RM55: Processing, Mechanical Properties, and Potential Applications of Oxide Dispersion-Ductilized Cr-Based Alloys

M.P. Brady, P. Sachenko, I.G. Wright
Oak Ridge National Laboratory, Oak Ridge, TN USA

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Resurgent Interest in Cr for High-Temperature Applications

- ADVANTAGES:
  - high melting point
  - good high-temperature oxidation and corrosion resistance
  - relatively low density
  - low coefficient of thermal expansion
- DRAWBACKS:
  - usually (<u>but not always</u>) brittle at room temperature
  - nitrogen embrittlement during elevated-temperature exposure
  - volatility--water vapor effects

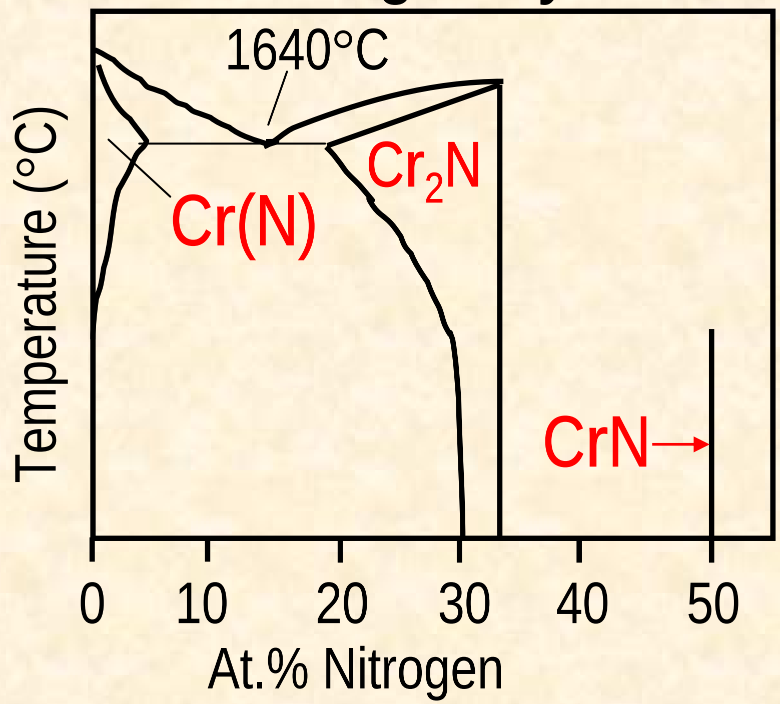
Issues for Cr Ductility at Room-Temperature

- Room-temperature brittleness of Cr mainly due to impurities, which raise the brittle-to-ductile transition temperature (BDTT)

- Nitrogen is particularly deleterious
  - high solubility at elevated-temperature; near zero at room temp
  - precipitates as fine, acicular, grain-boundary phase
  - as little as 5-10 wppm nitrogen can be embrittling

- Issues regarding dislocation initiation and motion also are important in causing the high BDTT of Cr

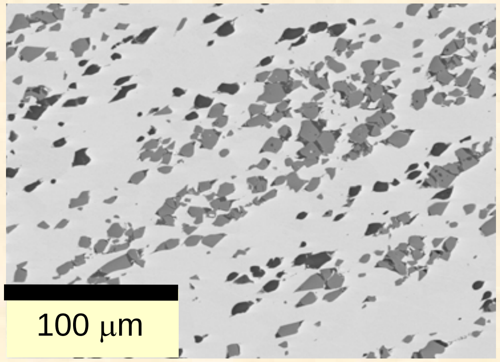
Cr-Nitrogen System



Bendix Corp. (Scruggs et al., mid-1960's) ductilized Cr via additions of MgO

- Additions of MgO to commercial-purity Cr powder
  - partially convert to $MgCr_2O_4$ during consolidation (100-500wppm C, N, S; >5000 wppm O)
- Measured 10-20% tensile elongation at room temperature
- Postulated that $MgCr_2O_4$ spinel getters nitrogen and other impurities

SEM Backscatter Micrograph



Cr matrix (light)
MgO (dark)
$MgCr_2O_4$ spinel (grey)

