Nanocrystalline Metals

Andy Howe, Corus RD&T
Super Bainite Workshop, 6/05/2010

"There has been a certain kind of madness that pervaded science over the past ten years, where the adjective 'nano' became notorious"

H Bhadeshia, MS&T 26, 4, 2010, p381

Ultra-Fine Metals

with a bit on nano

& with the emphasis on steel!

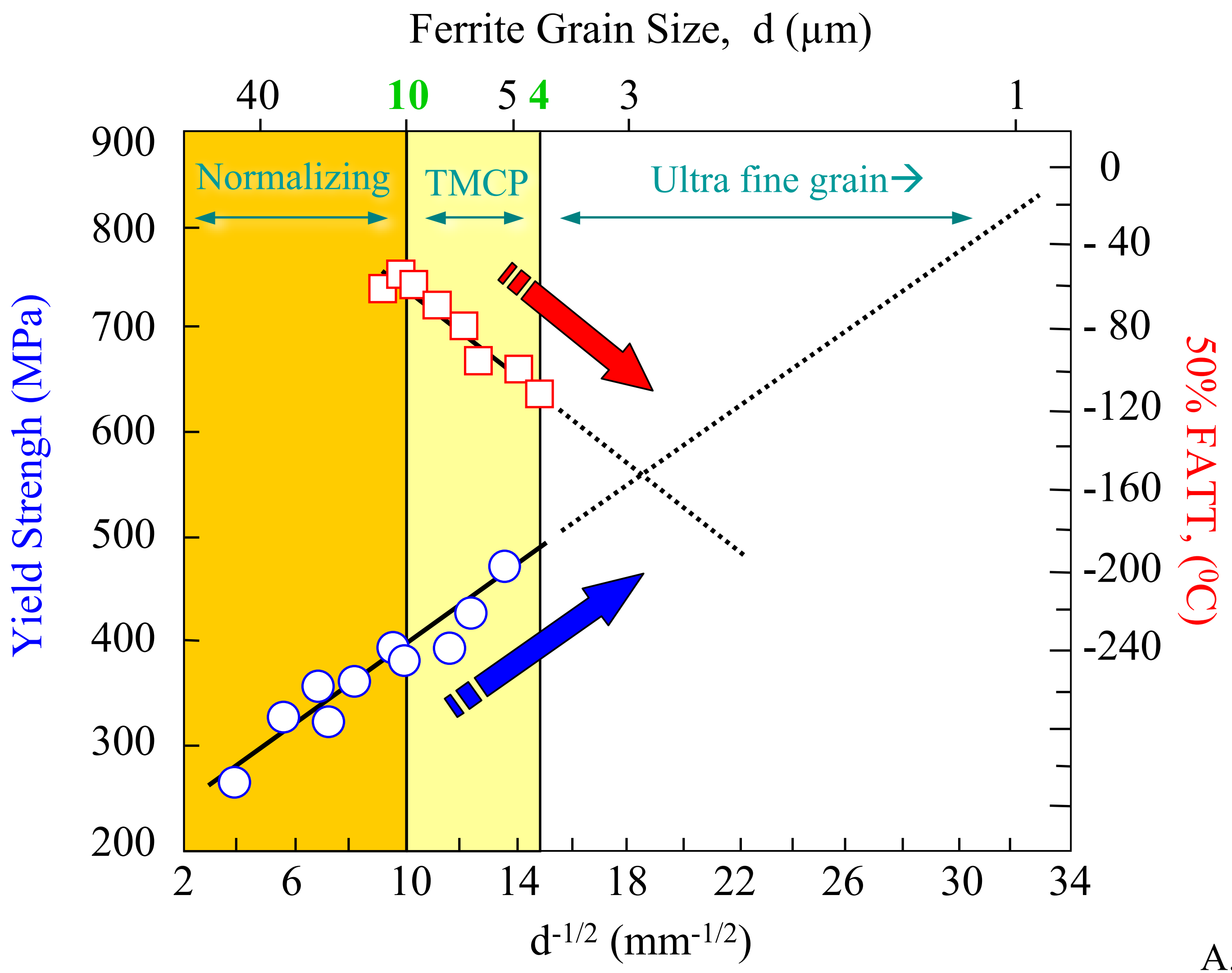
Andy Howe, Corus RD&T

Super Bainite Workshop, 6/05/2010

Outline

- Ultra-fine Ferrite
  - The metallurgical panacea
- “Reality check”
- Super Bainite!!
- Conclusions

Ultra-Fine Ferrite:
Further improvement of Strength & Toughness



A. Sato

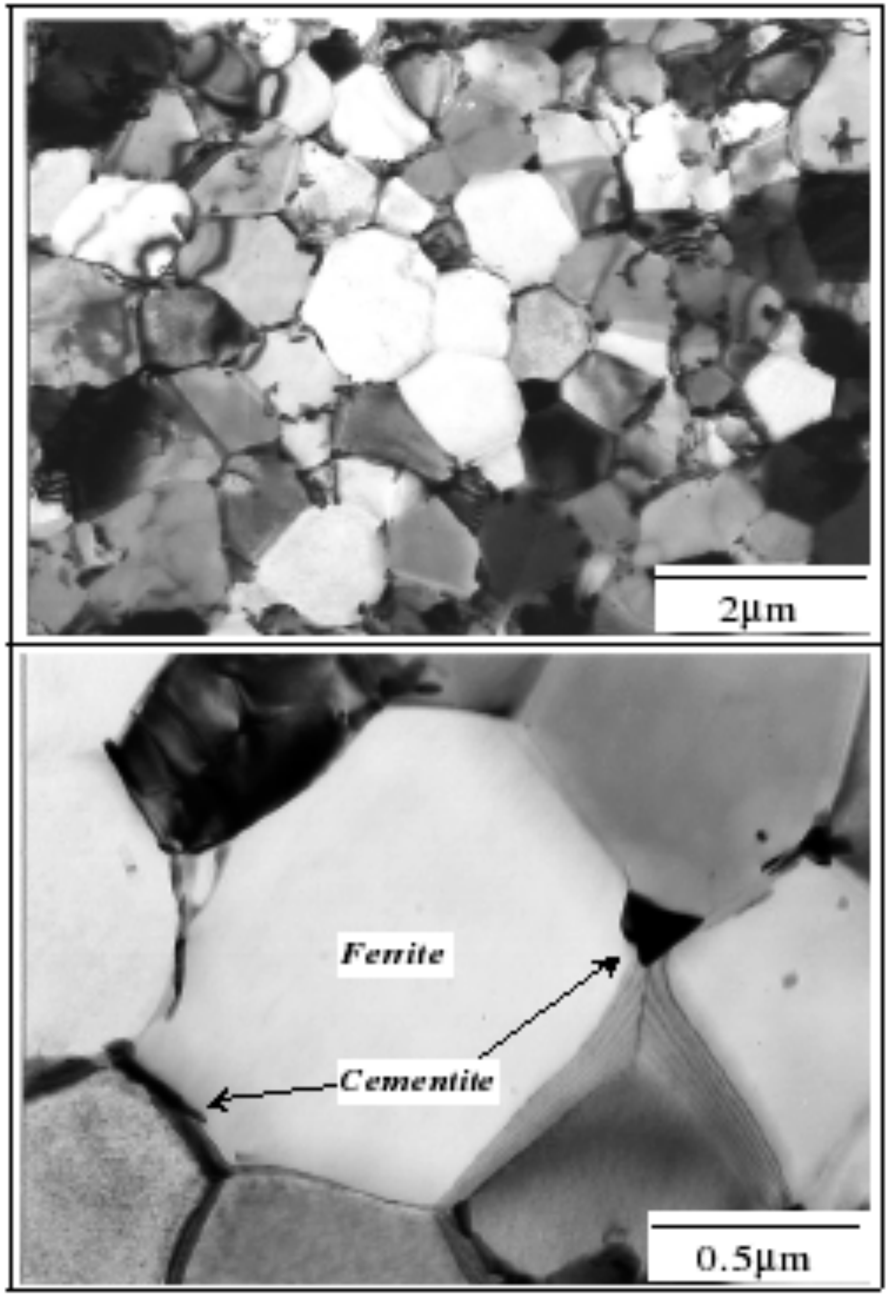
Ultra-Fine Ferrite

- Commercial production reached an apparent limit of about 4~5μm; even sub-4μm refinement of the austenite during hot rolling led to 4 μm+ ferrite grains
- Finer polygonal ferrite structures had, however, been produced in the laboratory, but were "shelved" as "academic"
- The subject was re-invigorated ~20 years ago with work primarily in Japan and Australia suggesting that ultra-fine polygonal grain structures should be amenable to bulk production after all
- Major international effort ensued, with large collaborative programmes in Japan, China and Korea

