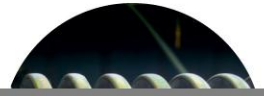


Deloro Stellite®

Coatings in the Valve Industry

Valve Manufacturers Association
Technical Seminar
8 - 9 March 2012, Houston

Contents

- Brief introduction to Deloro Stellite
- HVOF coatings
  - Process overview
  - Factors influencing coating quality
- Weld overlay coatings
  - Overview of various processes
  - Stellite hardfacing
- FusionStell™ coatings
  - Process overview
  - Engineered coating solutions

Deloro Stellite Group

Deloro Stellite is a global provider

of innovative solutions to challenging wear problems.

We deliver advanced wear protection

to extend the life of components

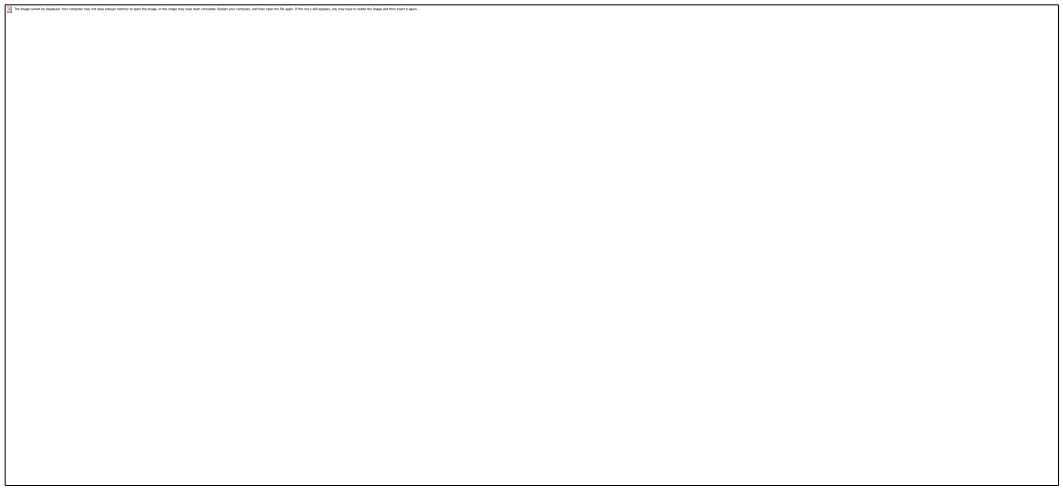
in demanding environments

where heat, corrosion and wear

are prevalent.

Deloro Stellite Group

- The company dates back to 1907 with the invention of a Co-Cr alloy called “Stellite”, known for its superior wear resistance
- Today it is a global company with $300m sales, operating out of 12 factories in 9 countries
- Industry leader for solving wear and corrosion problems, and a supplier to diverse industry sectors
- Portfolio of alloys and coatings for aggressive and demanding environments



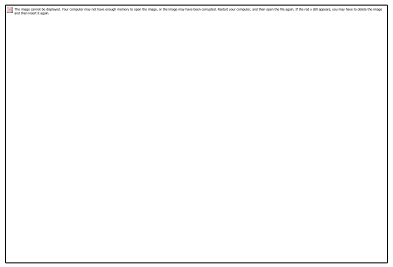
Provider of Wear Solutions

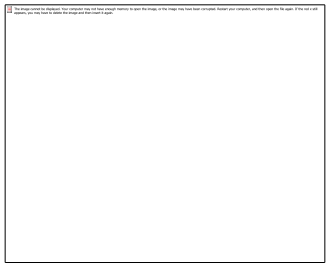
- Our ability to provide wear solutions in demanding environments is based on a wealth of experience & know-how of wear problems
- Deloro Stellite has around 200 alloys and an extensive materials data-base for material selection in a wide range of applications
  - Each alloy has its own characteristics and properties
- We match the alloy characteristics with the service conditions
  - What type of wear?
  - What is the operating temperature?
  - Is it an environment with a combination of wear and corrosion degradation?
- Use field service experience and application know-how to select most suitable alloy and manufacturing route
  - Custom alloy development capability for new applications

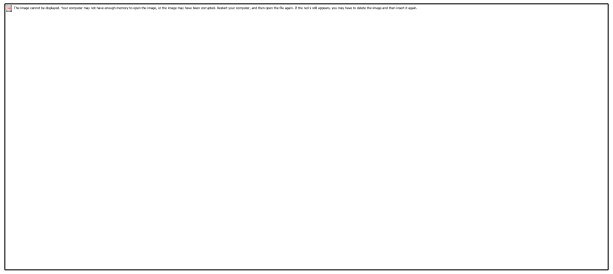
Suite of Processes

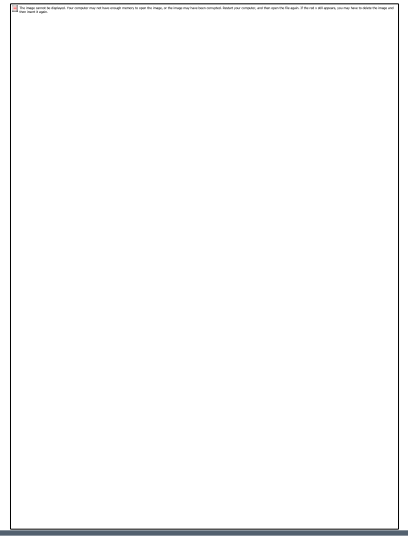
Manufacture of components for high wear applications

- Variety of casting processes available within our network of six foundries
  - Sand casting
  - Centrifugal casting
  - Investment casting
  - Resin shell casting
  - Vacuum casting
- Machining and finishing of hard alloys to high surface finish specs
  - Modern machine shops at various locations
- Powder metallurgy products
- Wrought products
- Prototyping and Rapid Product Development









Suite of Processes

Wear-Resistant Coatings

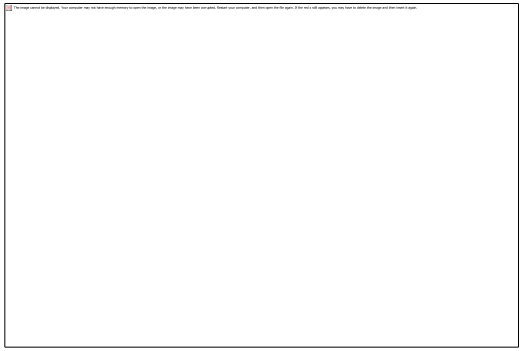
- HVOF coatings
- Plasma Transferred Arc (PTA) welding
- Tungsten Inert Gas (TIG) Welding
- Submerged Arc Welding
- Metal Inert Gas (MIG) Welding

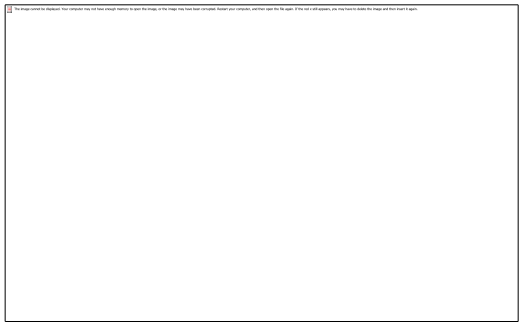
Wear-resistant materials

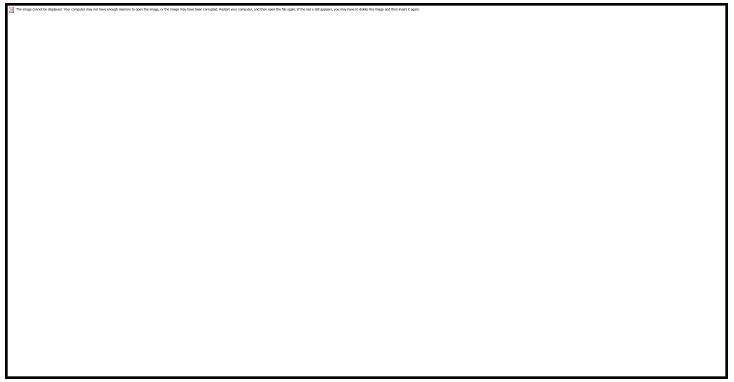
- Cobalt and Nickel welding consumables
  - Power, rod, wire & electrodes
- HVOF thermal spray powders

Coating equipment systems

- Jet-Kote® HVOF coating systems
- Starweld® & Hettiger® Plasma Transferred Arc (PTA) welding systems