- Typical composition: (93-97)Cr-(3-6)MgO-0.5Ti wt.%
- Sintered and extruded

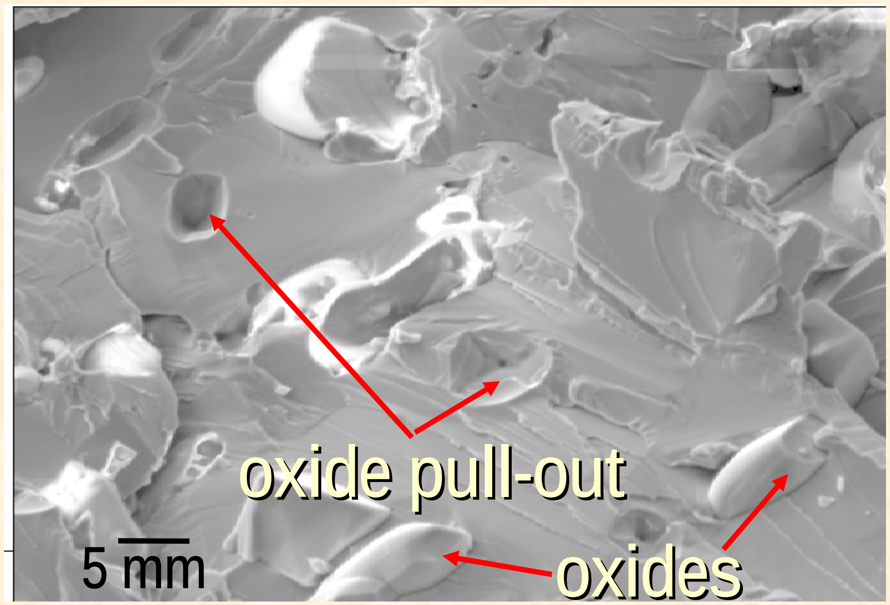
- ORNL testing measured 8% room-temperature tensile elongation
  - piece of original Scruggs alloy; 600 grit finish, $3.3 \times 10^{-3}\ s^{-1}$ strain rate
- Ductility was notch- and strain rate-sensitive

ORNL studied reasons for the observed ductility

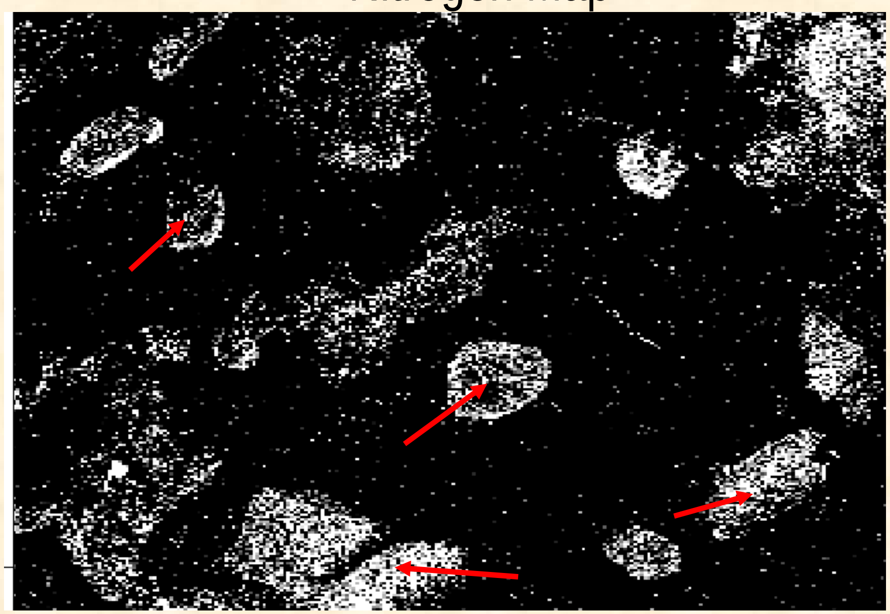
- Impurities (C, N, S) segregated at oxide dispersion/Cr matrix interfaces, not in spinel phase (as previously thought)
- Impurity precipitates also were observed at oxides in as-sintered and as-hot-pressed material (not seen after extrusion)

—Auger Maps of In-Situ Fractured Cr-MgO Alloys—

SEM of Fracture Surface



Nitrogen Map



- Opens possibility for other (non spinel) oxides to ductilize Cr

Recent Development Efforts for Oxide-Dispersed Cr alloys

Goal was to explore the effects of:

- Processing
  - temperature (impurity segregation, oxide coarsening)
  - magnesium salt precursors (instead of direct addition of MgO)

- Other oxide dispersions
  - non MgO
  - non spinel-forming

- Alloying of Cr matrix

Hot pressing at higher temperature resulted in improved ductility and lower yield strength

Cr-6MgO wt% Hot Pressed at Various Temperatures
[tensile properties at $3.3x10^{-3}$ s^{-1}, 600 grit (US) finish]

T°C	Elongation %	Yield Stress MPa	Microhardness (Vickers)	Ultimate Tensile Strength, MPa
1300	1.9	324	183	345
1450	3.5	255	156	324
1590	5.6	207	—	310

- Consistent with original work of Scruggs: temperature driven-impurity segregation to oxide dispersions ($MgO/MgCr_2O_4$)

Post hot-press annealing was not effective in improving ductility

Room-Temperature Properties of Cr-6MgO Hot-Pressed at 1300ºC as a function of annealing at 1500ºC in vacuum

