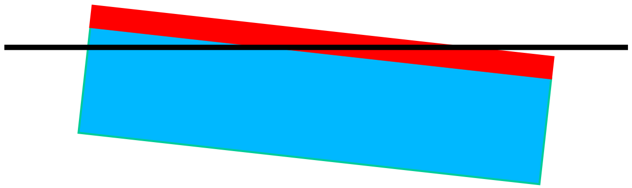
Atom maps of stable Y-, Ti- and O-enriched nanoclusters in oxide dispersion strengthened ferritic steel

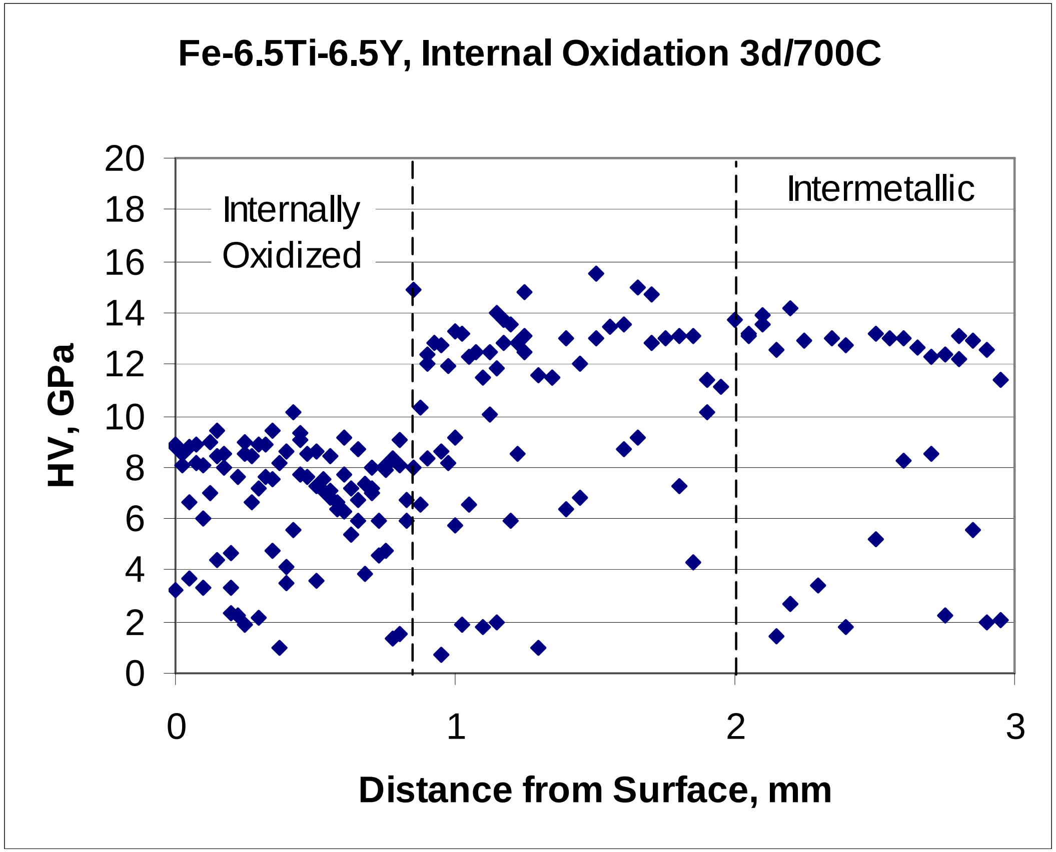


a) 100 x 100 x 90 nm^3 volume containing 23 Y-, Ti- and O-enriched nanoclusters
b) 4-nm-thick slice showing the nanoclusters aligned along a dislocation
c) 20 x 20 x 20 nm^3 selected volume containing an individual nanocluster.

M.K. Miller, C.L. Fu,
D.T. Hoelzer and C.T. Liu

Nanohardness (100nm depth) of Fe-6.5Ti-6.5Y (at%) coupon cut at an angle to the internal oxidation zone





Internal oxidation of Fe-6.5Ti-6.5Y at 600°C: substantial hardness increase - particles smaller than 20 nm