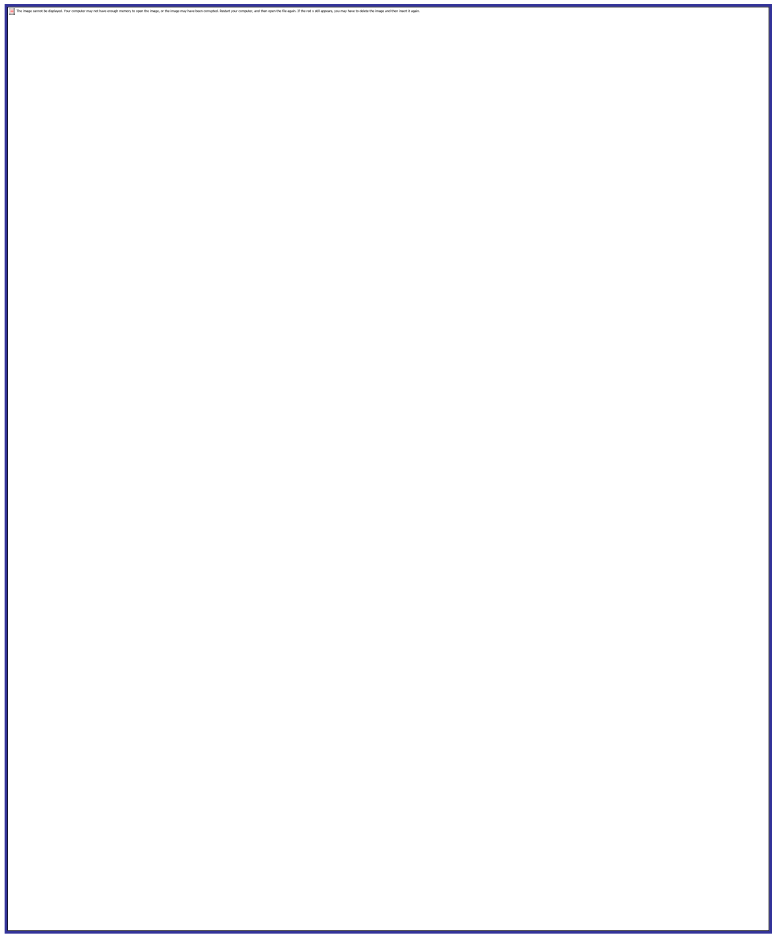




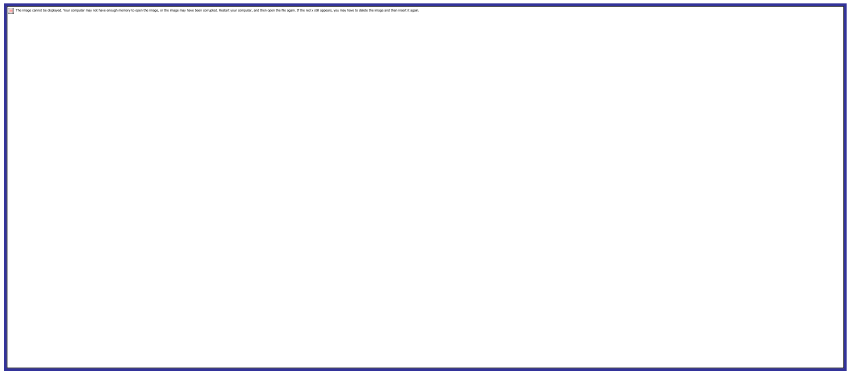


HVOF coatings

Principle of Thermal Spray

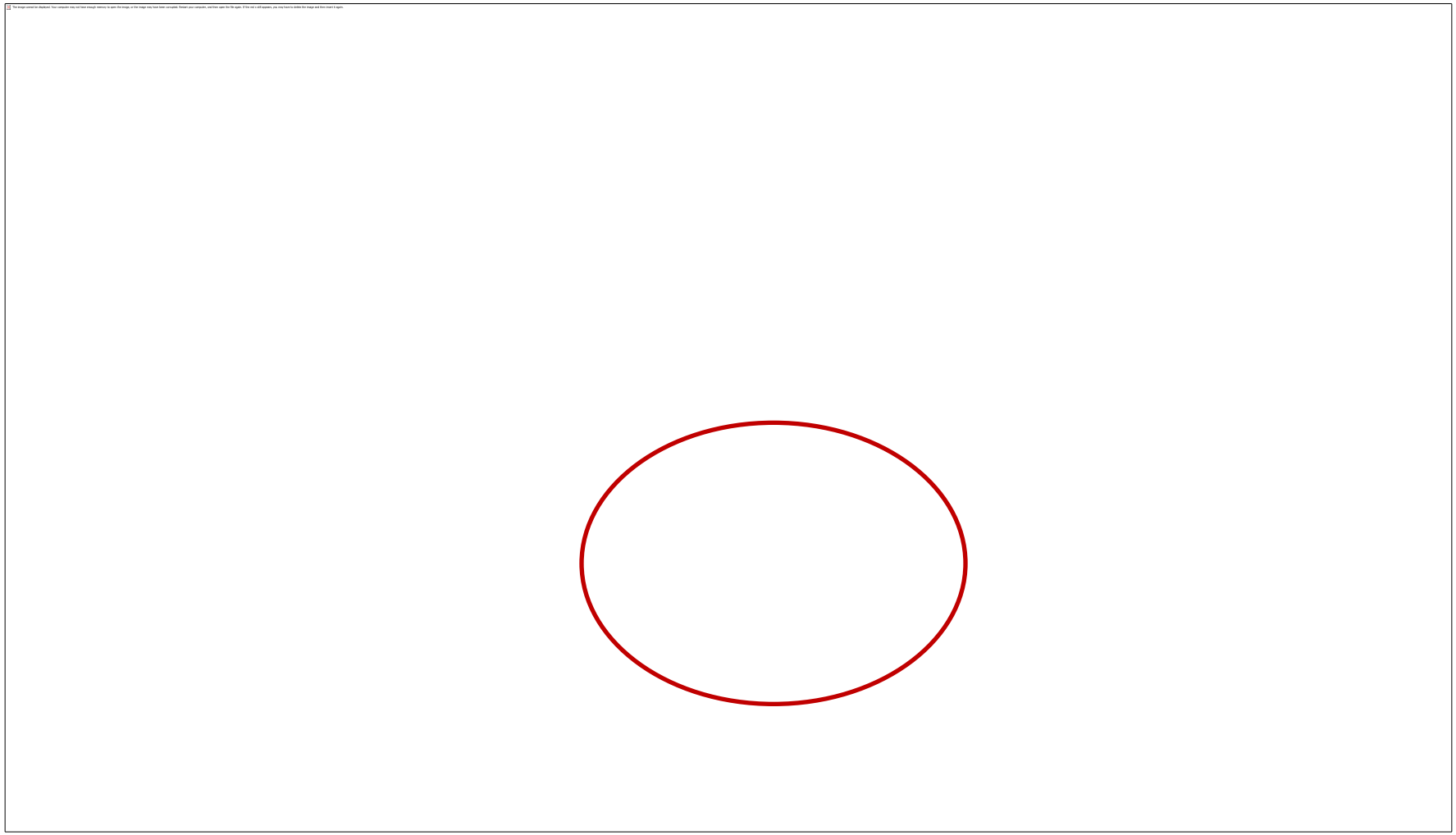


- Balance *kinetic energy* (velocity) and *thermal energy* (heat) by dwell in flame
- Extremely high particle velocity generating heat/bonding on impact due to mechanical deformation

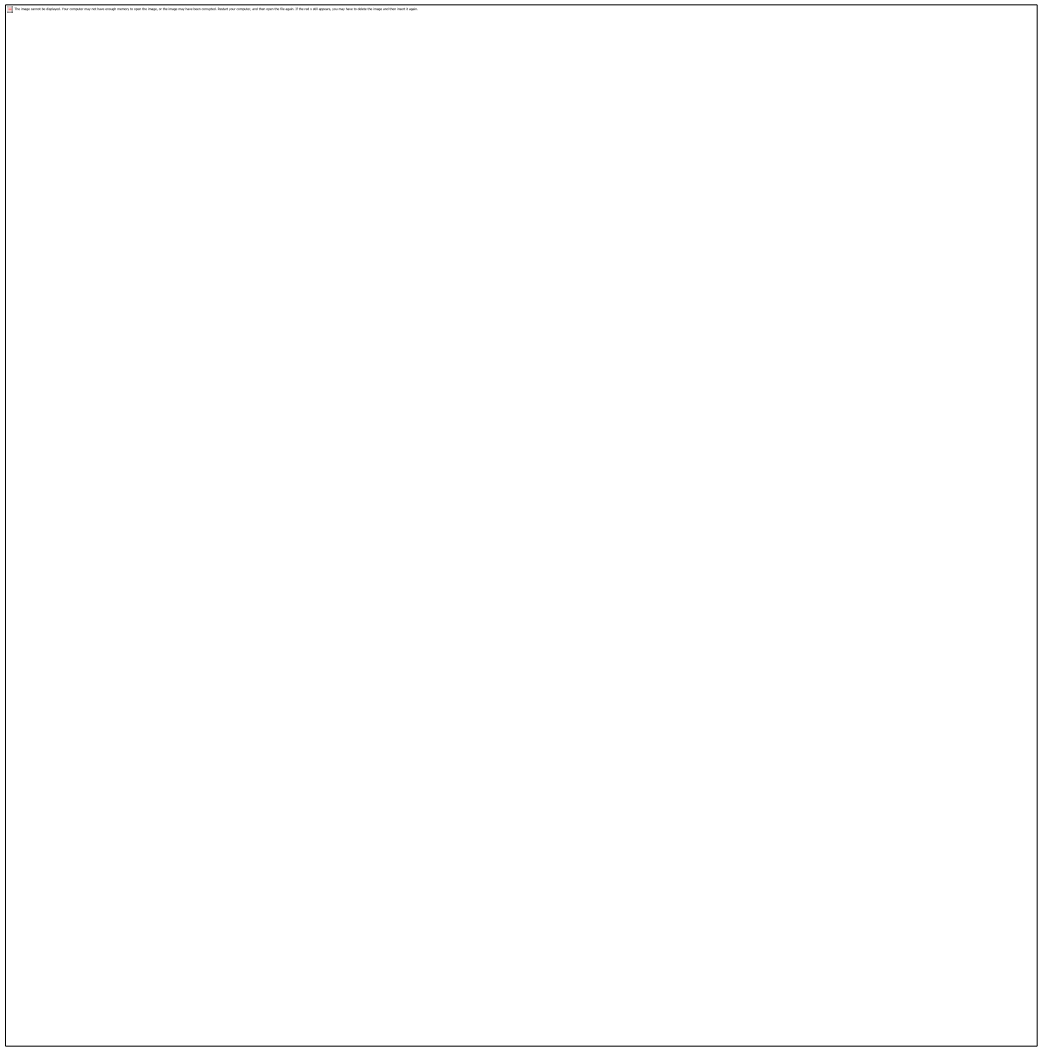


Figures used in this document are courtesy of ASM® International, TWI U.K. Ltd. and Gordon England.

Types of Thermal Spray Processes



Features in Thermal Spray Coatings



- Flame and Plasma Spray coatings have a greater tendency to form oxides, porosity and unmelted particles than HVOF coatings
- HVOF generally produces a denser coating with less oxides

Advantages & Limitations of Thermal Spray Coatings

Advantages

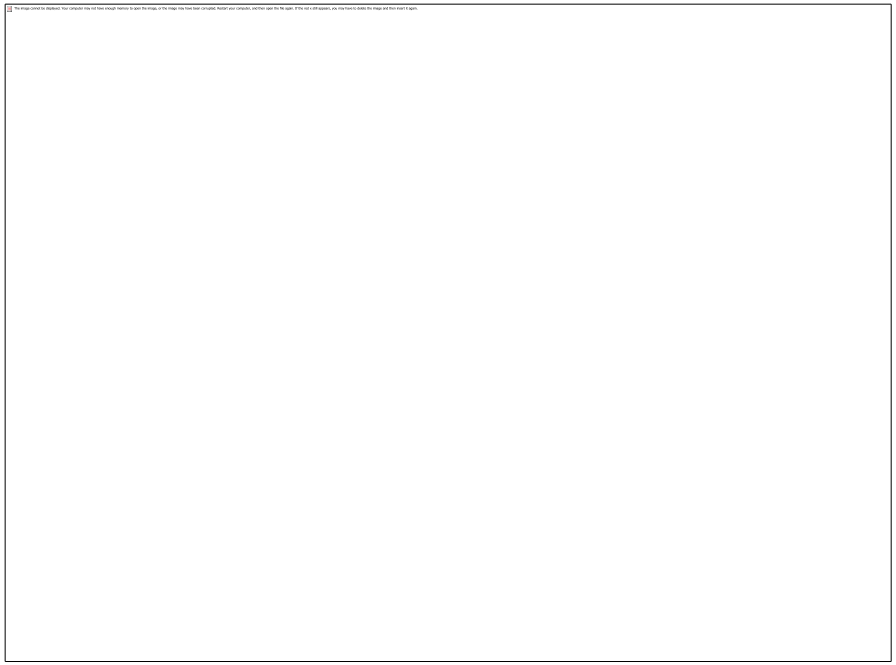
- Minimal heat input into substrate, <150°C and no dilution
- No change in properties of substrate, base material retains heat treatment
- Alloys which are difficult or not recommended to be welded can have coatings applied to them
- Coating compositions can be applied not possible by welding
  - Tungsten-carbide, Chromium- carbide, and ceramic coatings

Limitations

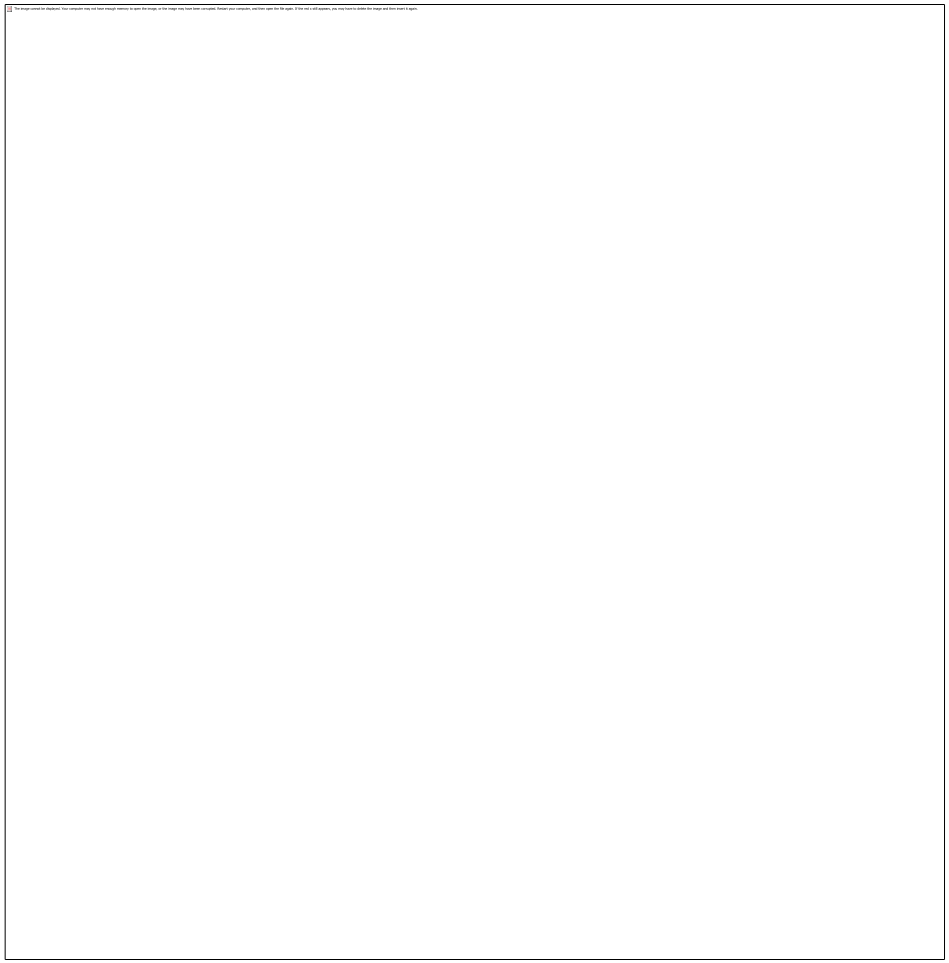
- Coatings adhere by a mechanical bond, which is not as strong as the metallurgical bond of a weld deposit – Lower impact resistance
- Complex geometries such as inside diameters where low spray angle would be necessary leads to lower coating quality
- Only materials that are available in the correct powder/wire size can be used as coatings

The birth of HVOF

- Jim Browning develops first portable, continuous spray (non-detonation) process in 1981 with coating quality comparable to the D-gun