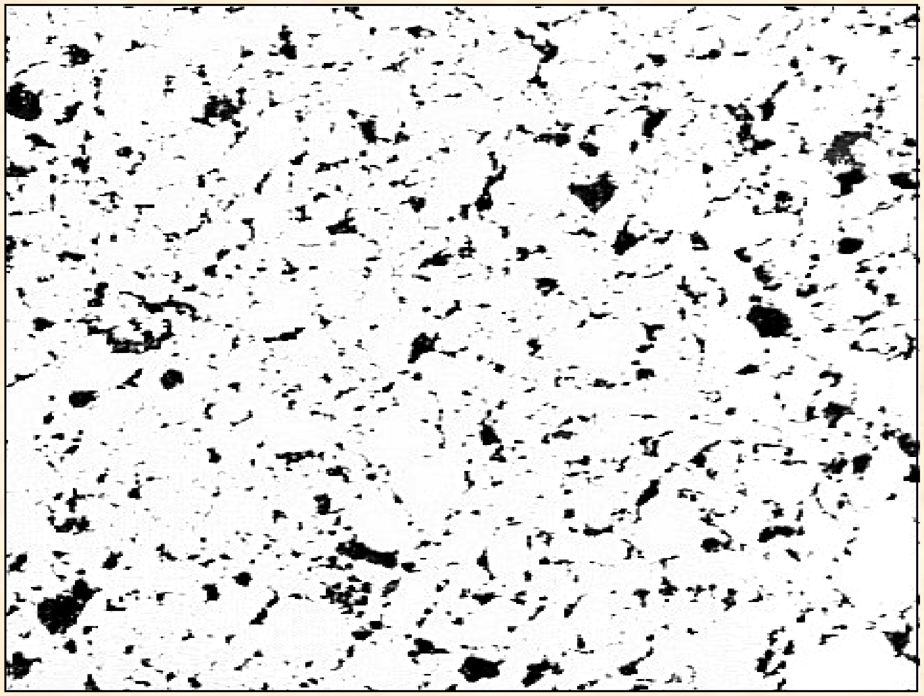
Annealing time, h	Elongation %	Yield stress, MPa	Fracture stress, MPa	Microhardness of matrix (Vickers)
0 (as-HP)	1.9	324	345	183
2	2.8	214	296	149
10	0.6	169	186	142

- Annealing decreased yield/fracture strengths and softened the matrix, but eventually degraded ductility