~And a little feasibility study in Europe…

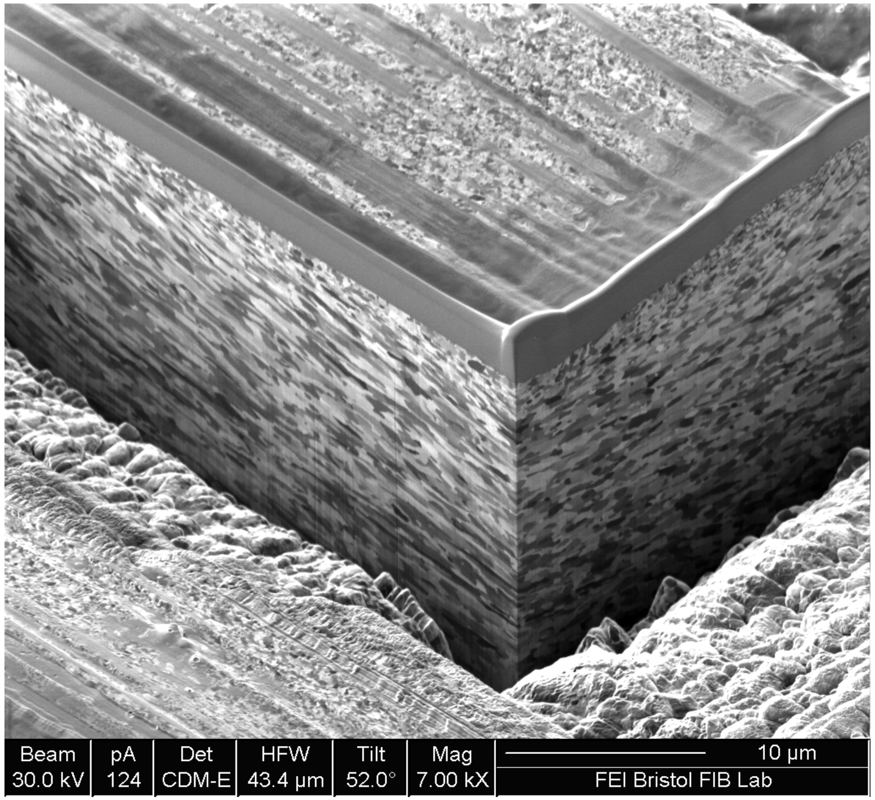
Ultra-Fine Ferrite

- Polygonal ferrite
  - Wakita, Sumitomo
- Almost dislocation-free
- Apparent potential to coarsen very quickly but pinned by cementite, and by the network of triple points / quadruple points



Ultra-Fine Ferrite

- ***Cheaper and easier production!***
- ***No need even for micro-alloys!***
- ***Perfect for re-cycling!***
- ***Simply roll iron to whatever strength you want!***



FIB-cut and imaged sub-micron IF steel

Corus – UoManchester

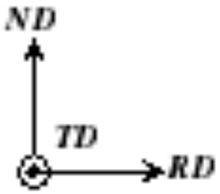
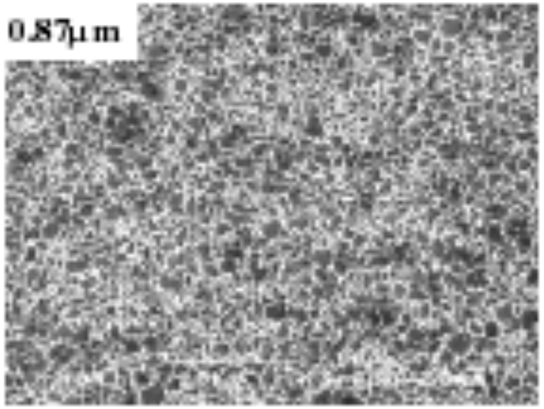
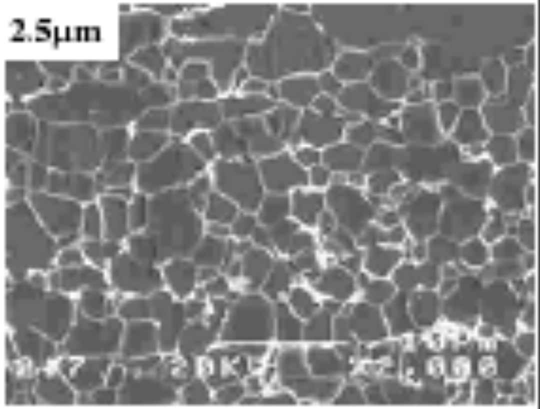
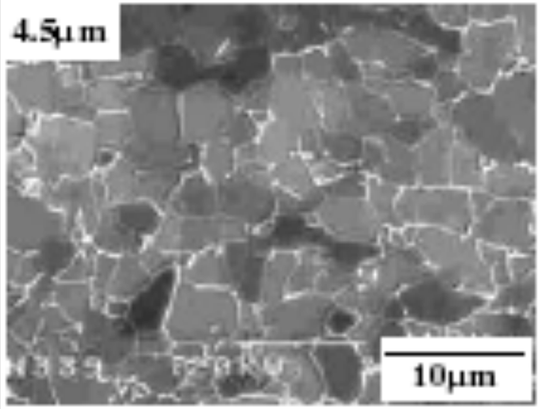
+FEI Bristol

Ultra-Fine Ferrite:
EC Feasibility Study

- Corus / Manchester / RWTH / CRM / CSM feasibility study; EC 2001
- The old 5μm barrier can be broken through several routes
  - e.g. Sub-micron IF steel, Corus/MMSC
- But expensive processing and/or new plant required
  - e.g. asymmetric rolling, Nakayama
- Issues on hitting target strength range, plasticity, welding, *and toughness*
- Back-track to 2 or 3μm for single phase polygonal structures
- Concentrate on refinement of dual phase structures
  – Dual Phase ferrite/martensite, and non-pearlitic ferrite/carbides aggregates
- Consider applications where the poor plasticity is not a problem
- Consider localised refinement

Making the #@%$ stuff!

