Manufacture of ODS Alloys by Mechanical Alloying ... History & Perspective

Huntington Alloys

Special Metals Corporation

a PCC Company

The Evolution of Oxide Dispersion Strengthened (ODS) Alloy Products

- Thoriated Tungsten – 1910
- SAP Aluminum –1950
- Thoriated (TD) Nickel – 1960
- TD Nichrome ~ 1965
- Mechanical Alloying – 1967
- Reaction Milled Aluminum – 1970
- Competitive MA Producers ~ 1985

ODS High Temperature Alloys

– Superior strength in an ODS material requires recrystallization

– Nanometer size grains must convert to millimeter or centimeter size grains

– Texture and grain aspect ratio are very important for optimum creep strength

– For most applications recrystallization is accomplished by conventional static heat treatment

ODS High Temperature Alloys

– Gas turbine blade applications require directional recrystallization (an exceedingly slow process)

– Production of MA-ODS single crystal blades was unsuccessful

– The recrystallized grain structure is sensitive to composition, milling conditions & thermal / mechanical processing conditions.

The Mechanical Alloying Process

- **Mechanical alloying is a true “cold” alloying process**
- **In principle any combination of elements can be combined, regardless of conventional phase diagrams**
- **Alloying takes place by repeated welding and fracturing of powdered raw materials. A proper balance of welding and fracturing is an essential part of the process.**
- **Length scale decreases progressively during the process**

The Mechanical Alloying Process

- Metal enters a nanocrystalline or sometimes an amorphous state.
- Oxide dispersion strengthening is achieved by adding a fine oxide powder which gets enfolded in the alloy layers
- Any insoluble oxide can be used (Yttria is preferred for iron and nickel base alloys due to its stability)
- The oxide strengthening can be supplemented with γ' age hardening as achieved in MA6000.

Mechanical Alloying Process Scale-Up

- **All known MA processes use some form of an energized ball mill**
- **Initial Inco experiments and most published academic work use a “spex mill”, multi-axis, vigorously shaken canister to produce a few grams of powder, in a few hours.**
- **First scale up was to an “attritor”, a mechanically stirred mill to produce up to about 100 lbs of powder in 24 – 48 hours.**
- **Commercial scale-up to gravity-assisted ball mills increased unit production to 3000 lbs. in a milling time of 50 - 150 hours.**

Mechanical Alloying Process Scale-Up

- **Larger mills are theoretically possible but, wear, vibration, structural integrity, heat extraction and product uniformity are potential problems.**
- **In principle any powder can be used as feedstock. However, in actual practice, proper selection of compatible powders is necessary.**
- **In processing, powder size control is essential. Too much welding may cause the mill to seize. Too much fracturing produces pyrophoric powder**

Commercial Production

- The MA process was invented at Inco's corporate research lab. Commercial production was established at the Inco Alloys plants in Huntington, WV, USA and Hereford in the UK. Haynes (then Cabot Corporation) was licensed but never entered commercial production. Metalwerk Plansee and Dourmetal independently developed their processes.

- Initial manufacturing involved powder making via 100S attritor, blending, canning, extrusion and rolling to bar for the manufacture of vanes and bands for GE engines for USAF.

Commercial Production

- Later gravity ball mills came into use
- Subsequent development led to procedures for making plate, sheet, tube and wire that include HIP, forging, and slab rolling.
- SMWL-Hereford concentrated on iron-base alloys and age-hardened “superalloys” (MA956 & MA6000)
- SMC-Huntington concentrated on nickel-base solid-solution alloys (MA754 & MA758)

Ball Mills for Production of MA Alloy Powders

Powder Screening / Sieving

ODS Problems – Process-Related

- **Maximum product size is limited by TMP, not powder production unit size.**

- **The alloy's fabrication requirements proved too specialized and complex for contract fabricators. Each prototype farication was an R&D project**

- **The cost for MA ODS products lies primarily in fabrication, yield and predictability rather than the basic cost of making powder.**

ODS Problems – Process-Related

- **Powder batches may need to be blended to make commercially useful size intermediate products**
- **Recrystallization to desired grain structure is difficult to reproduce in both mill product forms and fabricated components**
- **Continuous coil strip production has never been attempted**

ODS Problems – Process-Related

– **Each alloy requires a unique set of raw materials and process conditions which makes screening of candidate alloys tedious**

– **Reactive metal powders require special handling and may be pyrophoric.**

– **High energy mills are difficult to maintain in commercial production environment**

ODS Problems – Alloy Related

– **Joining -** Loss of strength in fusion welding. Brazing (TLP), diffusion bonding and explosion bonding have been moderately successful. Friction stir welding is interesting?