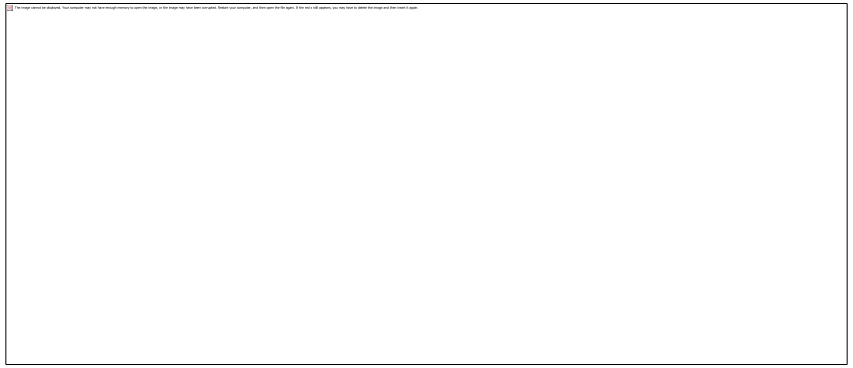


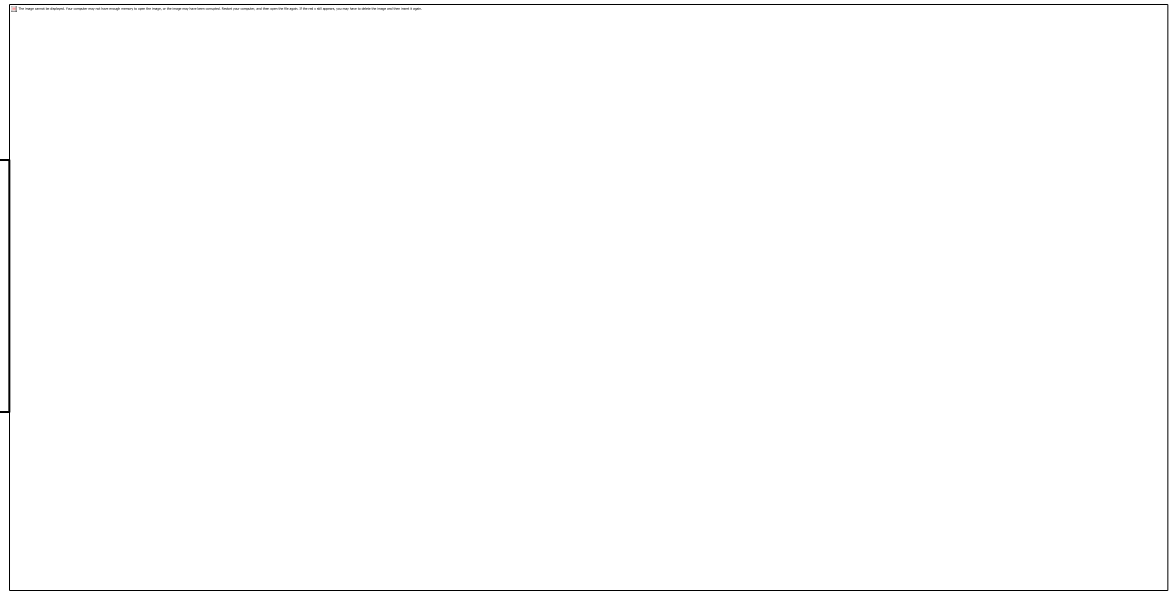
D-GUN Commercialized 1953



The HVOF Process

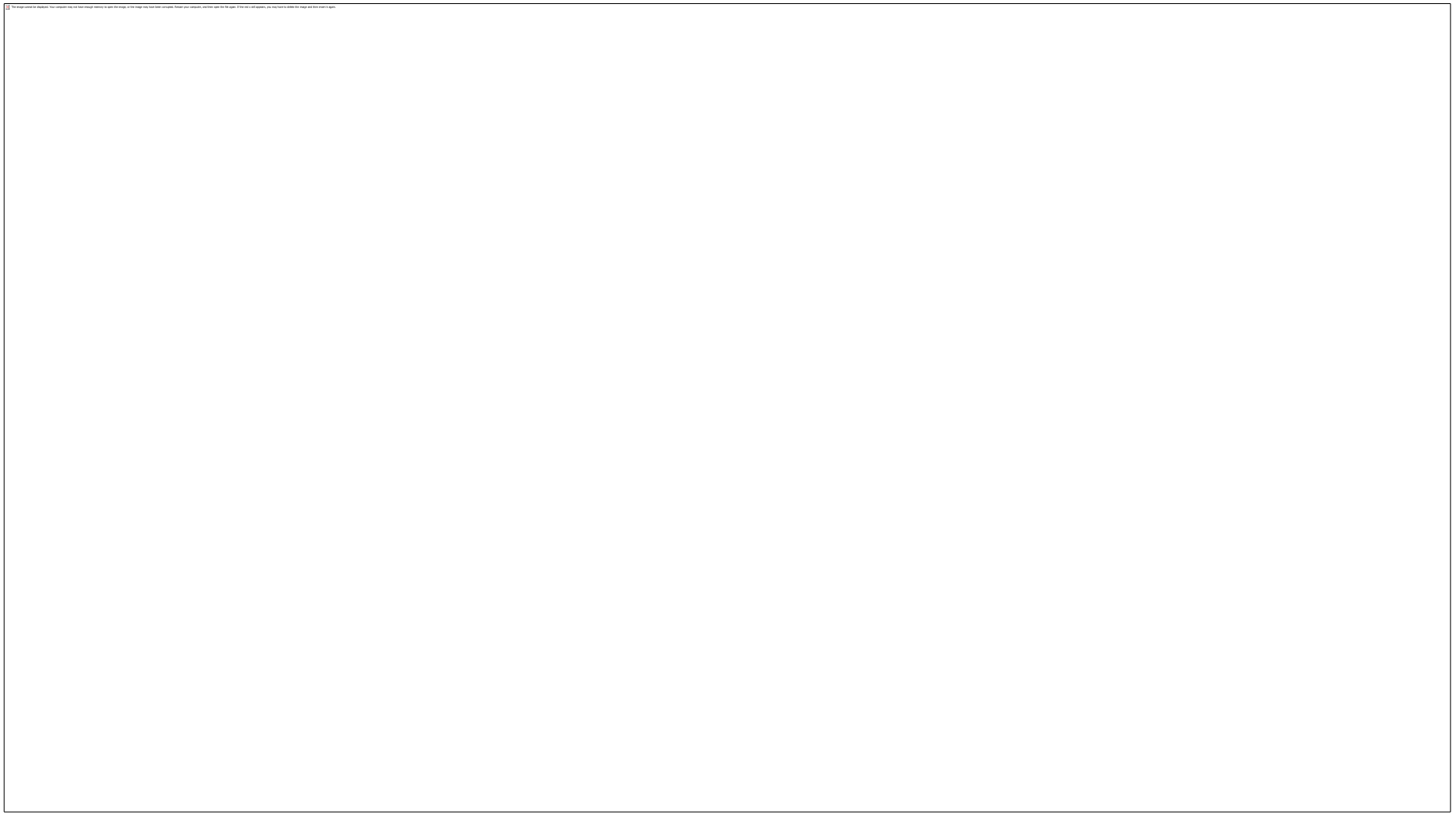
- **High Velocity Oxy Fuel**
- **Supersonic flame**
- **Lower temp than plasma spray**
  - Ideal for carbides (no decomposition)
  - Not for ceramics (too high melting point)
  - Good for metals, alloys





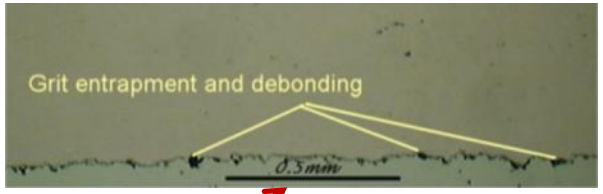
Ideal for high density wear resistant coatings

Many Factors Influencing Coating Quality



So What's Important?

- **POWDER**
  - Quality – consistency between batches
  - Type of powder – all tungsten-carbides are not the same!
  - Powder feed rate and settings



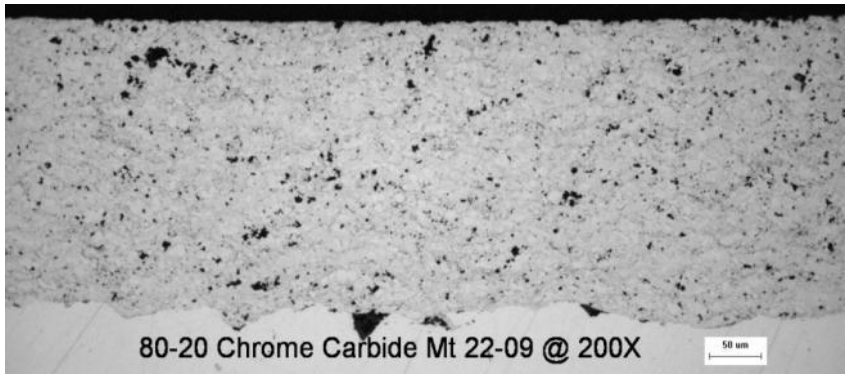
- **SUBSTRATE SURFACE**
  - Cleanliness (proper degreasing)
  - Roughness (correct grit blasting with clean alumina grit)
  - Interface (over-blasting results in too much grit in bond line)
  - No moisture or oxides on the surface (max. 4 hours wait before spraying)

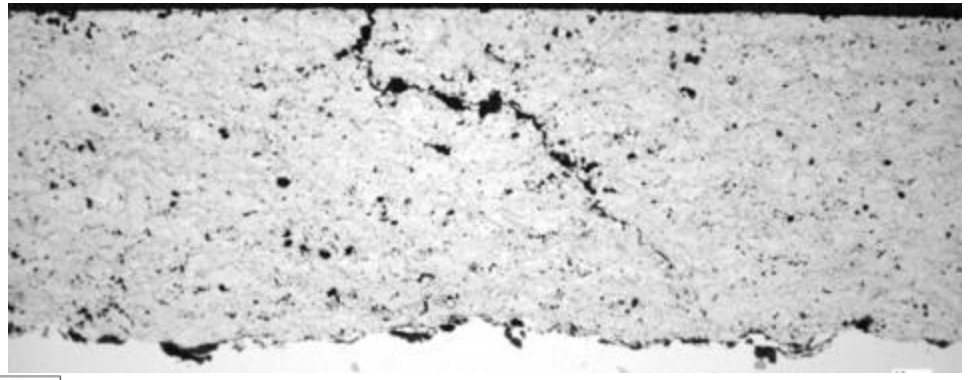
- **SPRAY PARAMETERS**
  - How to heat and accelerate the powder (gas flow settings)
  - Correct angle and stand-off (robot programme & rpm)
  - Spray program (thickness of each layer, heat into substrate, dwell time on part)

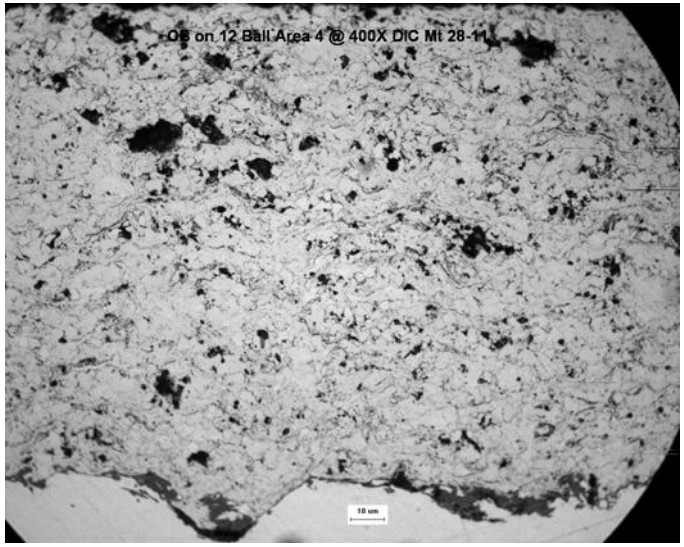
The same powder can be sprayed with different parameters resulting in coatings with completely different properties

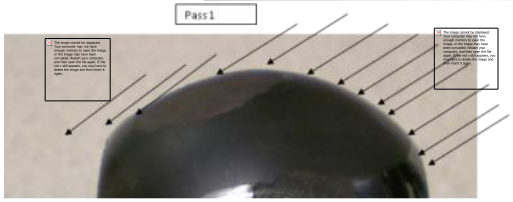
Spray parameters – Effect of Spray Angle

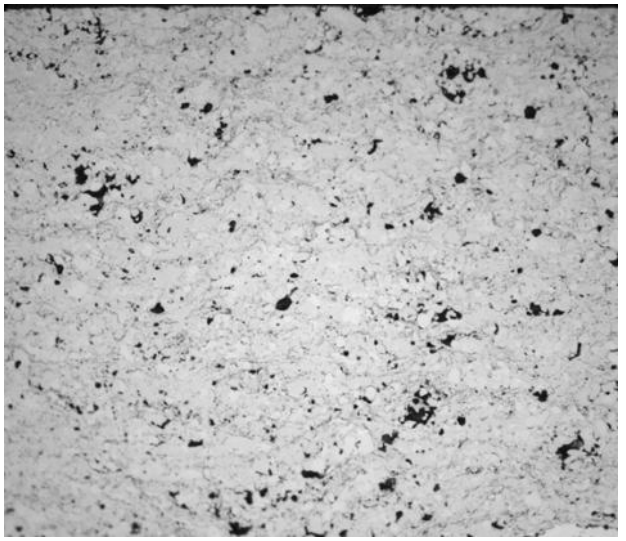
Coating quality depends on spray angle – robotic manipulation for complex geometries
(images of same coating on different sections of a ball valve)