Coarsening of spinel/MgO particles likely contributed to the decreased ductility

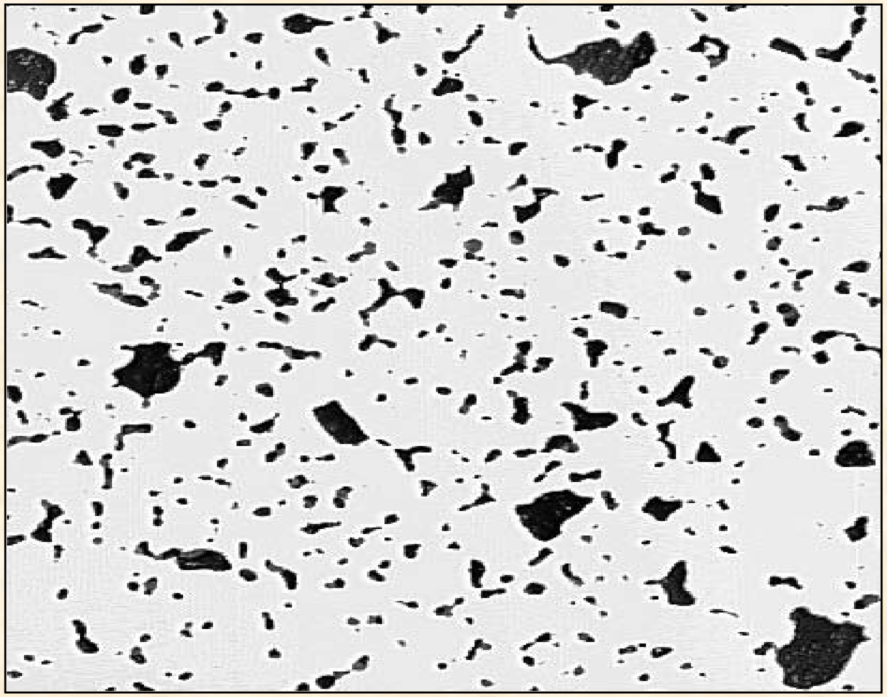
Optical Cross-Sections

As-Hot Pressed



0.1mm

10 h, 1500°C Anneal



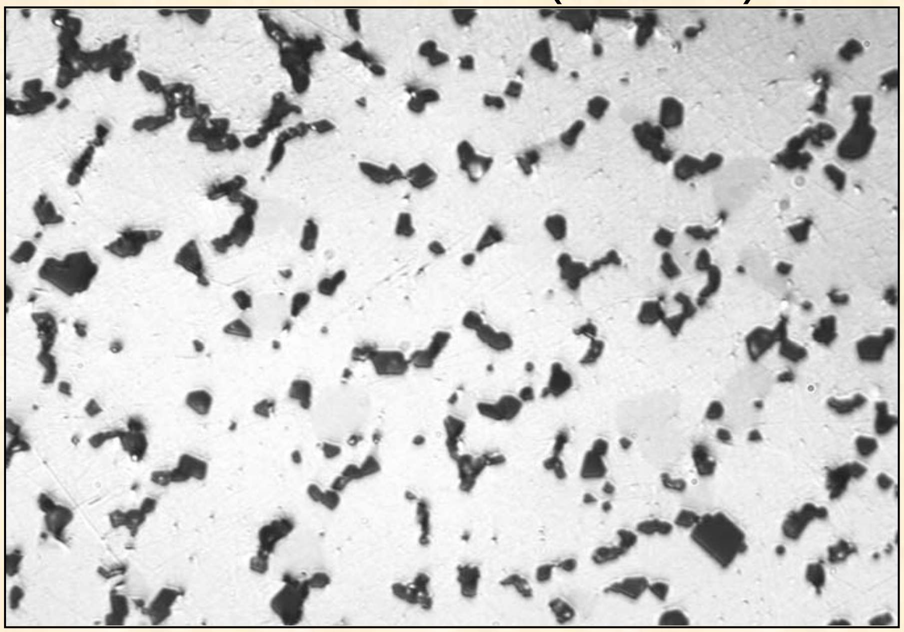
0.1mm

- Coarsening was surprising: Mg is essentially insoluble in Cr
  - is grain boundary transport needed for coarsening?

Magnesium acetate as a MgO-precursor yielded fine, evenly-distributed spinel

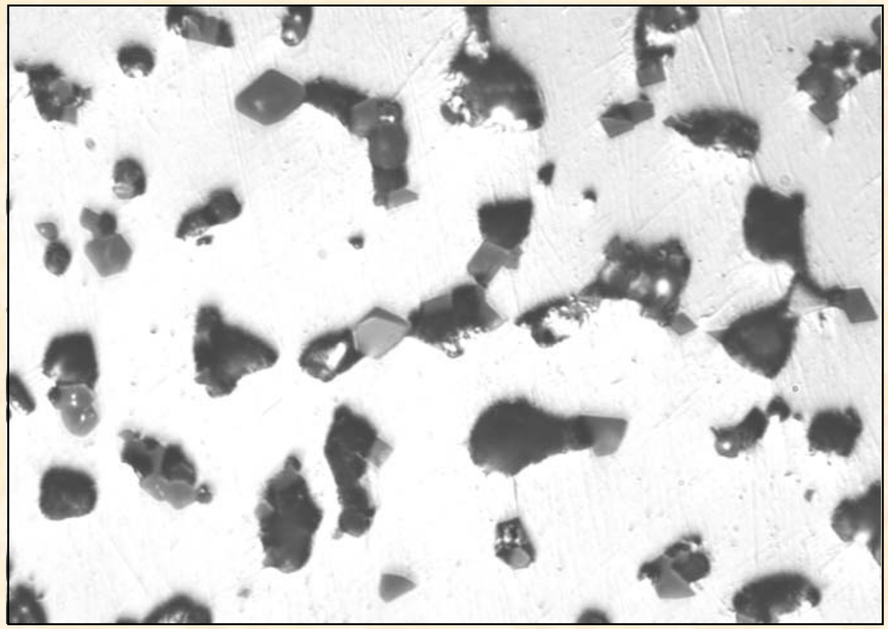
Optical Cross-Sections

As Hot Pressed (1450°C)



10 microns

+Annealed 2hrs at 1500°C



10 microns

No tensile ductility: totally brittle!

- suspect increased carbon impurities from acetate
- dispersions too fine?
  - all spinel may not be beneficial

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Different oxide dispersions were explored to gain insight into key factors for ductilization

These had a range of CTE, hardness, stability/solubility with Cr/Cr_2O_3:

- Non Spinel-Formers (w/Cr_2O_3):

  La_2O_3, TiO_2, Y_2O_3, ZrO_2 (partially- and fully-stabilized)

- Spinel (MCr_2O_4) Formers:

  Fe_3O_4, Mg_2TiO_4 (from MgO + 0-2 wt.% Ti), NiO, ZnO

- Pre-Synthesized Spinels:

  $MgCr_2O_4$, $MgAl_2O_4$

- Perovskites:

  $MgTiO_3$, $SrTiO_3$

Room-Temperature Tensile Properties of Selected Oxide-Dispersed Cr alloys

	Highest elongation %	Yield stress, MPa	Fracture stress, MPa
Pure Cr	1.5	179	165
Cr-6MgO	5.6	207	310
Cr-6TiO_2	—	—	241
Cr-6Y_2O_3	—	—	283
Cr-6La_2O_3	—	—	407
Cr-2TiO_2	1.4	214	255
Cr-2ZrO_2	2.2	214	303

- Only TiO_2, ZrO_2, 'Cr_2O_3' imparted ductility
  - not as effective as MgO, or Mg_2TiO_4 (from MgO + (0-1)Ti)
- Some significantly increased alloy fracture strength (La_2O_3, Y_2O_3)
  - much finer dispersions than with MgO