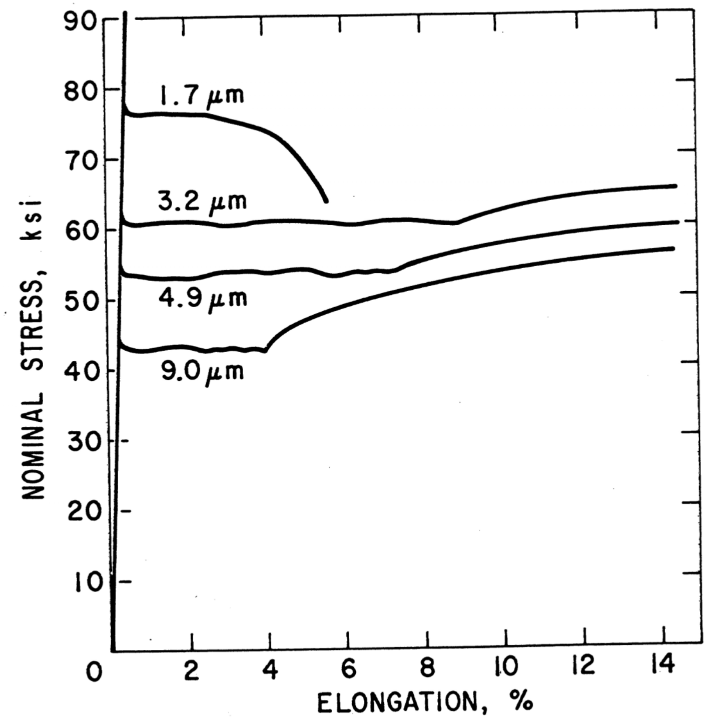
- Various methods, but all basically requiring investment in new, very high load, AC plant, and preferably with asymmetric rolling

Process	SSMR	Compact mill	Conventional mill
Reduction in finish rolling	50%-40%-50%	50%-50%-50%	30%-30%-30%
F2-F3 interpass time	0.17 sec.	1.0 sec.	0.6 sec.
Cooling process	Inter-pass cooling and rapid cooling after pass	Conventional	Conventional
SEM images  ND TD RD	0.87μm 	2.5μm 	4.5μm  10μm

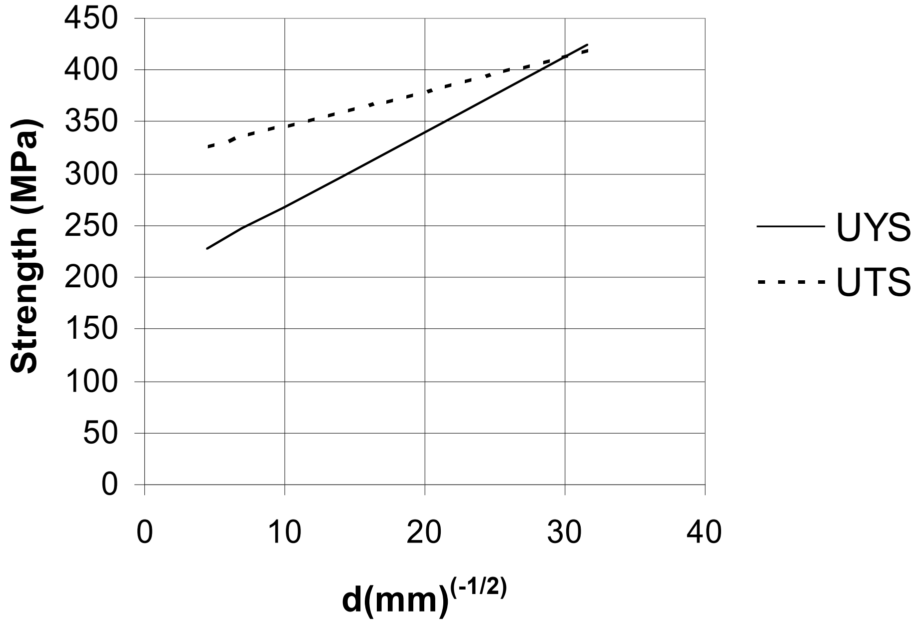
Wakita et al, 2005: SSMR process, Environmentally Conscious Ultra-Fine Grained Steel Consortium, JRCM

Ultra-Fine Ferrite:
Ductility

- The "shelved" academic work had already shown that there were problems here
- Indeed, it could be inferred simply from the classic Hall-Petch equations



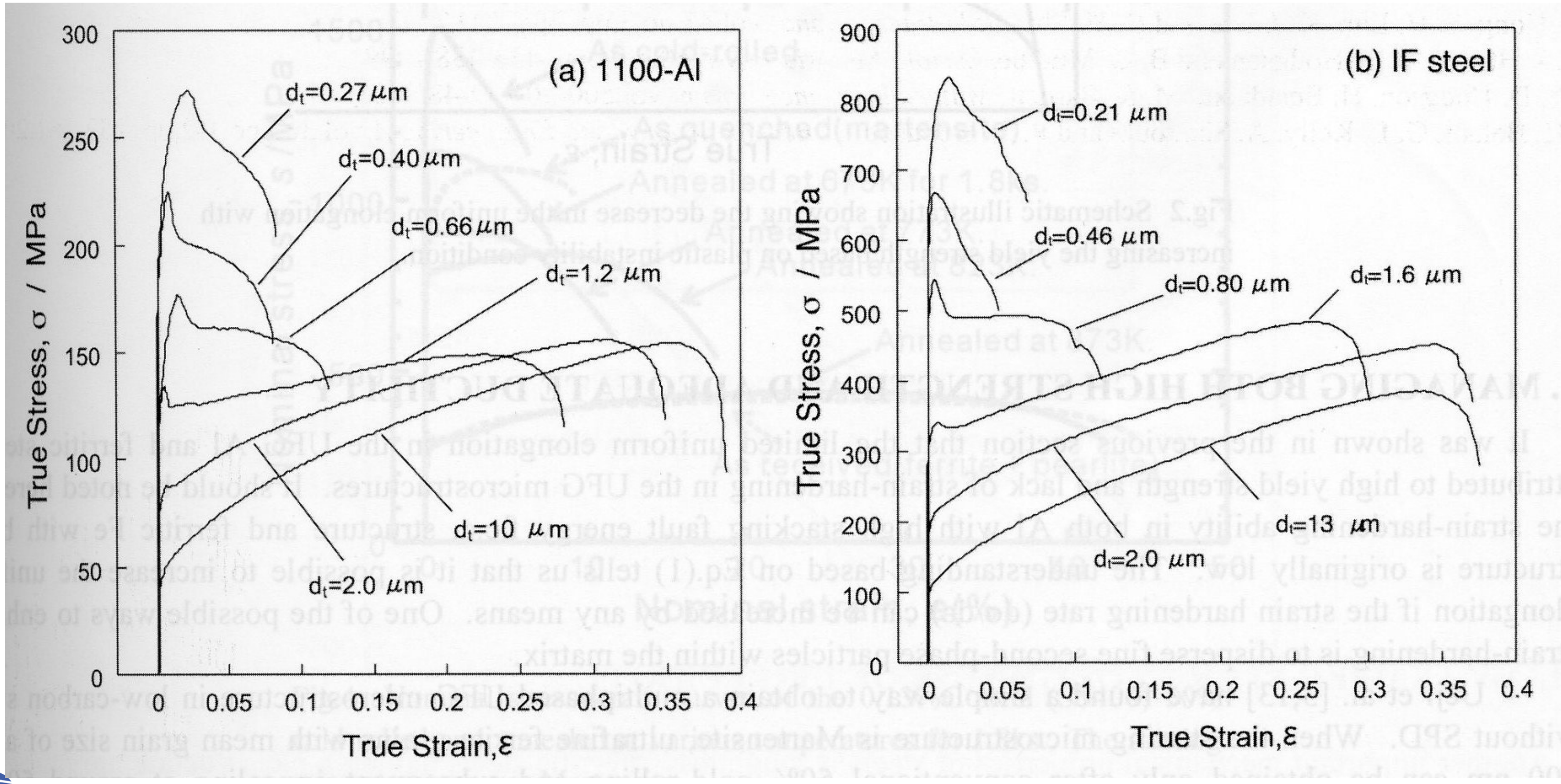
Stress/strain plots, Morrison, 1970



Convergence of σ_y and UTS from Hall-Petch equations

Ultra-Fine Ferrite: Ductility (2)

- And not just steel: Inherent in the fine grain size's limited capacity for dislocation activity