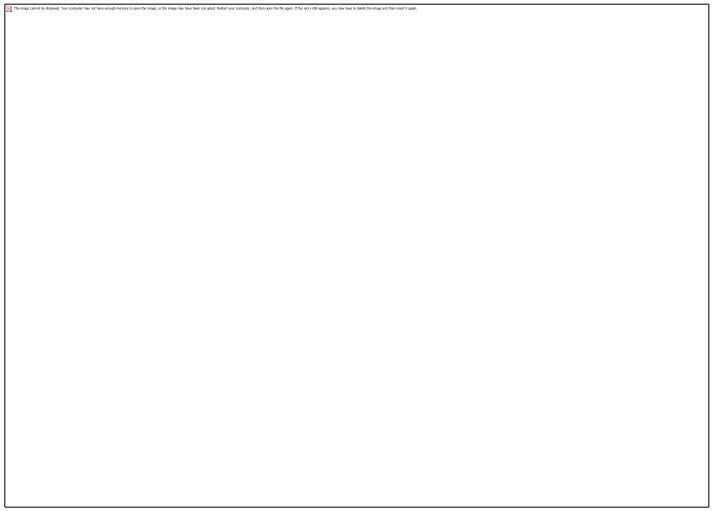




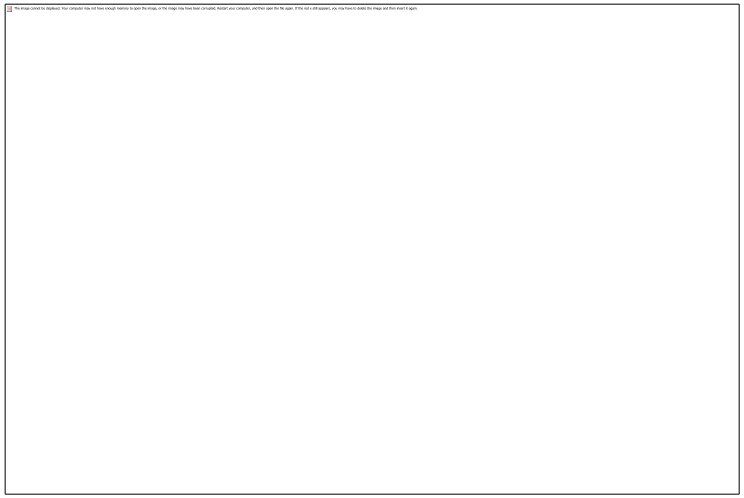


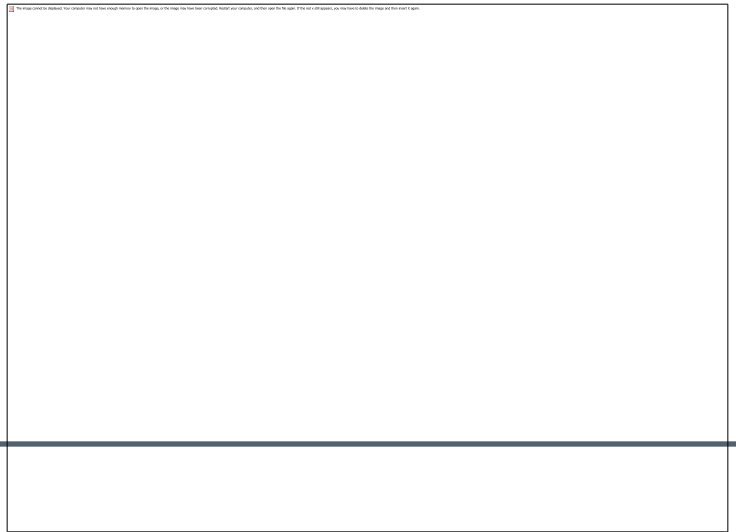
Spray Parameters – Type of Torch

Coatings deposited with Propylene torch



Cr_3C_2/NiCr



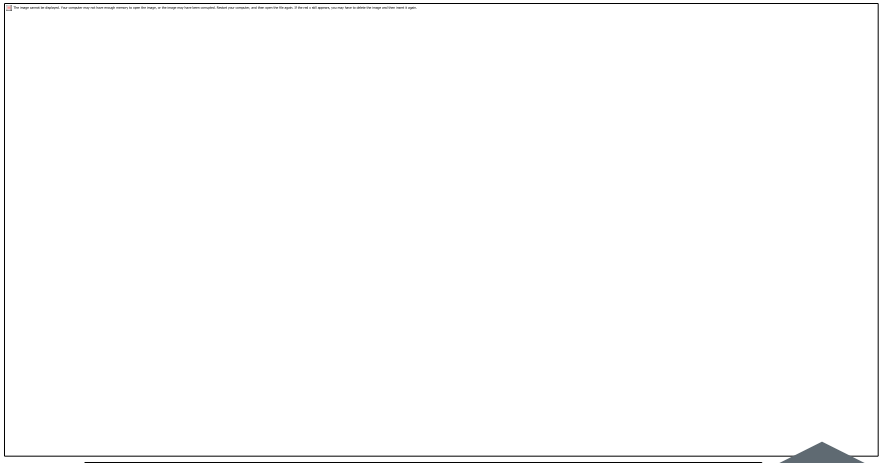


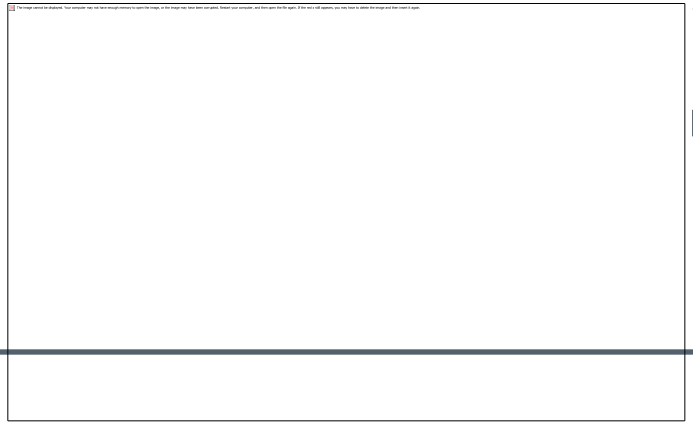
Stellite 6

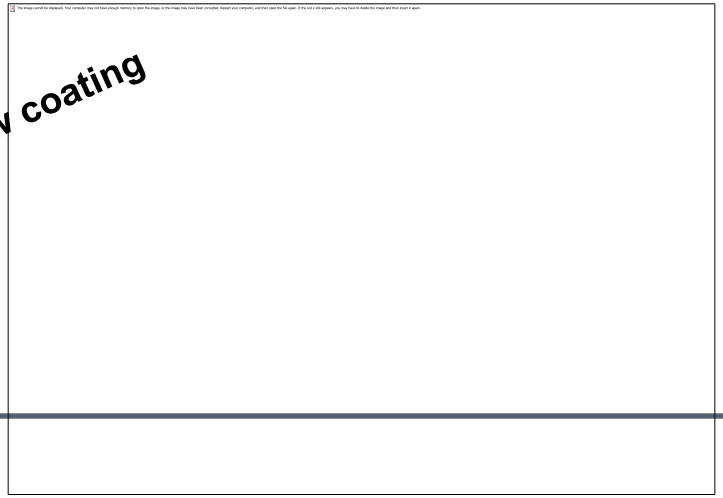
Coatings deposited with hydrogen torch

The right coating for each application

- Cr-carbide coating for a super-critical steam application
  - Coating failed due to low thermal shock tolerance in severe environments
  - Problem solved by *developing* coating to increase *toughness*
  - Furnace fused NiCrSiB coating provides acceptable coating toughness, but not as good erosion resistance as WC composite coating

