New Nano-Particle-Strengthened Ferritic and Martensitic Steels by Thermo-Mechanical Treatment

R. L. Klueh, N. Hashimoto, P. J. Maziasz Metals and Ceramics Division Oak Ridge National Laboratory

Euromat 2005, Prague, Czech Republic September 6, 2005



Ferritic/Martensitic Steels For Elevated-Temperature Service

Steels developed for fossil-fired power plants

- Advantages: thermal properties and economics
- Limitations: upper temperature limit on strength
 - Steels limited to 550-600°C
- Steels proposed for nuclear applications fission and fusion power plants
 - Advantages demonstrated for fast reactors in 1960s
 - Steels adopted for fusion applications



Ferritic and Martensitic Steels for Fusion Reactor First Wall

- Ferritic/martensitic steels were chosen because of advantages over austenitic stainless steels:
 - Thermal properties
 - Higher thermal conductivity
 - Lower thermal expansion
 - Lower void swelling during irradiation



Choice of Steels for Fusion

- First steels were commercial Cr-Mo steels (HT9, mod. 9Cr-1Mo, 2¼Cr-1Mo) from powergeneration industry
- Reduced-activation steels were developed for fusion for easier nuclear waste disposal
 - Mo, Nb, and Ni were eliminated—long-life isotopes
 - Cr-W steels were developed to replace Cr-Mo steels
 - 7-10Cr-2WVTa steels were developed in Japan, Europe, and the United States



7-12% Cr Steels Have Tempered Martensite Microstructure

- Austenitized and air cooled (normalized) to produce martensite
- Tempered to increase ductility and toughness

Sandvik HT9: Normalized-and-tempered





Microstructure Limits Elevated-Temperature Strength of Steels

- Large M₂₃C₆ particles pin subgrain boundaries
- Dispersion strengthening is by small MX particles (carbides, carbonitrides, and/or nitrides)
- Particles coarsen at elevated-temperatures
- Subgrain size increases and strength decreases

OAK RIDGE NATIONAL LABORATORY U. S. DEPARTMENT OF ENERGY



HCM12A Steel (N &T)



New Steels Required For Higher Temperature Applications

- Steels limited by elevated-temperature strength
 - Higher temperature operation required for better efficiency
 - Favorable properties of martensitic steels make them preferred candidates
- Present best <u>potential</u> replacement: Oxide dispersion-strengthened (ODS) steels
 - Fabricated by expensive/complicated mechanical alloying and powder metallurgy techniques
 - In development since 1960s



Strength Of Steel Is Determined By Composition And Microstructure

- Deformation creates and moves dislocations through matrix
- Strength improved by hindering dislocation movement
- Composition determines precipitates and solidsolution strength
- Microstructure effects (dislocation obstacles):
 - Precipitates (small, high-number density)
 - Grain boundaries and subgrain boundaries
 - Dislocations



High Strength Obtained From Large Number Of Small Obstacles

- Conventional steels: strength obtained by heat treatment to produce tempered martensite strengthened by precipitates
 - Large precipitates and low number density
- ODS steels: strength from high number density of small oxide particles
- New steels: strength from high-number density of nano-sized precipitates
 - Conventional processing vs. expensive powder metallurgy techniques of ODS steels
 - Conventional processing to eliminate anisotropy that has plagued ODS steels



Objective: Develop New Steels For Elevated-Temperature Service

- Use nitride (MX) precipitates for strengthening
- Obtain strength from high number density of small MX precipitate particles
 - maximize number of small MX particles
 - minimize number of large M₂₃C₆ particles
- Produce steels by conventional processing
- Creep strength adequate to 700°C (or higher)
- Computational thermodynamics used to devise compositions and processing of new steels





Thermo-Mechanical Treatment (TMT) Devised to Produce New Steels

- Thermo-mechanical treatment:
 - Heat to high temperature (1100-1300°C) to put all elements in solid solution in austenite
 - Cool to hot-rolling temperature (750-900°C)
 - Hot roll to introduce dislocations that act as heterogeneous nucleation sites for MX precipitation
 - Anneal to grow precipitates to optimum size
 - Air cool to form high-strength martensite matrix
- Strength from distribution of nano-sized MX nitride and/or carbonitride precipitates



TMT Process Applied to Nitrogen-Containing Commercial Steel

- Initial work: nitrogencontaining commercial steels (modified 9Cr-1Mo, etc.) were used
- Plates (25.4-mm thick) were available and processed by hot rolling
- Results used to verify capability of process

<u>100 nm</u>

Modified 9Cr-1Mo-New TMT

T-BATTELLE

Size and Number of Precipitates Depend on TMT Procedure



•Commercial modified 9Cr-1Mo Steel after two variations of new TMT treatment

500 nm



Precipitates Form On Dislocations During TMT



50 nm

•Dark-field image—HCM12A (12CrWMoVNb steel)



New Steel With High Number Density of Small Particles Produced

- Fe-9Cr-1MoNiVNbN steel 400-g ingot) was melted, cast, and TMT
- High number density of small precipitates



250 nm



Size and Number of Precipitates Depend on TMT Processing Procedure

Experiment	MX Precipitates	
1913 7 10 1013 7	Average Size (nm)	Number Density (m ⁻³)
Modified 9Cr-1Mo—N&T	32	7.9 X 10 ¹⁸
Modified 9Cr-1Mo—TMT1	7.2	8.9 X 10 ²¹
Modified 9Cr-1Mo—TMT2	7.3	2.1 X 10 ²¹
Modified 9Cr-1Mo—TMT3	8.0	1.9 X 10 ²¹
Fe-9Cr-1MoNiVNbN-1	4.0	1 X 10 ²²
Fe-9Cr-1MoNiVNbN—2	3.3	7.2 X 10 ²²

High number density of nano-size particles obtained



TMT of New Steel Composition Produced High Strength

- Excellent strength from small ingot
- This despite inability to obtain nitrogen concentration desired





TMT of New Steel Composition Produced High Strength

 Strength and ductility in tensile test are comparable to highstrength experimental ODS steel





TMT of New Steel Composition Produced High Strength



Strength and ductility comparable to high-strength experimental ODS steel



Creep-Rupture Life Of Modified 9Cr-1Mo Steel Improved By TMT

- Rupture life increased by ≈80 times by TMT
- Excellent ductility for high strength





Summary

- Process to produce nano-particle-strengthened martensitic steels are being developed
 - Present steels limited to 550-600°C
 - New steels should have use temperature >700°C
 - Steels developed for fossil-fired power plants and future nuclear fission and fusion power plants
- Initial work demonstrated possibilities:
 - Microstructures contain high number density of small precipitate particles
 - Steels show large increase in strength relative to steels produced by conventional heat treatment
 - Strengths are comparable to strong ODS steel