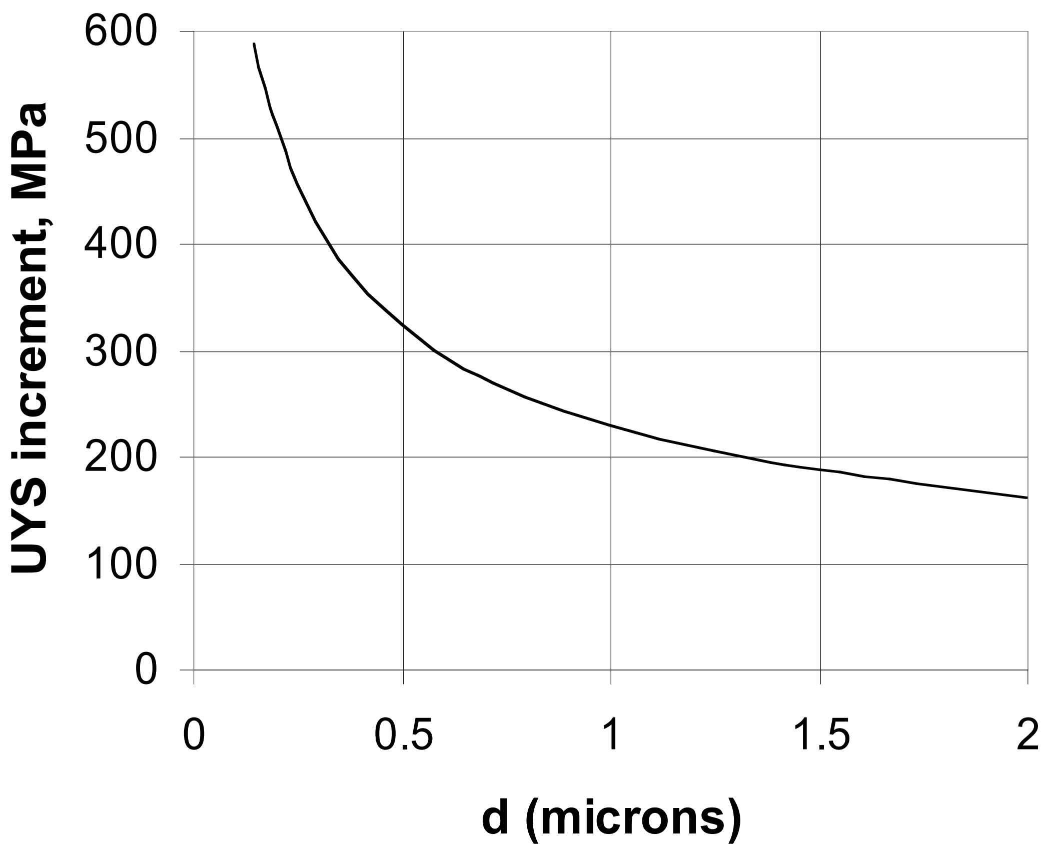
Tsuji, ICASS 2006

Ultra-Fine Ferrite: Ductility (3)

- Materials Science Forum, Vols 633-634, special issue, 2010, **Ductility of Bulk, Nano-structured Materials** (Fe, Al, Cu, Au…)
- **"The poor ductility of bulk nanostructured materials has indeed become a seemingly insurmountable obstacle to the widespread technological application of structural bulk nanostructured materials"**
- Various things to do, based on inhomogeneities
  - Second phases, even fine precipitates can help a bit
  - TRIP effect
  - Bimodal size distributions
  - Treat as you would making a Bulk Metallic Glass ductile
  - But still unlikely to match coarse/normal grain ductility
- Poor RT ductility in unconfined loading geometries.
- Beware how ductility is measured. Compression-v-tension. Temperature, strain rate effects. Uniform elongation and RoA much more meaningful than total elongation

Ultra-Fine Ferrite: Strength

- High strength, yes, but hard to hit a given strength range through $d^{-1/2}$

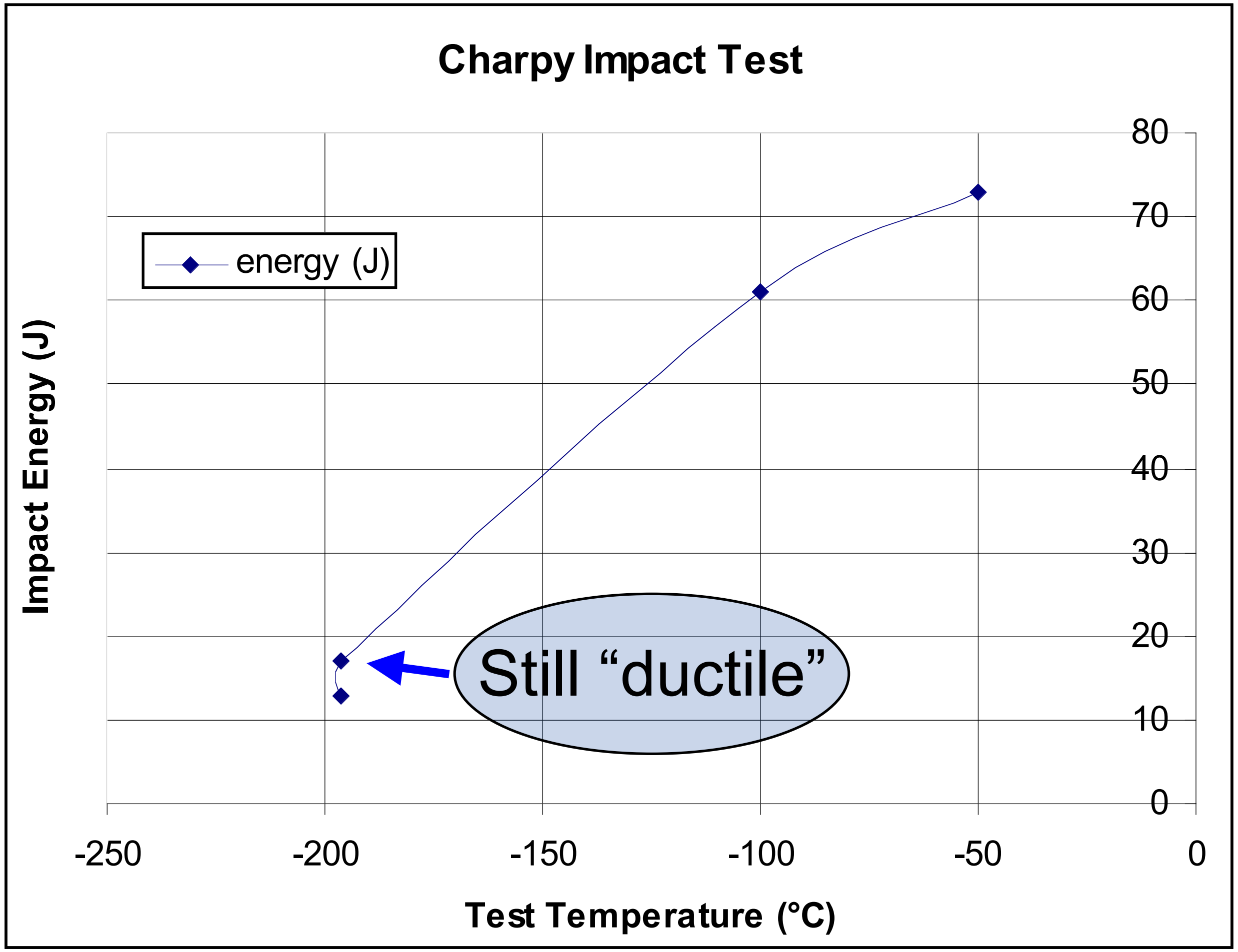


- And would it survive welding?
- But what about toughness?