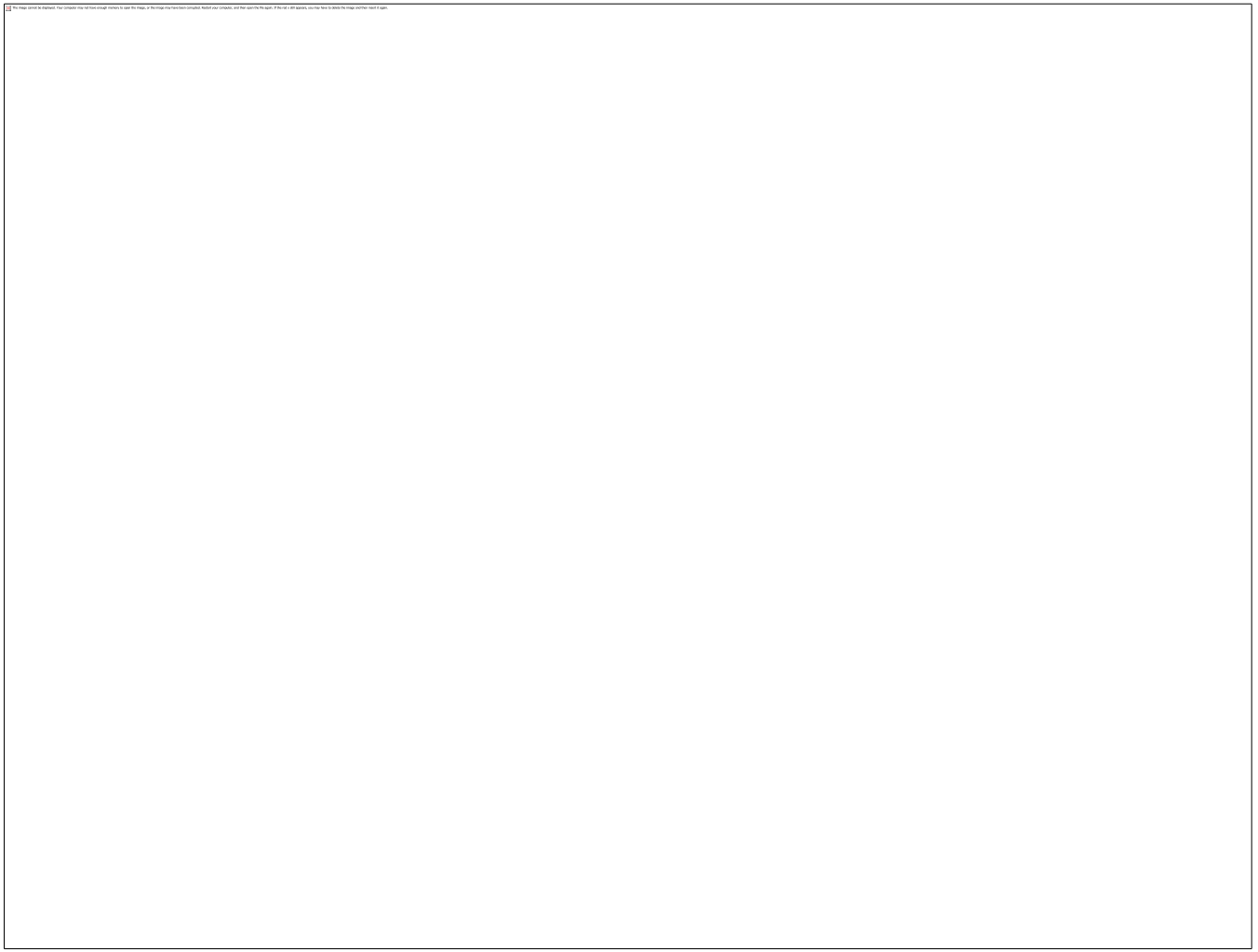




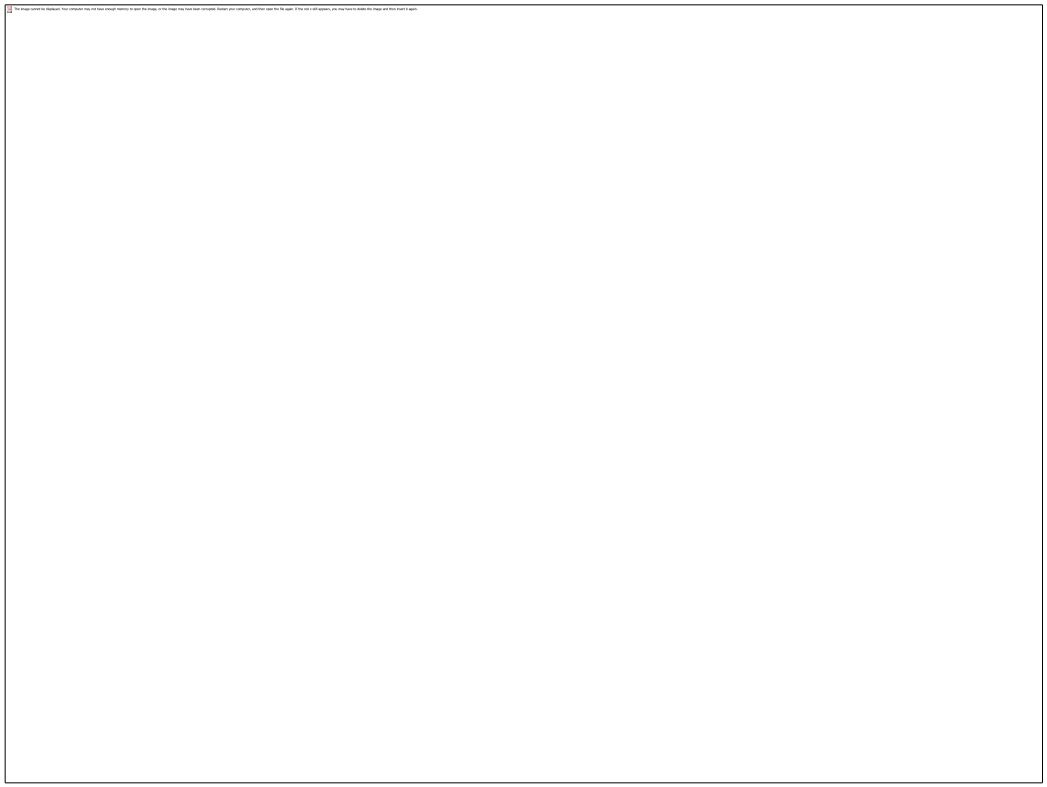


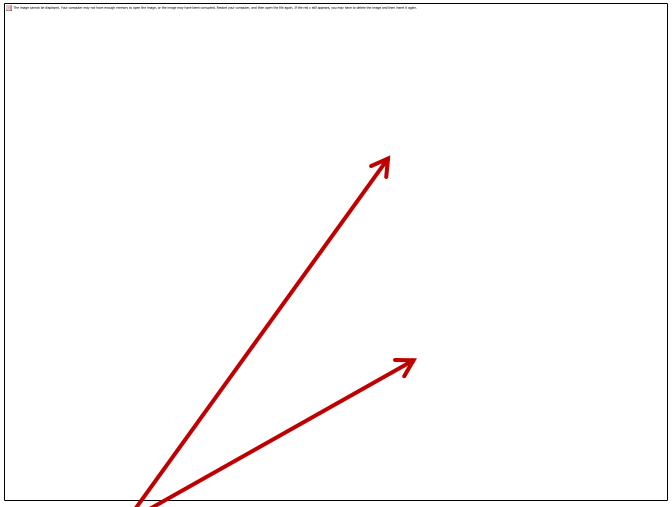
Powder Quality

- Shape (morphology)
- Particle size distribution
- Flowability
- Bulk Density



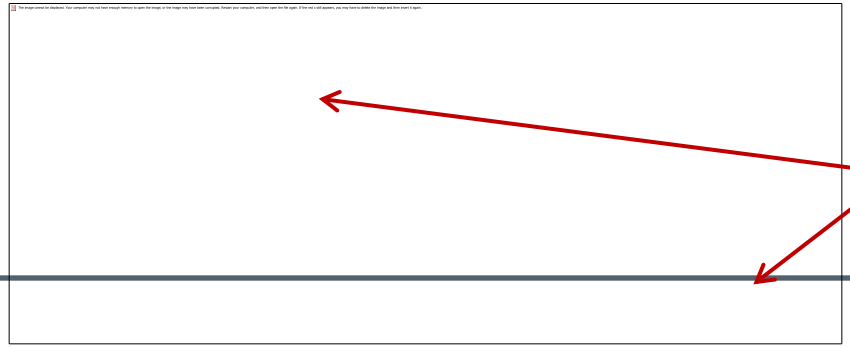
Gas atomized alloy powder





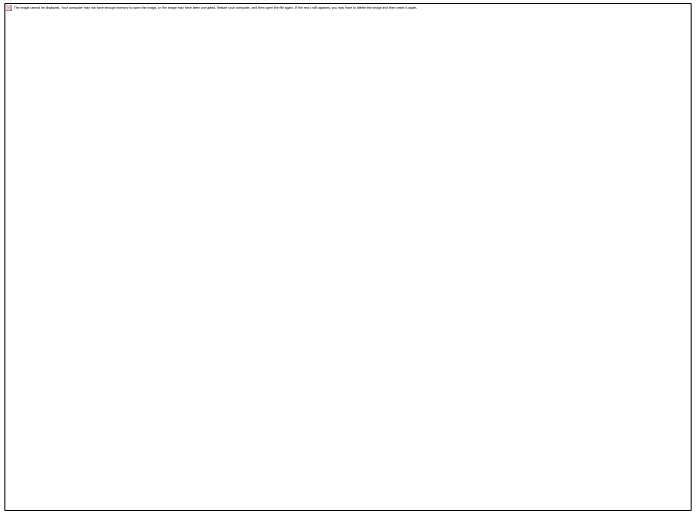
‘Dogbones’