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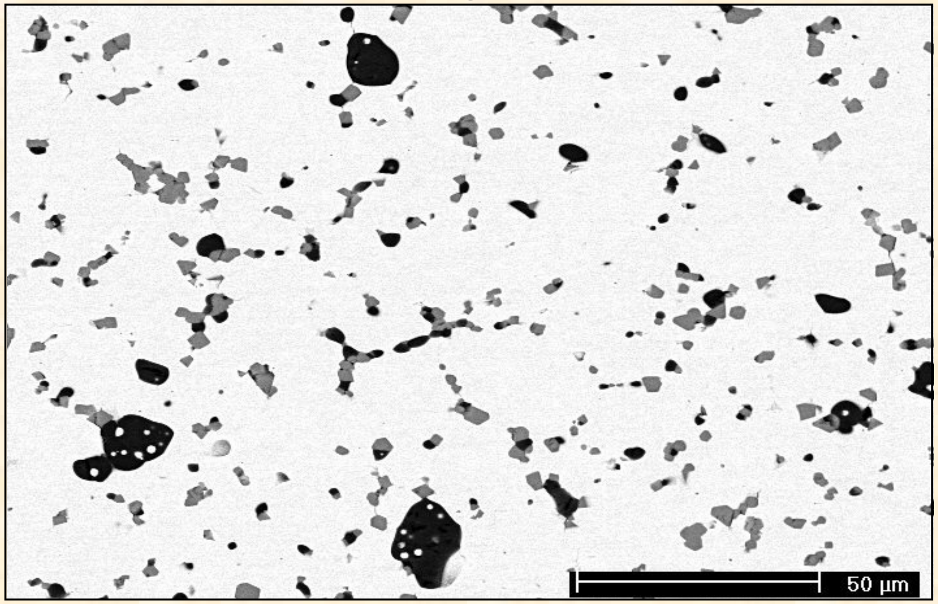
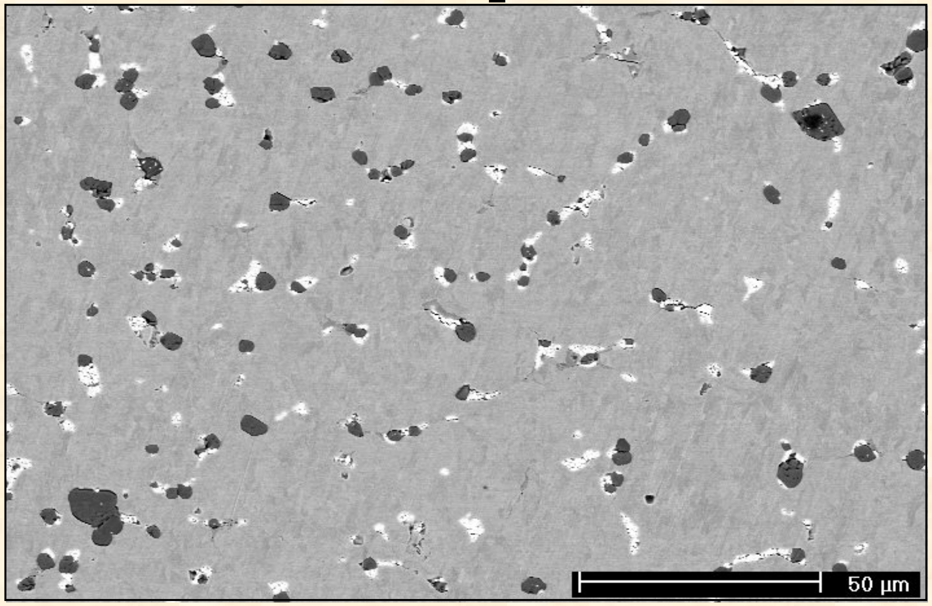
ZrO_2-dispersed Cr was similar to MgO-Cr

—SEM-backscatter images: hot-pressed at 1500°C, 2hrs—

Cr-3MgO wt%



Cr-3ZrO_2 wt%



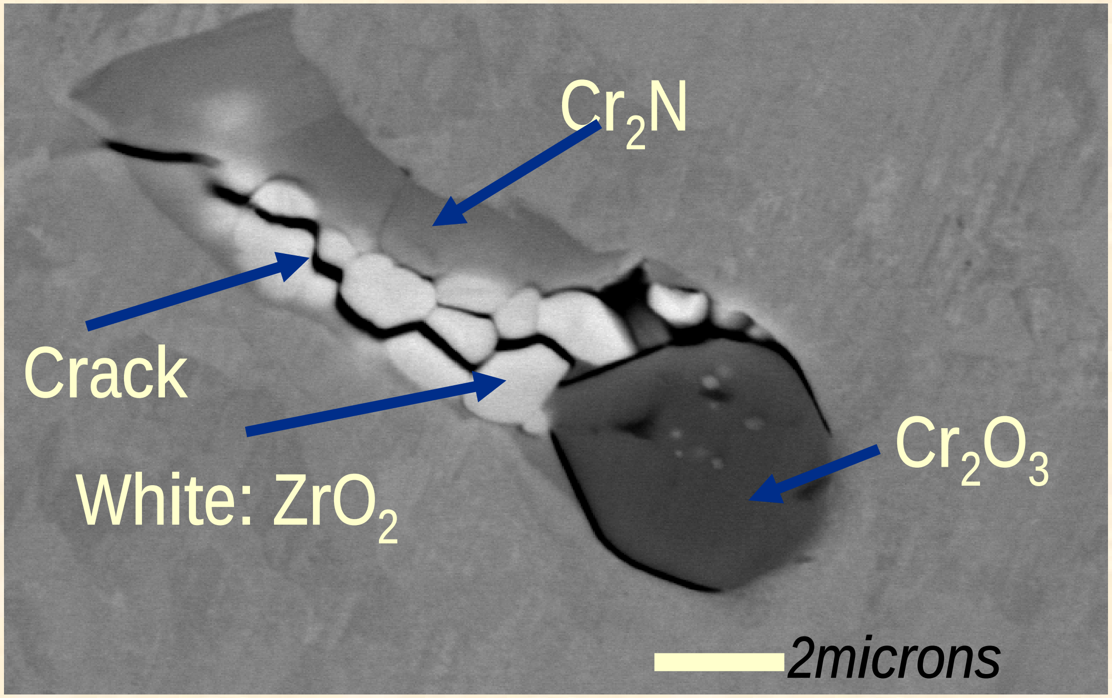
Grey particles-$MgCr_2O_4$
Black particles - MgO