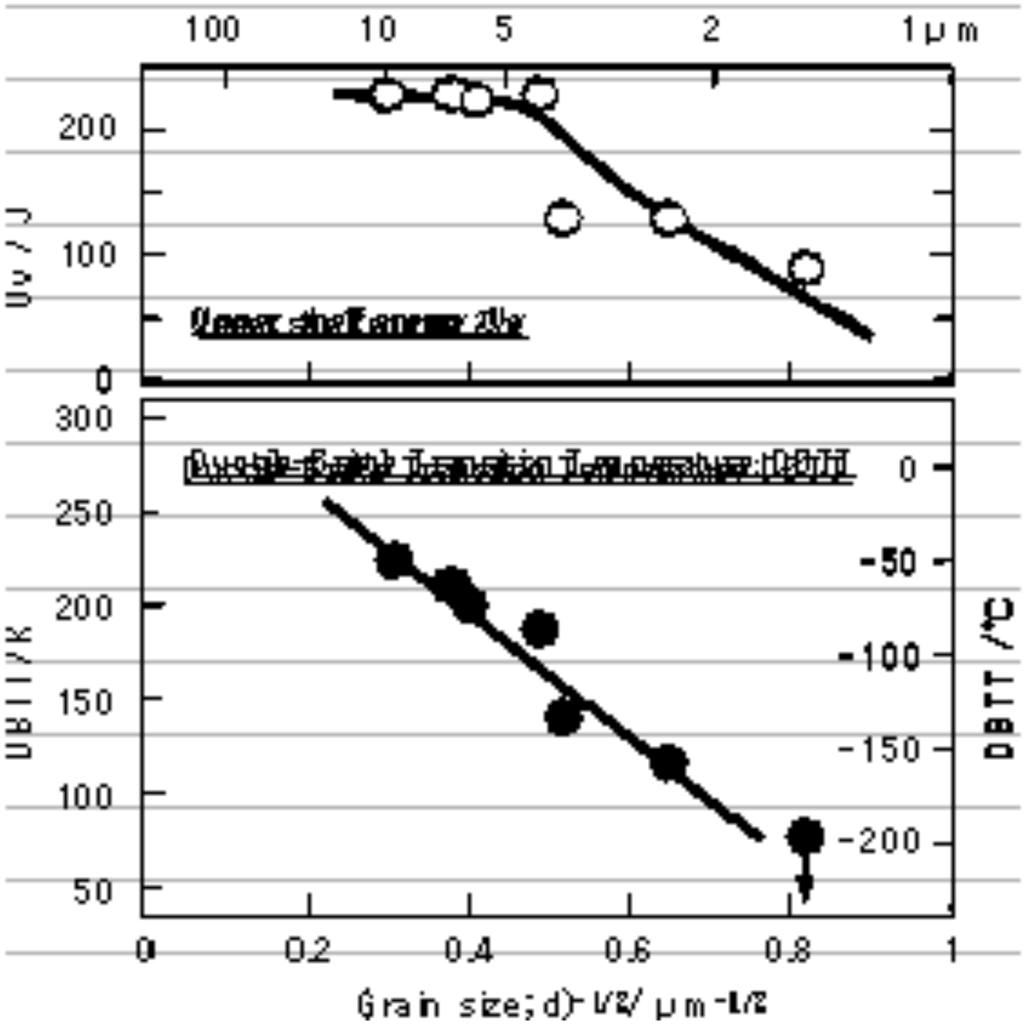
Ultra-Fine Ferrite: Toughness

Fine grains are only good for DBTT generally, not Upper Shelf Energy (or ductile K_{IC})

Sub-micron IF:
Low DBTT, but shelf energy falls to very low values even whilst still “ductile”

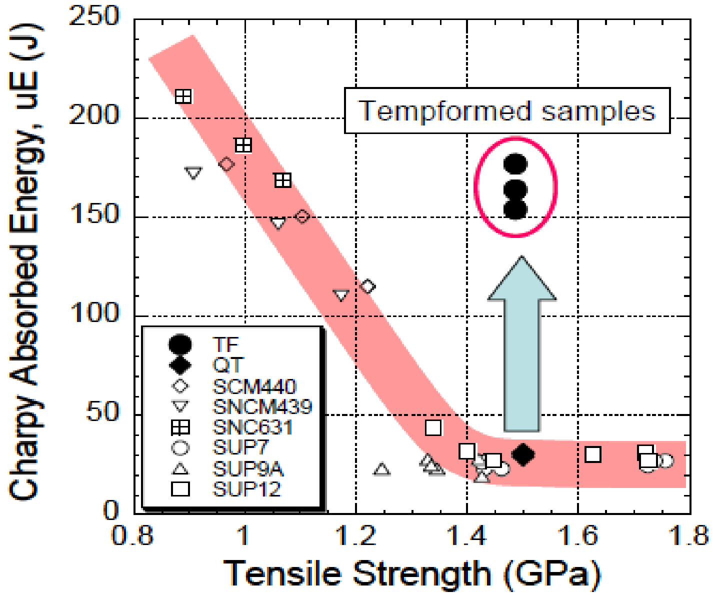


~And not just the Corus stuff…

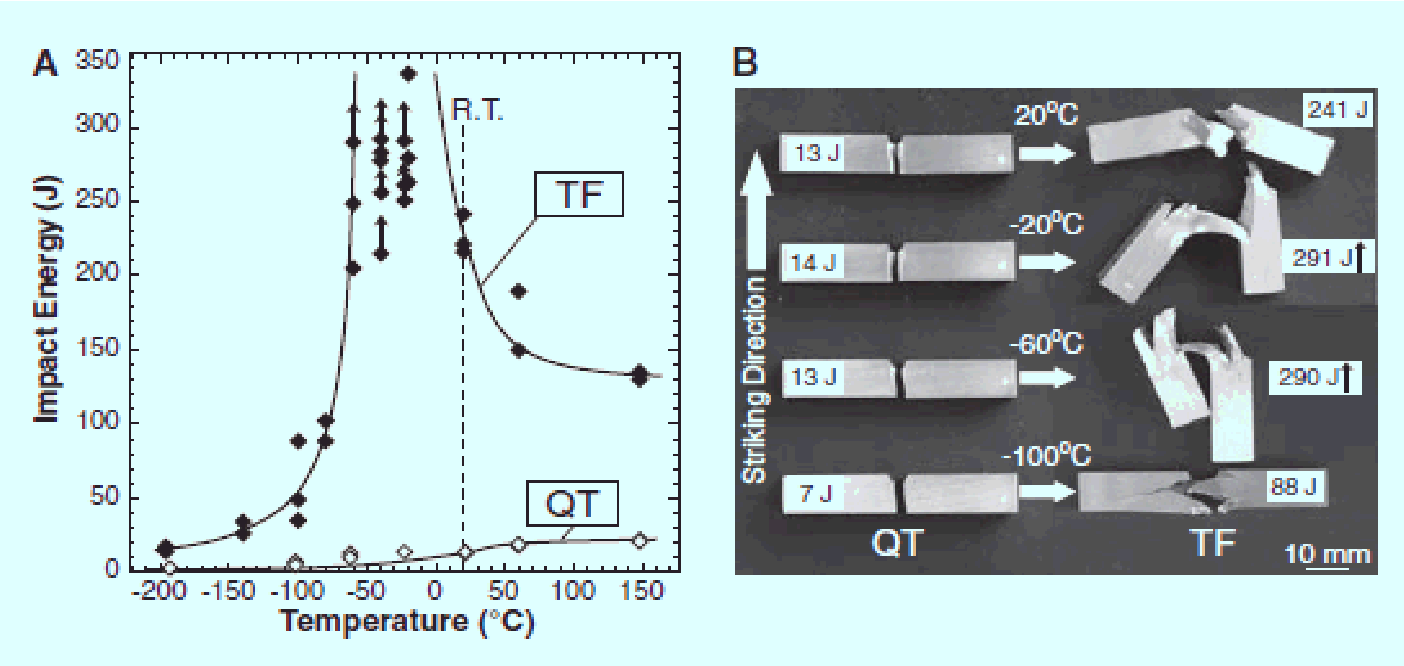


- Takaki, ISUGS 2005
- Plunging impact energy even though “ductile”
- Recommend > 5μm for good energies
- Very low DBTT

Kimura/NIMS 2007: Toughness problem solved?