Density variations

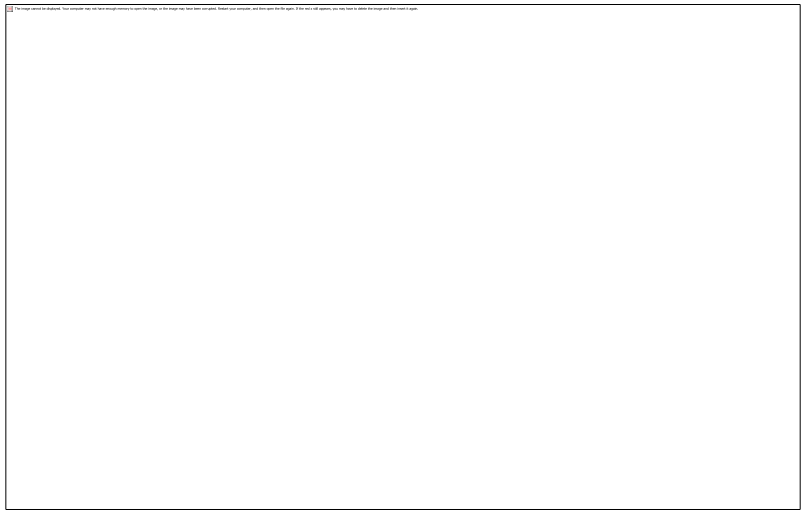


Satelites

Various WC-Co powders ➡ different coating properties



Cast (fused) and crushed



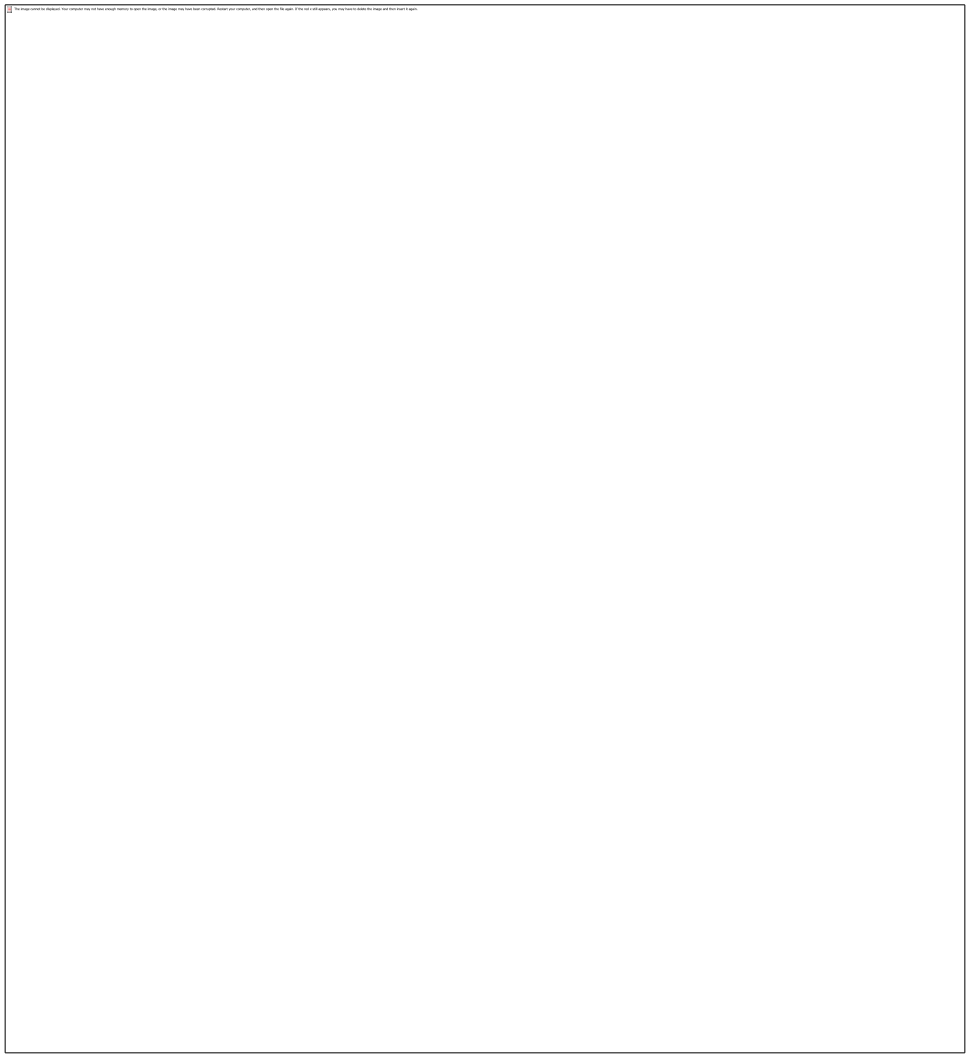
Agglomerated (spray dried) & sintered

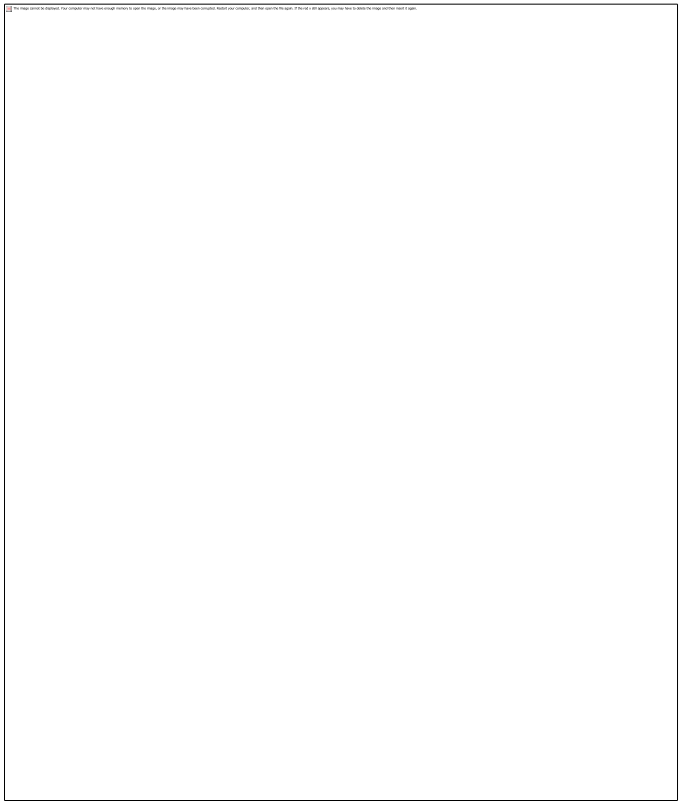
Sintered and crushed

Agglomerated & sintered & plasma densified

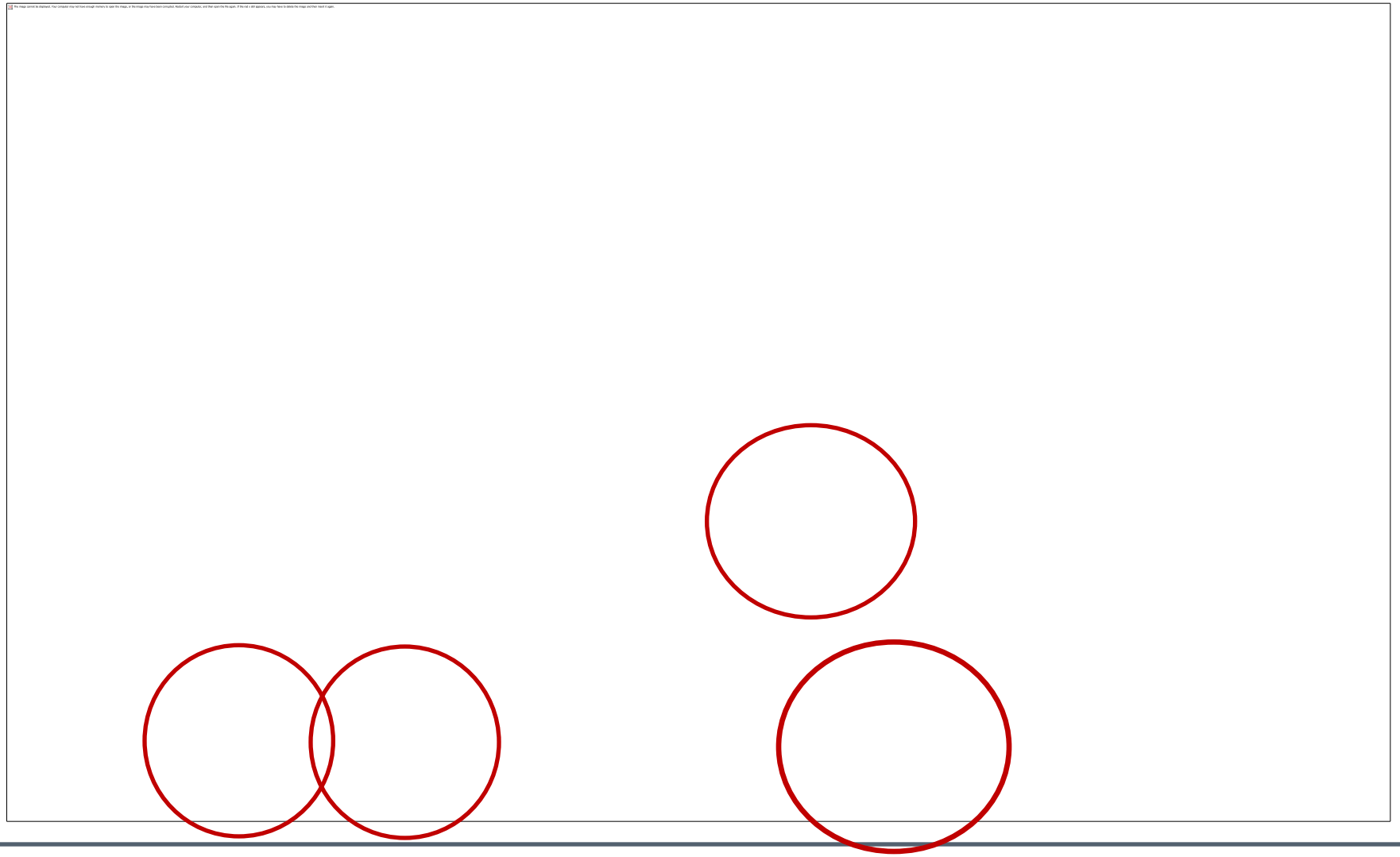
Contents

Weld Overlay Coatings





Cladding Methods – Overview



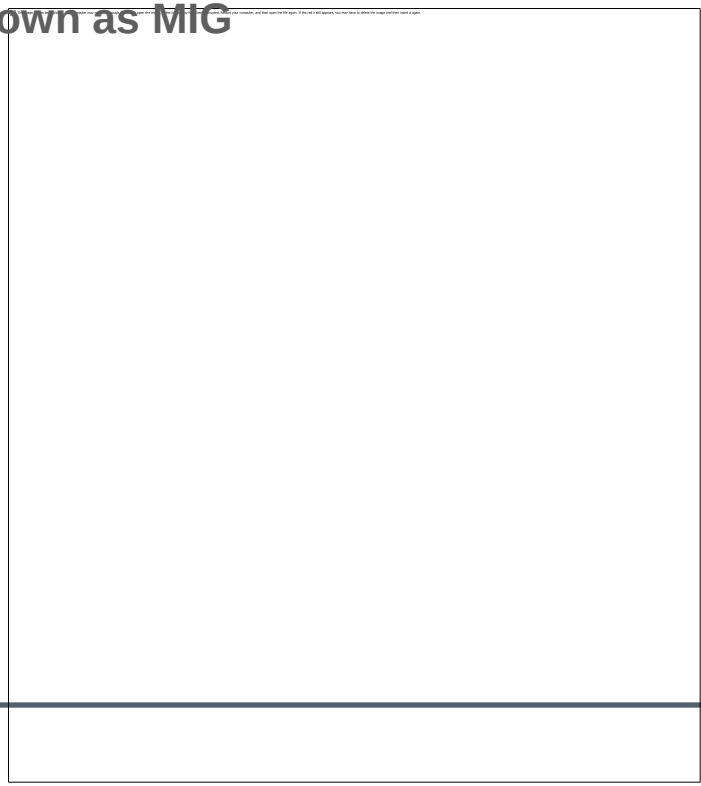
GTAW and GMAW Processes

Gas Tungsten Arc Welding

- Arc between electrode & work piece
- Consumable (welding rod) fed into arc
- Advantages simple manual operation and good control of welding arc
- Also known as TIG process

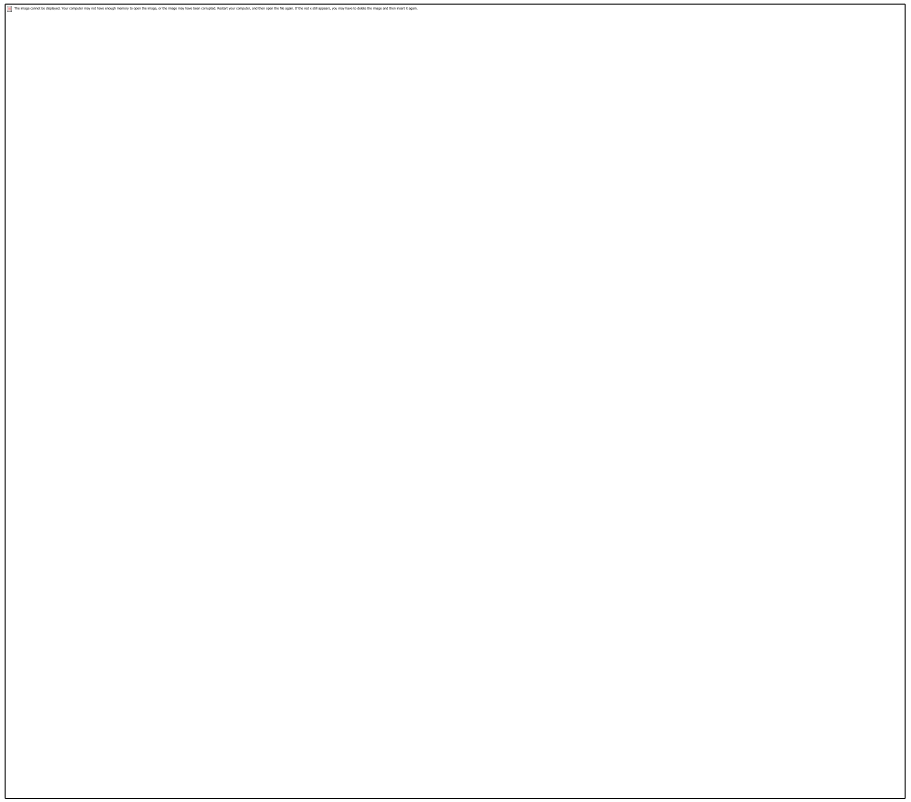
Gas Metal Arc Welding

- Arc between welding wire & work piece
- High deposition rates possible
- Process can be fully mechanized
- High deposition efficiency
- Also known as MIG



Plasma Transferred Arc (PTA) Process

- Arc between Tungsten electrode and work piece (similar to GTAW)
- Welding consumable is metal powder that is melted in the arc
- Main advantage process can be easily automated, providing high degree of reproducibility
- Wide variety of overlay materials possible
  - also combinations of materials (metals + carbides)



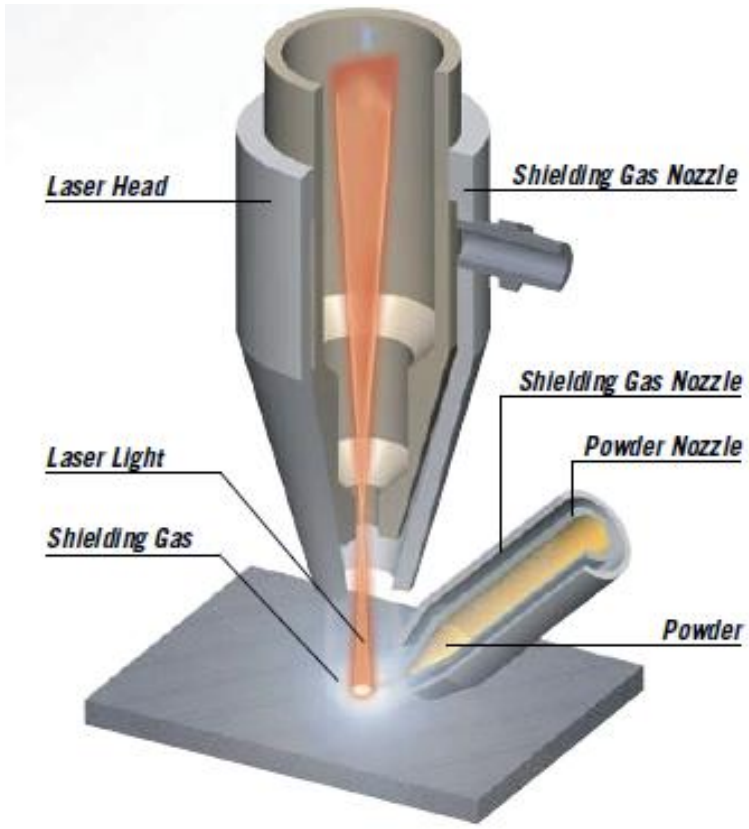
<u>Advantages</u> due to highly concentrated heat source:

- High deposit rates
- High powder utilization
- **Very low level of Fe-dilution**

Laser Welding

- Work piece heated with a laser beam
- Powder material fed into the laser beam and melted
- **Advantages:**
  - Narrow heat-affected zone
  - Fast cooling rate
  - Low heat input

  …….therefore
  - A finer microstructure
  - Usually higher hardness



A word of caution:

The fast cooling leads to a higher hardness, but in Stellite alloys that rely on time-dependent carbide growth during solidification for their wear properties, **it can lead to unexpectedly poor wear resistance**

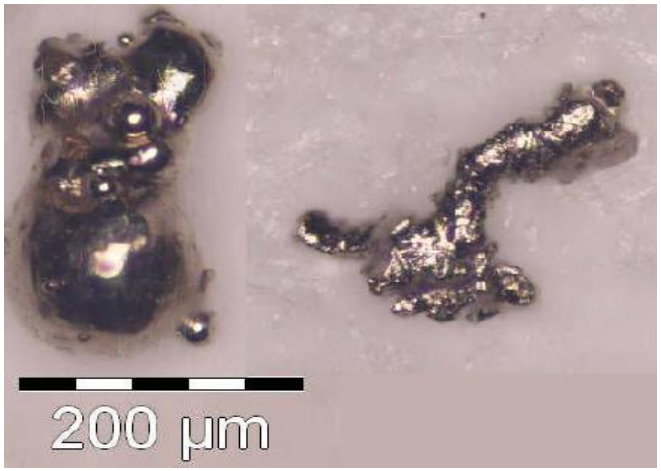
So What's Important?