White particles – ZrO_2
Black particles – Cr_2O_3

- Despite similar overall microstructures to MgO-Cr, no Cr_2O_3-ZrO_2 interaction

ZrO_2 particles in Cr matrix were polycrystalline, and were readily cracked

—optical cross section of Cr-3ZrO_2 wt.% after tensile test (1% ductility)—



- Crack initiation at ZrO_2 particles likely contributes to low ductility
- $MgO/MgCr_2O_4$ particles usually are single-crystal

Best results were obtained with MgO additions

—some phenomenological trends/factors are emerging—

- Optimal size/distribution of oxide-dispersed microstructure
  - too fine: may strengthen alloy, but lose ductility
  - too coarse: oxides may act as failure sites
- Oxide particle morphology is important
  - want single-crystals
  - want somewhat spherical, not elongated shape
  - not clear if faceting is helpful ($MgCr_2O_4$ is faceted; MgO is smooth)
    - effects on dislocation initiation?
- Oxide should be more stable than Cr_2O_3, and insoluble in Cr
  - Fe_3O_4, NiO are reduced (dissolved Fe/Ni hardened Cr)

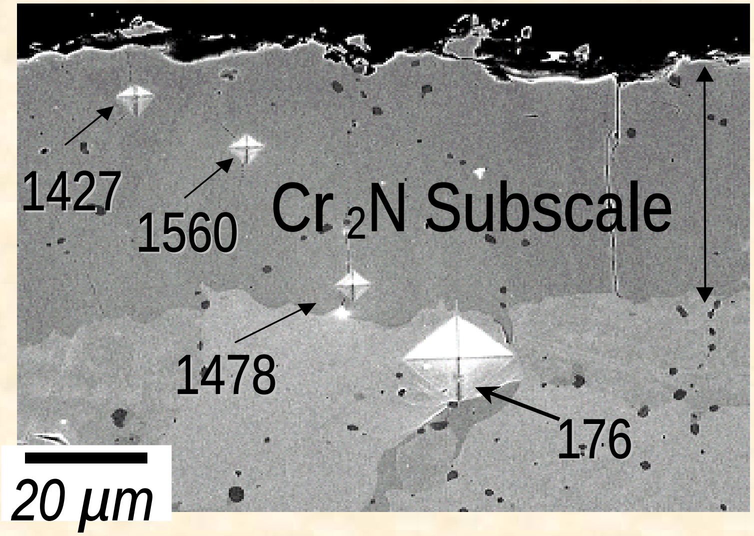
➢MgO appears to be the Ideal Choice

Alloying of Cr Matrix Phase

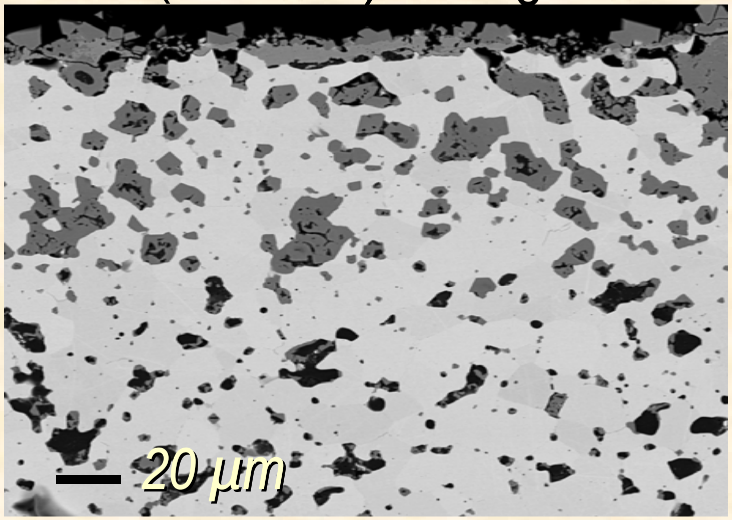
—interesting preliminary results with 45% Fe addition—

SEM cross sections after oxidation for 120 h (6 cycles) at 1100°C in air

Pure Cr



(Cr-44Fe) + 6MgO



- 3x increase in room-temperature yield strength to ~650 MPa
  - still shows some ductility (1.5%)
- Oxidation/corrosion tests suggest Fe retards rapid nitride subscale formation in air (possibly alters O/N permeability?)