- Non-polygonal UF ferrite from "tempformed" ferrite
- Large impact energy ***peak*** above transition
- High warm-deformation texture, easy cleavage, like an assemblage of strips making a Charpy specimen



Tsuji/Tanaka 2010: Toughness problem solved?

- ***High*** Charpy energy at low temperatures in **I**nterstitial **F**ree steel
- The fracture toughness increased while the DBT decreased in the specimens deformed by the ARB process
  - – Fracture toughness from 4-point bending at various temperatures
  - – Quasi-3D dislocation dynamics: dislocations absorbed by boundaries re-emitted on increasing strain – dislocation “source”, responsible for improved low temperature toughness
- Distinction from earlier results ?

Ultra-Fine Ferrite:
What happened next

- Corus: EU projects on rapid annealing of strip (Hudd, ~2μm) and UF high-carbon ferrite/carbide aggregates, for possible alloy steel substitution (Smith / Howe)
- Corus in-house: continuing refinement of Dual Phase strip
  – Note British Steel patent for UF DP alloy steel, 1982
- Extensive worldwide effort, moving on from *“how fine can we go?”* to
  - *“how do we make it attractive?”,* and
  - *“how do we make it economically?”*
- Four general themes apparent to make use of the extensive work on ultra-fine ferrite…

"Reality check"
(i) Back-track from "ultra-fine" to "very fine"

- Most of the claimed applications for "UFG" steels have actually been "VFG". 2~4μm is now common.
  - Step-changes drifting back towards the incremental improvements
- Also, use of "UFG approaches" for commercialisation of plain steels with typical microalloy grain sizes (5μm+), notably China

Fig. 5 Application examples of ultra-fine grain steel long products

Weng, Zhao, Dong, ICASS 2006

"Reality check" (i) Back-track from "ultra-fine" to "very fine"

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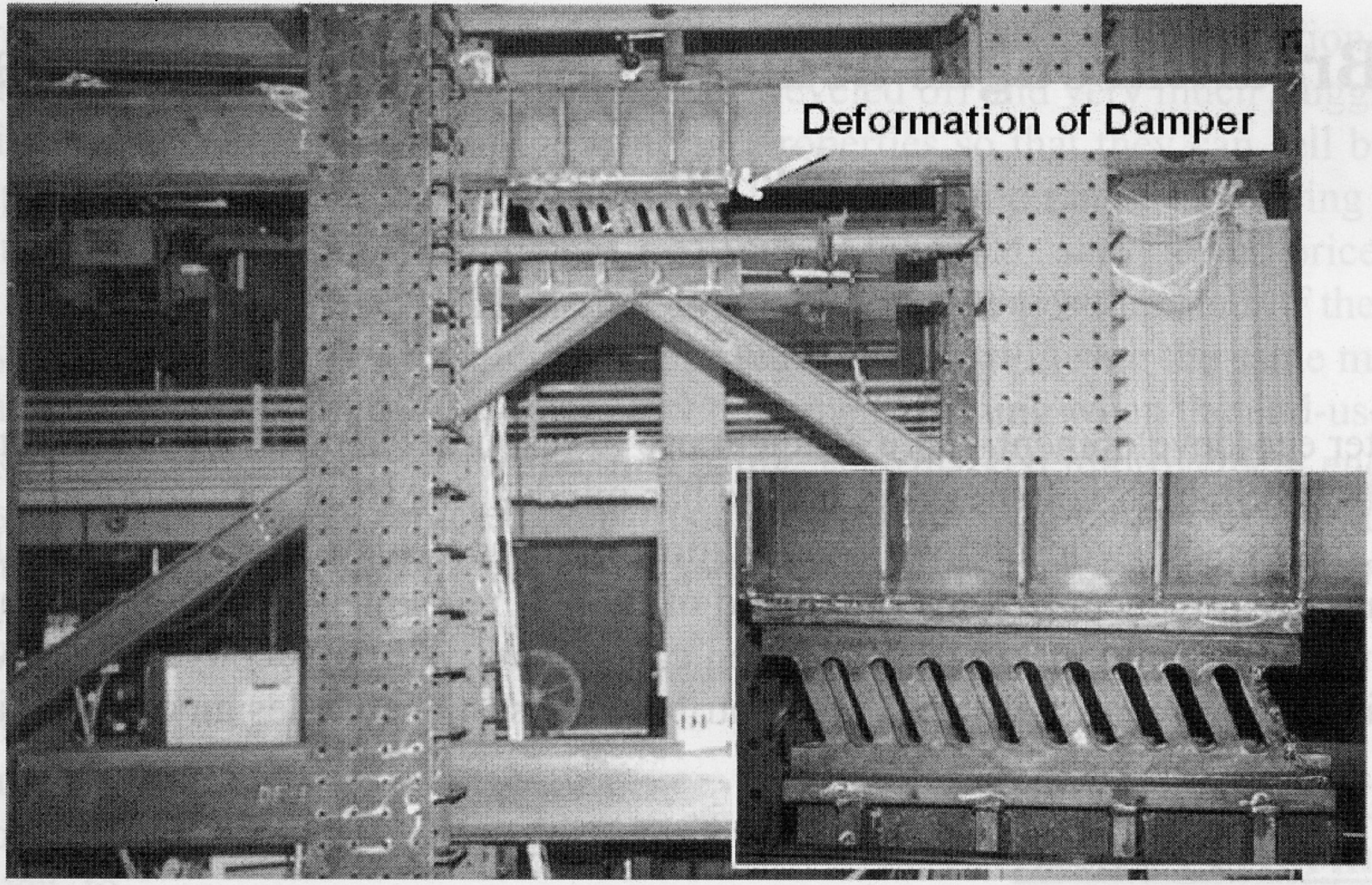
  - Step-changes drifting back towards the incremental improvements
- Also, use of "UFG approaches" for commercialisation of plain steels with typical microalloy grain sizes (5μm+), notably China
- Or maybe just mix fine grains with normal grains and hope to get the best of both worlds
  - Bimodal, or simply a very wide grain size distribution
    - Wang et al, Nature 2002, incl. Ma, cf:-
    - Ma 2006: this can be very difficult to engineer

“Reality check”
(ii) Employ where the poor plasticity is not a problem

- Applications where a high strength or dent resistance is wanted but formability or energy absorbance upon failure are not critical
  - But where a premium can still be charged!
- Girders etc: high energy absorbance wanted, low σ_y/UTS ratio
  - Employ cheap, stronger, high ratio primary members, with specific energy-absorbing components in the structure
  - Replace these components like a fuse, after the earthquake, with primary members having remained within their elastic limits

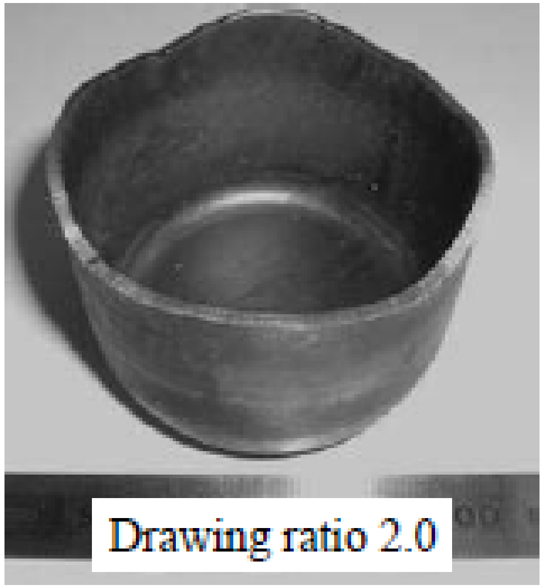
“Reality check”
(ii) Employ where the poor plasticity is not a problem