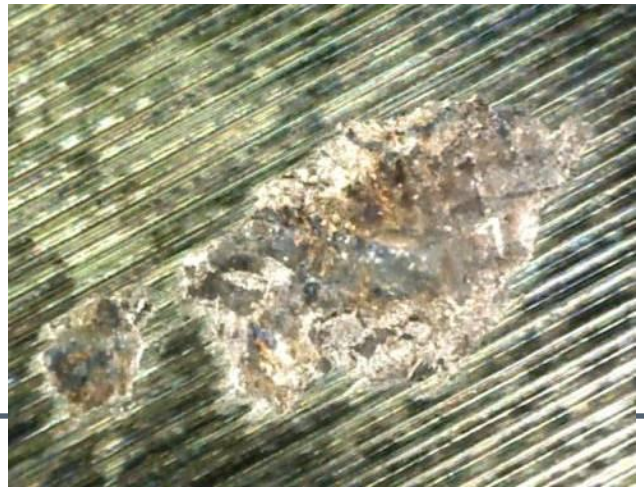
- **POWDER**
  - Quality – consistency between batches, no oxides
  - Particle shape and uniformity – Hall flow rate
- **SUBSTRATE**
  - Pre-heat (varies for different alloys)
  - Cooling rate
  - Post-weld heat treatment
- **WELDING PARAMETERS**
  - Selection of hardfacing material and welding process
  - Heat input (Fe-dilution)
  - Heat-affected zone (HAZ)
  - Welding parameters (inter-pass temperature, feed rate, oscillation, etc.)
  - Reproducibility (manual welding vs. automated process)

The same alloy can have very different properties depending on hardfacing method selected

Powder Quality

- Powder quality is one of the most important aspects to obtain good weld overlays……but often neglected by weld operators
- Particle shape and uniformity is critical for powder flow, constant feed rate, and weld pool stability
- Undesirable powder particle shapes
  - Requires more carrier gas that disrupt the arc
  - Lead to pulsing powder feeding
- Oxidized particles lead to increased slag and defects in the coating





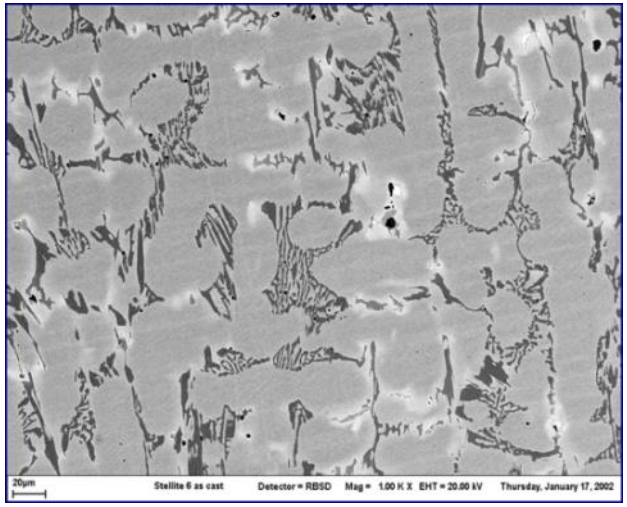
Stellite® Alloys

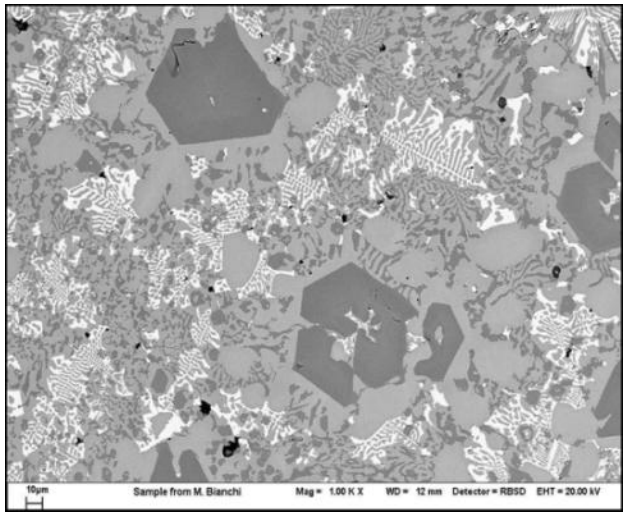
- Family of alloys that exhibit excellent resistance to wear and corrosion
  - Main constituents of Stellite alloys are Co, Cr, W, Mo, C
  - Hardness from 32 – 63HRC
- Known for their properties in high temperature applications
  - Excellent resistance to galling & metal-to-metal adhesive wear
  - Particularly in the absence of lubrication
  - Low coefficient of friction gives good sliding wear properties
- Variety of manufacturing methods, including various casting and surfacing proceses
- Good corrosion resistance due to high Cr content (28 – 32%)
  - Corrosion behaviour similar to 316 stainless steel

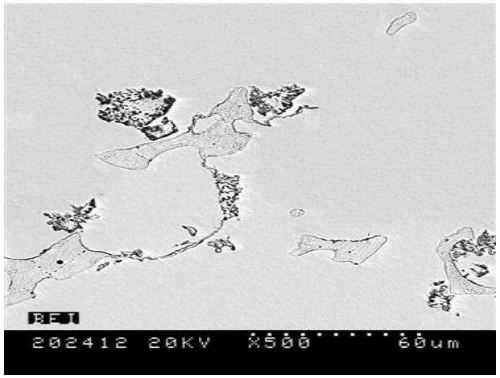
Alloy Selection

Two types of Stellite alloys

- Carbide type - C > 0.8%
  - Strengthened by carbides of Cr, W, Mo
  - Hypo-eutectic ($M_{23}C_6$ carbides) – **Stellite 6**
  - Hyper-eutectic (M_7C_3 carbides) – **Stellite 1**
- Solid Solution type - C < 0.4%
  - Co,Cr, Mo alloys (no W) – **Stellite 21**
  - Co, Cr, Mo, Ni (low W) – **Ultimet**
  - Work hardening provides wear resistance

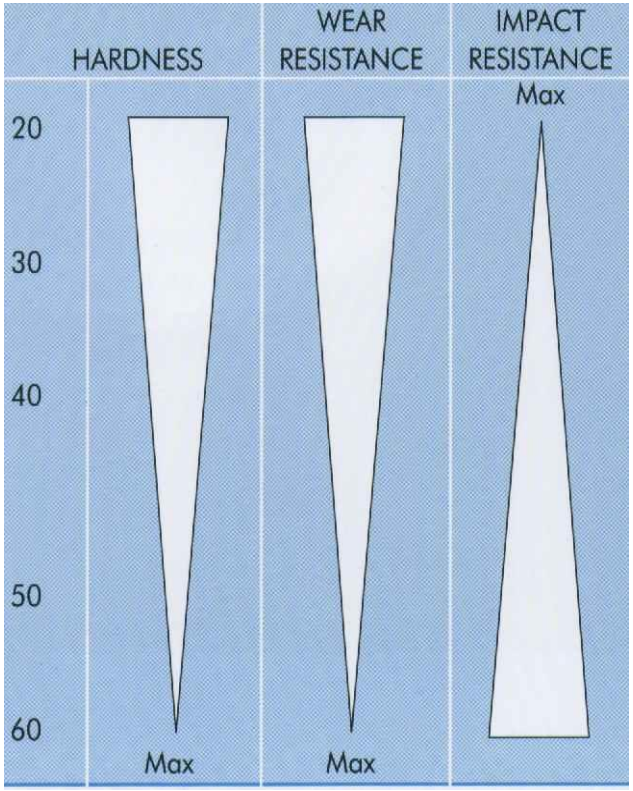




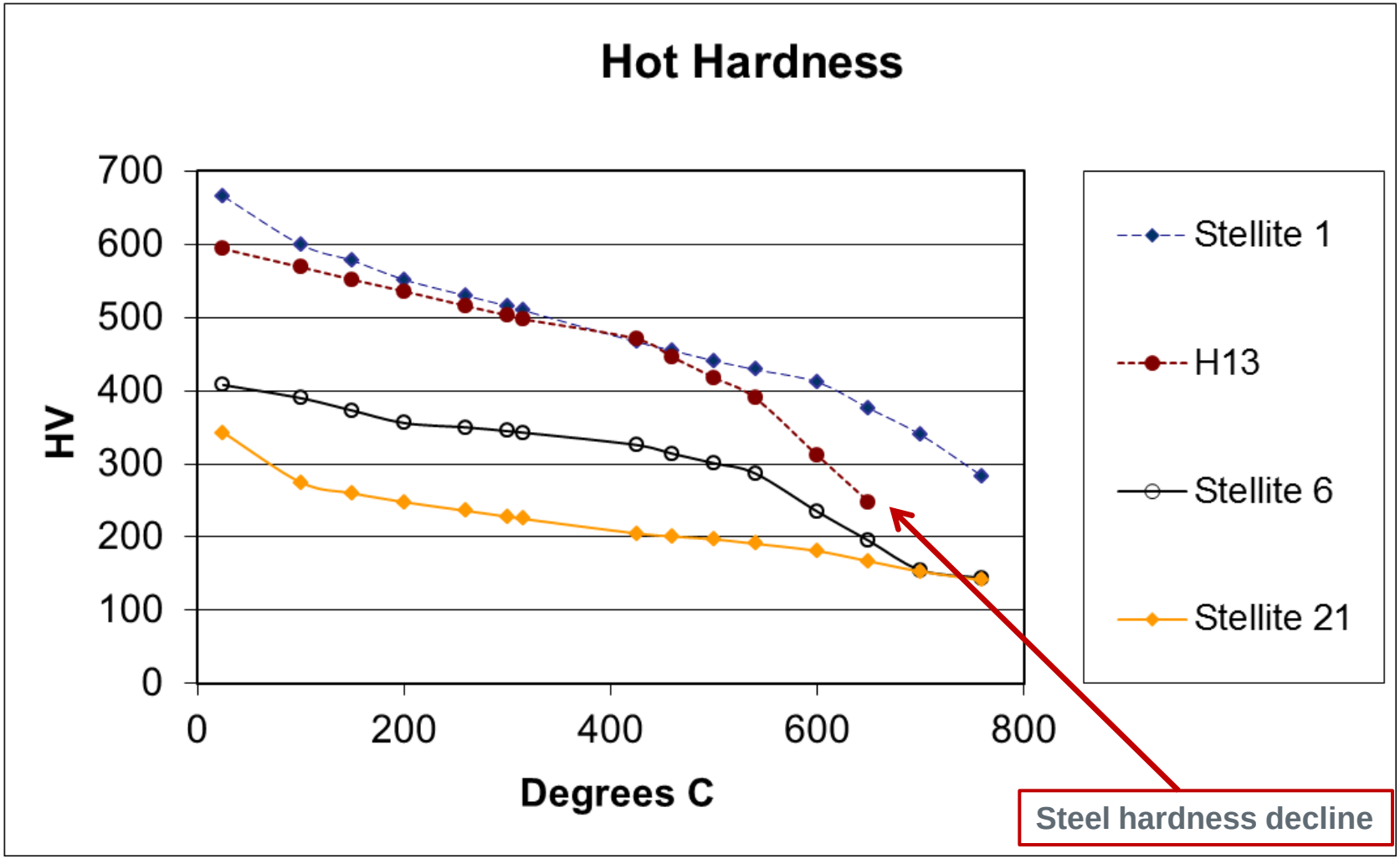


Hardness vs. Ductility

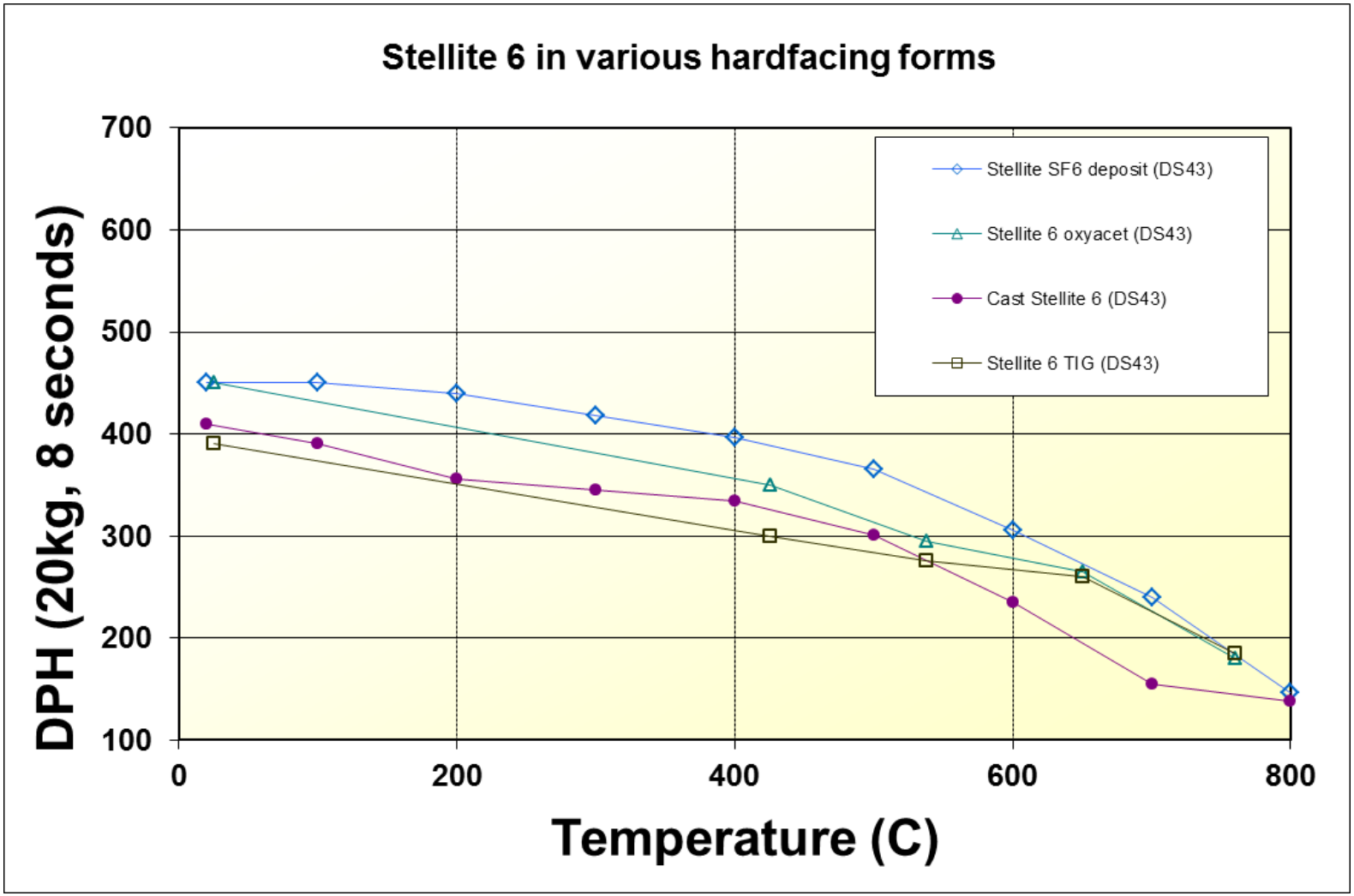
Alloy	Composition	Hardness
Stellite 21	27Cr, 0.2C, 5.5Mo	32 HRC
Stellite 6	28Cr, 1.2C, 5W	42 HRC
Stellite 4	31.5Cr, 1C, 14W	47 HRC
Stellite 12	29Cr, 1.85C, 9W	49 HRC
Stellite 1	33Cr, 2.45C, 13W	55 HRC
Stellite 20	22Cr, 2.45C, 17.5W	57 HRC
Stellite 100	33.5Cr, 2C, 18.5W	63 HRC