– **Oxide Loss in MA956 -** Catastrophic oxidation (“Black Rot”) results in local loss of protective alumina layer. Alumina oxide palls with thermal cycling due to expansion mismatch.

– **Dealloying -** Oxidation or evaporation of Al and Cr at high application temperatures, problem in thin sheet

ODS Problems – Alloy Related

- **Stability -** Y_2O_3 dispersoid is not stable at temperatures near melting. It can coarsen and convert to an intermetallic compound (YAG), a less effective strengthener.

- **Directional Properties -** Certain grain boundary orientations in ferritic alloys are inherently weak. Combined with strong texture, this is basis of poor hoop strength in tube.

- **DBTT -** MA956 has ductile-brittle transition temperature above room temperature. This has implications for handling during cold processing and impact toughness

ODS Problems – Alloy Related

– **Processing Difficulties -** Nickel base alloys are very difficult to cold work and recrystallize. Opposite is true for iron-base.

– **Ductility -** In the unrecrystallized state the alloys are brittle at low temperatures, but superplastic under some hot working conditions.

Current Status of MA Alloys at SMC

SMC/HBE – Huntington, WV, USA - Six large and one small production ball mills and several experimental mills. The latter have not been used in over ten years. A few large mills are operable and an order for MA758 is currently being processed. Only nickel-base alloys were commercially produced in Huntington. Most of the technology and knowledgeable engineers are still here.

Current Status of MA Alloys at SMC

SMWL – Hereford, UK - Mill has been dismantled. All iron-base alloy production and all age-hardened nickel-base alloy was at SMWL. Sheet and wire rolling and tube making technology resides at SMWL and all knowledgeable engineers have left the company. Some of the pedigreed excess powder was sold in US for DOE projects. None is left.

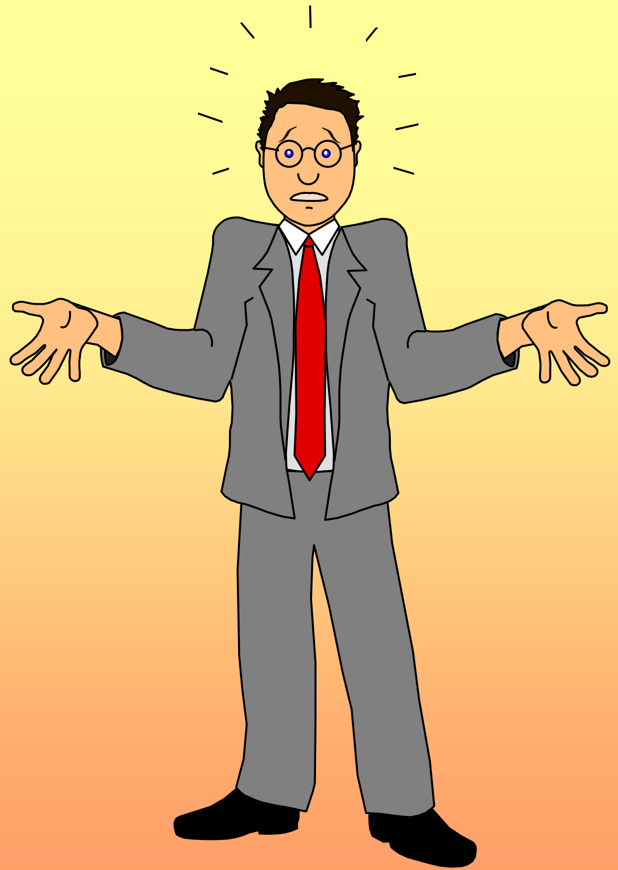
Current Status of MA Alloys at SMC

Special Metals Corporation – SMC has withdrawn from the commercial MA ODS alloy business and is entertaining orders only on a target of opportunity basis. This situation is unsustainable in the long run and unless a substantial market appears soon, the existing capability will vanish.

Summary

- **MA ODS alloys offer unique combination of engineering properties**
- **Inco R&D made significant contributions to MA ODS alloy technology – product and process development and application.**
- **While some equipment and personnel are still “intact”, it is doubtful that production will resume without immediate development of major product requirements.**

Questions ???



Thanks !!!