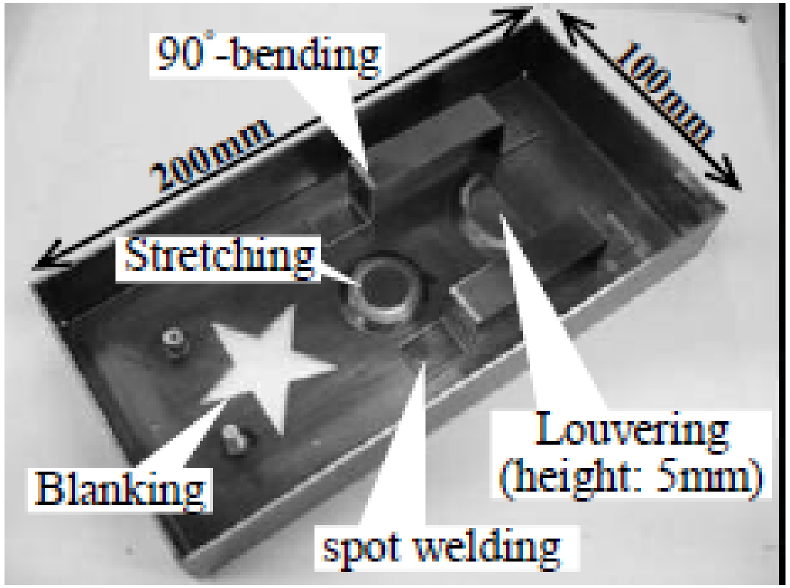
- Even so, this approach has used VFG rather than true UFG
    - W-Y Choo, ICASS 2006



“Reality check”
(ii) Employ where the poor plasticity is not a problem (2)

- Strength, ductility and formability depend on the stress state: e.g. form the components in channels (caliber rolling) rather than by flat rolling
- Project Proteus / Japan: UFG can still be formed into components where Ludering/YPE is not an issue - Wakita et al, ISUGS 2007
  - 700MPa @1μm example: any more attractive than traditionally ductile DP?

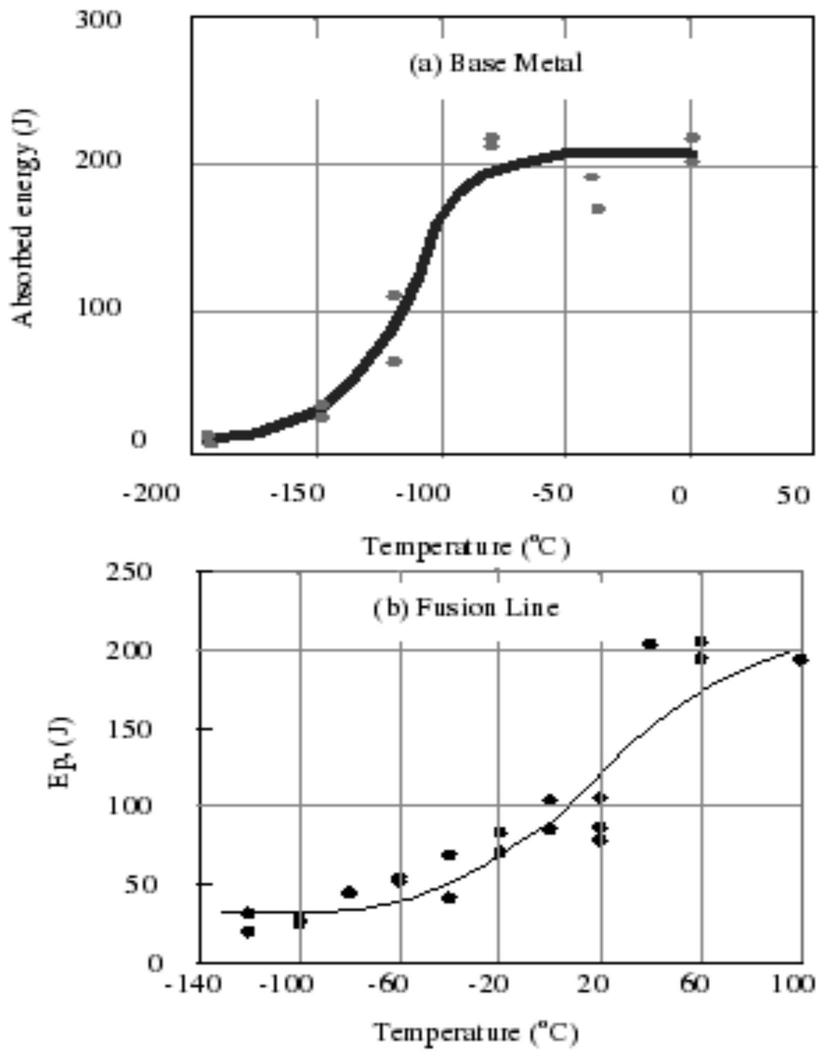




“Reality check”
(ii) Employ where the poor plasticity is not a problem (3)

- Maybe “UFG” can be <u>better</u> in some cases: better than what would be a poor material at conventional grain sizes

- NIMS/Japan, 0.8%Si,0.8%Al weathering steel, avoiding Cu & Ni but usually problems of embrittlement with Si/Al. Not evident in very fine grained material

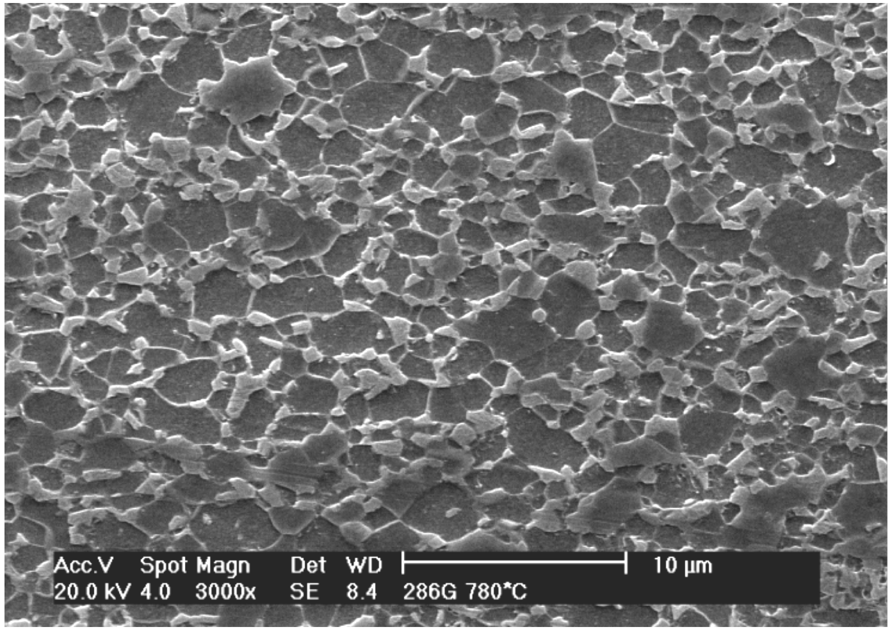


“Reality check”
(iii) Counter the problems with hard second phases

- The UFG problem was encapsulated by the question:
  “Why does the steel industry want another hard, brittle phase when it already has martensite?”