Application Activities with Cr-MgO and Related Alloys

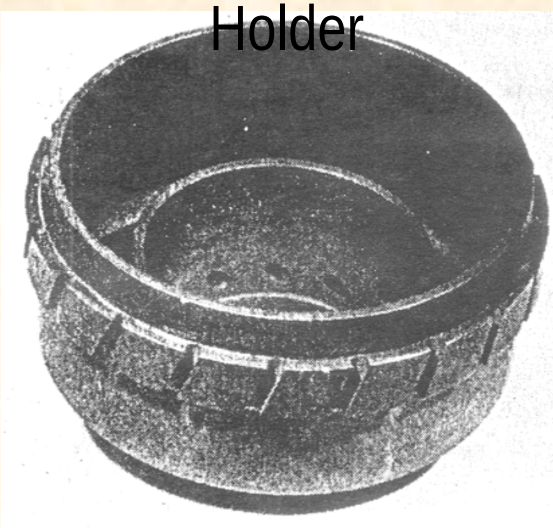
- Collaboration with Plansee for exploration of scale-up issues for manufacturing Cr-MgO alloys using appropriate industrial processes
  - see poster paper RM104

- Applications
  - original gas turbine applications--overtaken by superalloys
  - exploration for in-orbit repair of space shuttle
  - thermo-wells in aggressive, high-temperature environments (carburizing; molten salts)
  - *Application X (high MPt)*

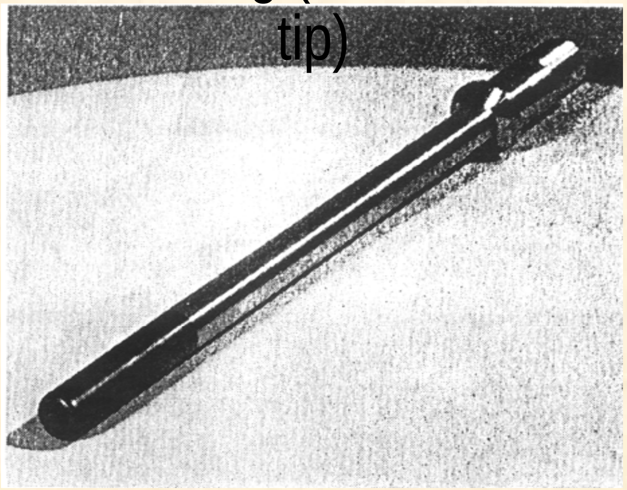
Mechanical properties of Cr-MgO alloys are sufficient for component manufacture

Components From Bendix Work in the 1960's

Gas Turbine Flame Holder



Thermowell for Ethylene Cracking (carburized tip)



Space Shuttle In-Orbit Repair for Heat Shield

MgO addition imparts resistance to re-entry conditions

– pure Cr melted and failed after 15 seconds
– Cr-6MgO-0.5Ti survived 15 minute torch exposure intact

Pure Cr

Cr-6MgO-0.5Ti

Macros of ~ 2.5 x 1.5 cm flat coupons
after 15 minute torch re-entry simulation test (ATK Thiokol)

Need to successfully manufacture and demonstrate sufficient ductility (bend radius) in <u>Cr-MgO foil</u>

– strength goal of 34 MPa at 1650°C
– Cr-MgO is borderline

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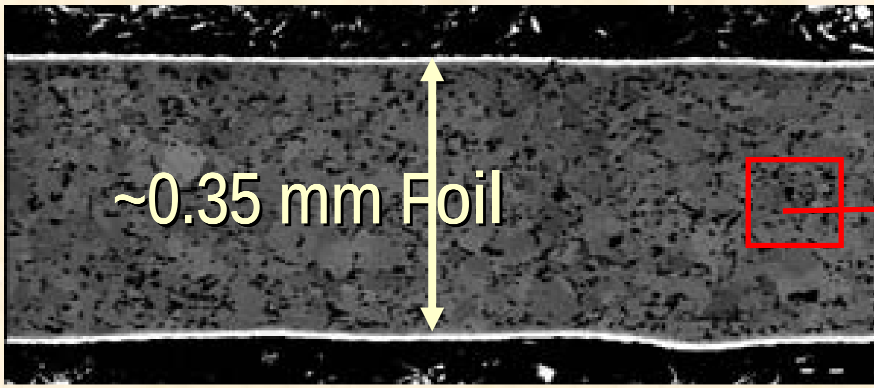
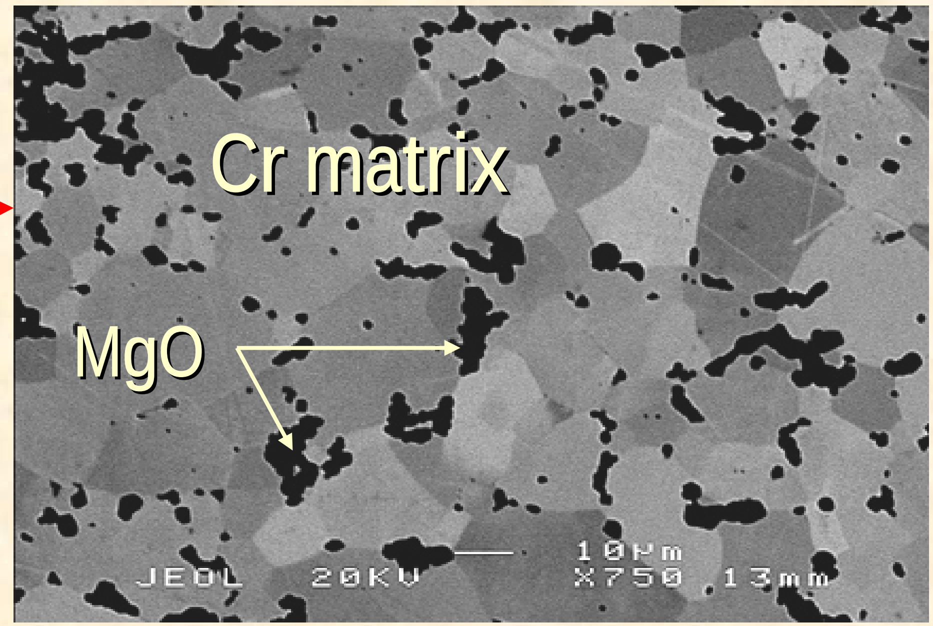
NASA Langley RC demonstrated feasibility of Cr-MgO coatings and foils