"Reality check"
(iii) Counter the problems with hard second phases

- The UFG problem was encapsulated by the question:
  "Why does the steel industry want another hard, brittle phase when it already has martensite?"
- The solution? *–mix it with martensite!*
  - Merging with ongoing incremental work
  - Bridges, buildings, line-pipe, automotive…
  - Indications that VFG is still better than UFG
    - (Song et al, 2006)
- EU Study example, CRM, 860MPa with 10% e_u

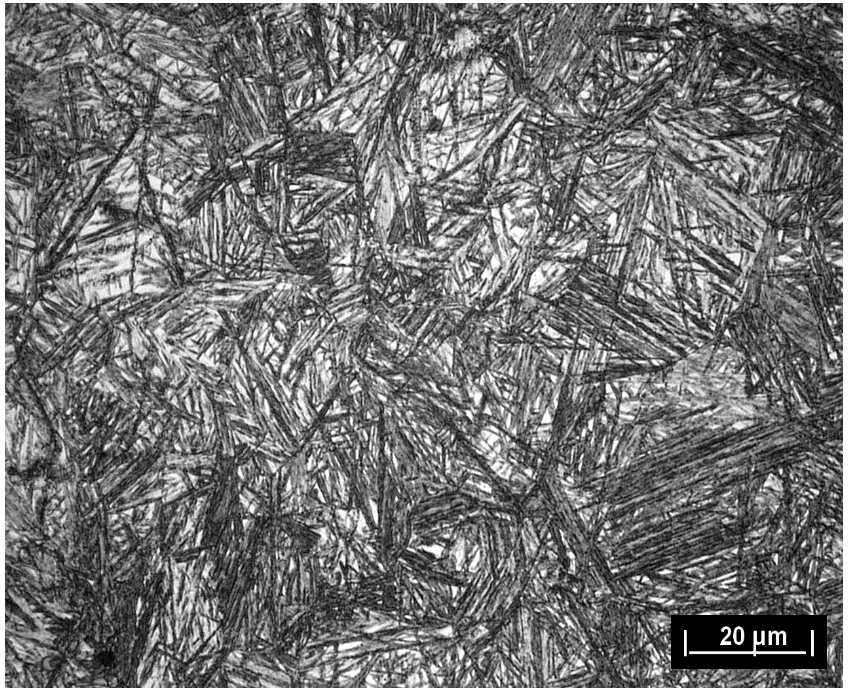


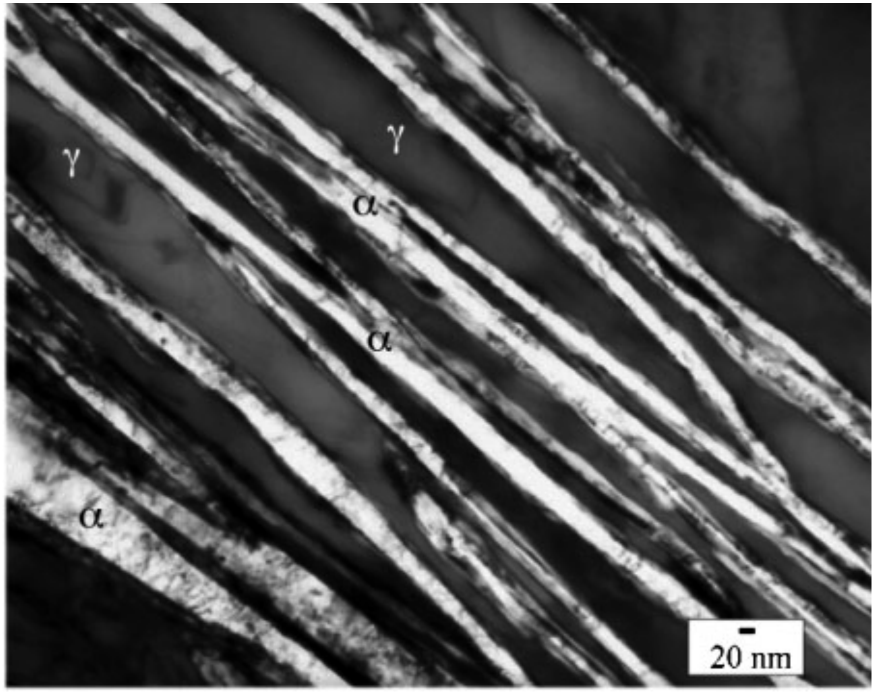
- Other hard second phases similarly
  - Ferrite/cementite aggregates as before
  - Also, fine precipitates appear to promote more dislocation activity than plain UFG exhibits. Arguably better for RoA than elongation

"Reality check"
(iii) Counter the problems with hard second phases (2)

- Or maybe mix with a phase which <u>becomes</u> martensite
  - metastable austenite (TRIP)
- And why stop at 2-phases?
  - UF Complex Phase, including TRIP
- By this time, we're no longer dealing with polygonal structures
- Martensitic steels: Already:-
  - Very/ultra-fine structure
  - Residual austenite films (to improve toughness)
  - Nano-precipitates (at least as tempered)
  - Ausformed: warm worked austenite as per some UF Ferrite approaches but then quenched: further refinement, better strength-ductility combination
  - Cf. the reverse; working martensite then heat up for UF (Tsuji patent)
- And, of course…

Super Bainite !!





- Optical: Corus/DSTL

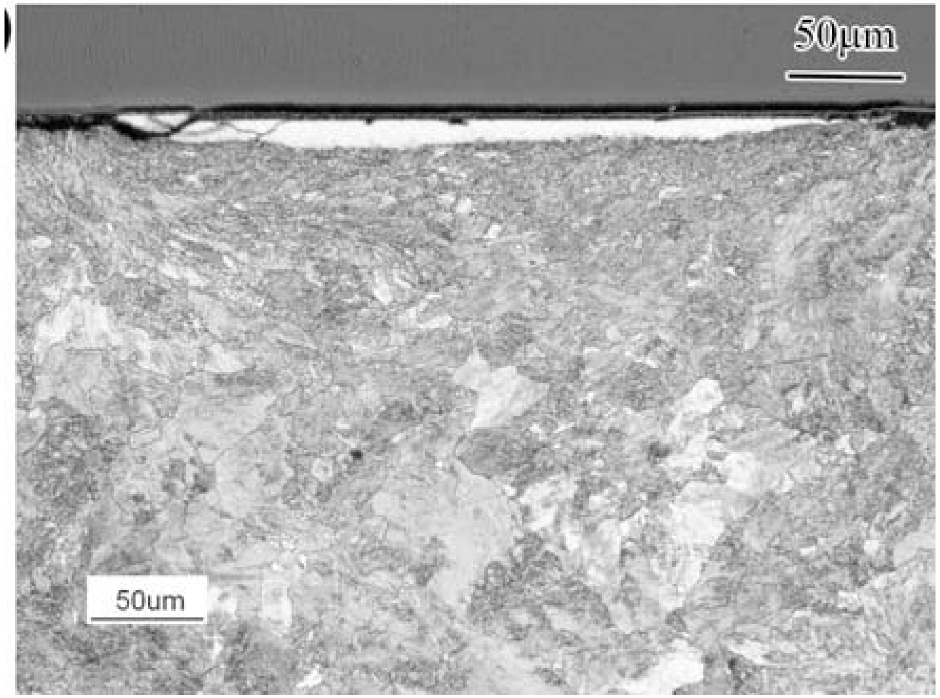
TEM: Mateo & Bhadeshia, Cambridge

Super Bainite goes Global

- General revival in bainitic steels generally, and
- Super Bainite style steels, in Europe and worldwide

"Reality check"
(iv) Local use of ultra-fine microstructures

- Ongoing research but:
- Hiarrest product commercialised for some time
  - 1-3μm surface grains on ship plate T Ishikawa, Nippon Steel Tech. Report, Jan 2000, **81**, 109-113
- Easier to achieve than bulk UFG
  - Cooling rate, shear strains, etc
- And nano-"grains" in heavily drawn wires



- Long-running battle over whether White Band / White Etching Layer on rails is supersaturated nano-scale ferrite or martensite, though recent APFIM work strongly suggests it's martensitic
  - •Takahashi, Acta Materialia 58 (2010) 3602–3612

TATA STEEL

Conclusions

- Some “true” / polygonal 1μm-grain products are being commercialised but are certainly not a metallurgical panacea
- It *can* be done in bulk, but is difficult to do, and does not offer an attractive combination of properties for general products
- 2-3μm products have now entered the mainstream, incremental advances into this area accelerated by the grand UFG projects
- The UF technology has also promoted plain steels matching micro-alloy grain steels
- Fine phase mixtures, and not just polygonal, are the most promising materials for high strength in combination with other useful properties, and still with plenty of scope for development


Thank you!
20 µm