Cross-Section of NASA Langley RC Cr-6MgO Foil

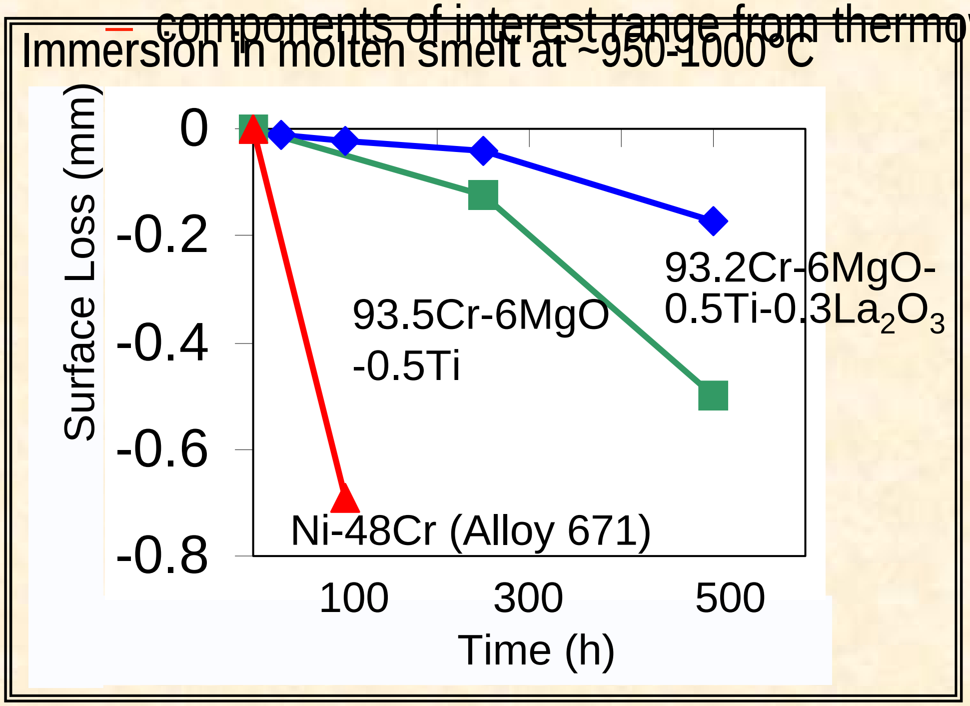




- Successful at first attempt; MgO distribution yet to be optimized
- Spin-off possibilities for Cr-MgO as coatings for aggressive, high-temperature environments?

Molten salt resistant alloys are needed for developmental black liquor gasifiers in the paper and pulp industry

- Gasification or burning of black liquor produces ‘smelt’ (high alkali molten salts)
  - ~70Na_2CO_3-22Na_2S-4Na_2SO_4-4KCl wt %
  - temperature range: 750-1000°C
- Current alloys are aggressively attacked in molten smelt
  - components of interest range from thermowells to brackets, inserts, and spouts



- In lab tests: Cr-MgO superior to Alloy 671, but still borderline for black liquor gasifier application
- Potential for thermowells in other hot corrosion environments

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In Summary
Why does MgO ductilize Cr?

- Manages impurities
  - MgO/spinel particles act as preferential sites for segregation/precipitation of nitrides

- Stabilizes a fine-grain structure
  - use of high consolidation T & relatively slow cooling provides time for segregation, and formation of coarse, blocky nitrides
  - provision of dislocation source?

- MgO/spinel are poor strengtheners
  - relatively coarse, soft particles

- MgO/spinel is very stable/inert
  - Mg has no significant solubility in Cr
  - spinel is more stable than Cr_2O_3

- Other oxide particles are not as effective because
  - exert stronger ODS effect
  - contaminate the matrix (stability vs Cr)
  - produce a less optimized particle size and morphology after processing

Acknowledgements

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