Maintain Hardness at High Temperatures



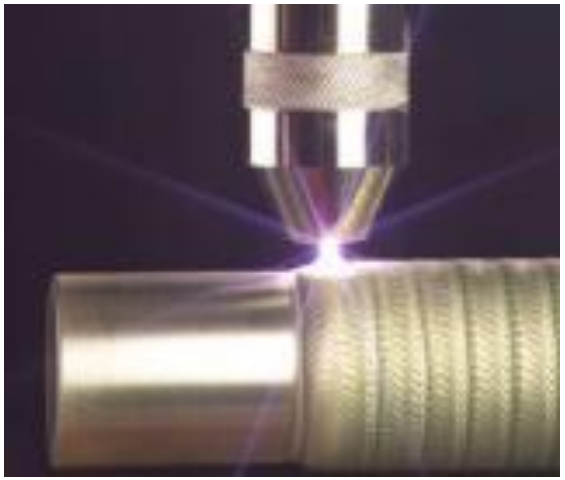
Effect of deposition method on Hardness

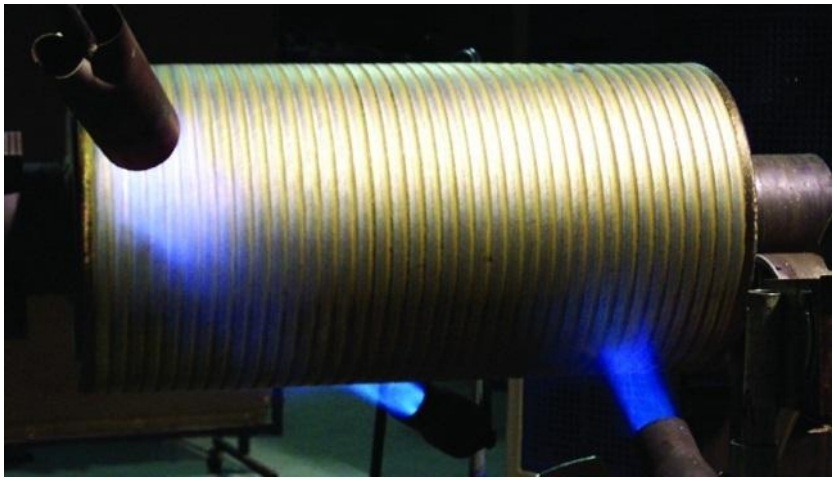


Stellite Hardfacing

Metallurgical issues related with hardfacing of various classes of steels:

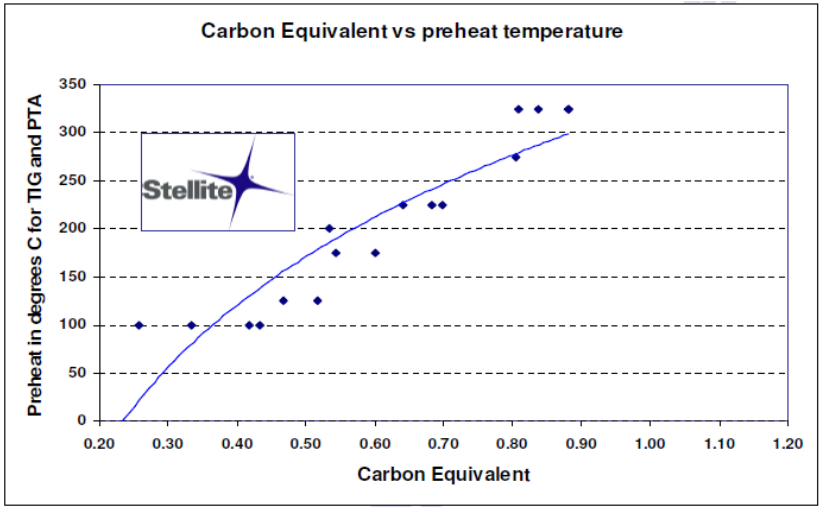
- **Carbon steels**
- **Alloy steels, Martensitic steels, Tool steels**
- **Austenitic Stainless steels & duplex stainless steels**





Stellite Hardfacing of Steels

- Weldability directly related to their hardenability
  - Resulting in the formation of brittle heat affected zone (HAZ)
- If the part is cooled too fast, or pre-heat is too low, then HAZ zone is quenched from austenitic to brittle semi-martensitic structure
- Weldability of steel (tendency to form martensitic) based on C level
- Martensitic formation unavoidable when C is above 0.5%
  - Post-weld HT essential to temper brittleness in HAZ and prevent cracking

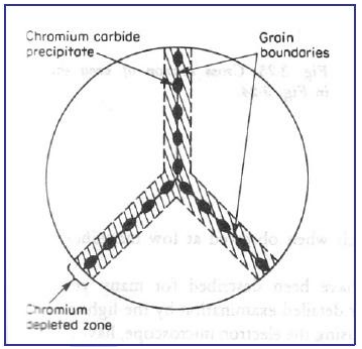


- Alloys with C above 1% generally a hardfacing challenge

Stellite Hardfacing of Stainless Steels

Austenitic Stainless Steels

- Unlike other steels, no formation of brittle martensitic in HAZ
- Difficulty is diffusion of C from Stellite into alloy in HAZ, forming carbides at the grain boundaries – sensitization
- The result is a decrease in corrosion resistance
  - Solution a Ni-based buffer layer to inhibit C diffusion



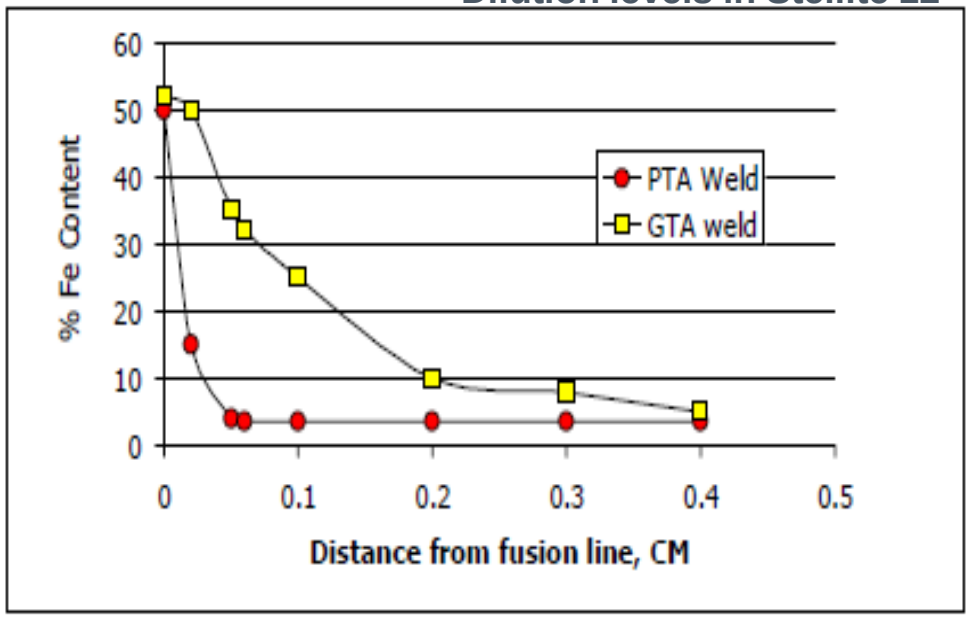
Duplex Stainless Steels

- Both sensitization and embrittlement occur during typical welding cycle due to formation of secondary brittle phases
- Welding parameters with minimum time in embrittlement range
  - Minimum pre-heat; fastest cooling rate, low inter-pass temperatures
  - Apply ductile Ni-based buffer layer with little or no pre-heat to shield substrate

Why is Fe-Dilution important?

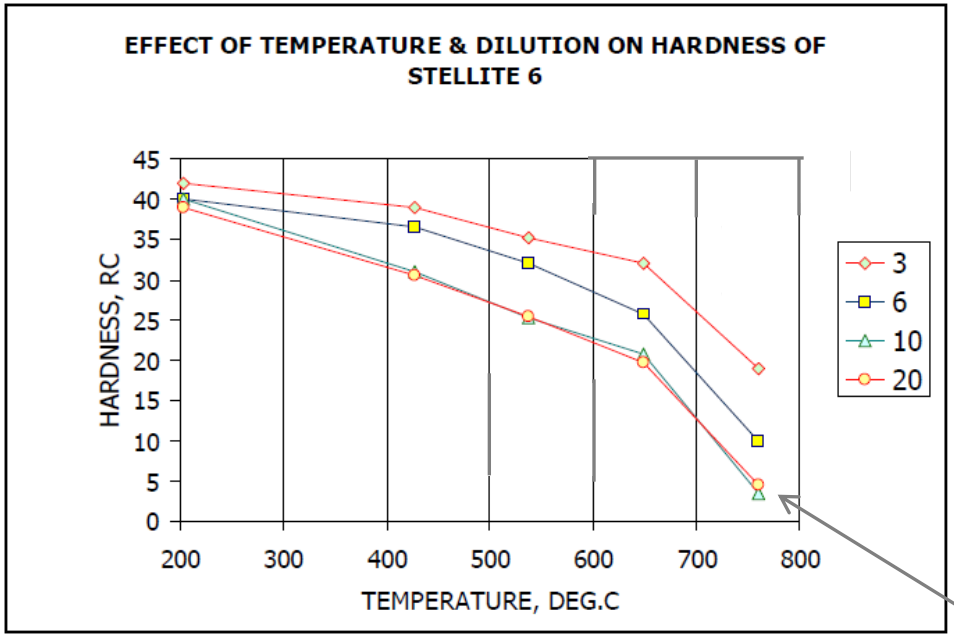
- Dilution of Stellite weld overlays from substrate is inevitable
  - Dilution is amount of Fe or Ni (when using IN625 butter layer) in the Stellite
- Dilution in Stellite generally has the following effect:
  - Decreases the hardness – more pronounced at higher temperatures
  - Decreases the corrosion resistance
  - Decreases the wear resistance
- What are acceptable?
  - General guideline dilution should be kept below 20%
  - With max 10% in the 2nd layer
  - And a 3rd layer to reach 5%

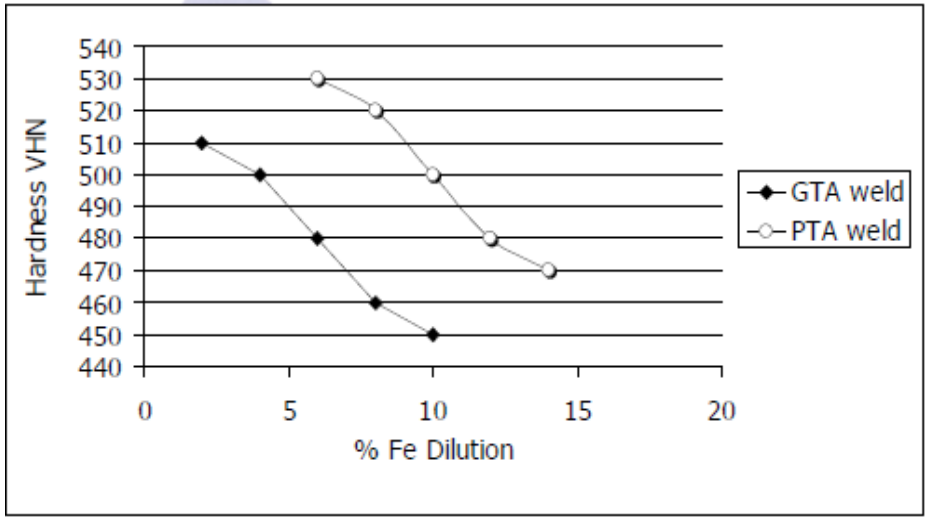
Dilution levels in Stellite 12



Hot Hardness and the Effect of Dilution

- Hardness drops linearly with dilution up to levels of about 15%
  - Trend is more profound the higher the temperature
- Hot hardness is very important to ensure good wear resistance at higher operating temperatures

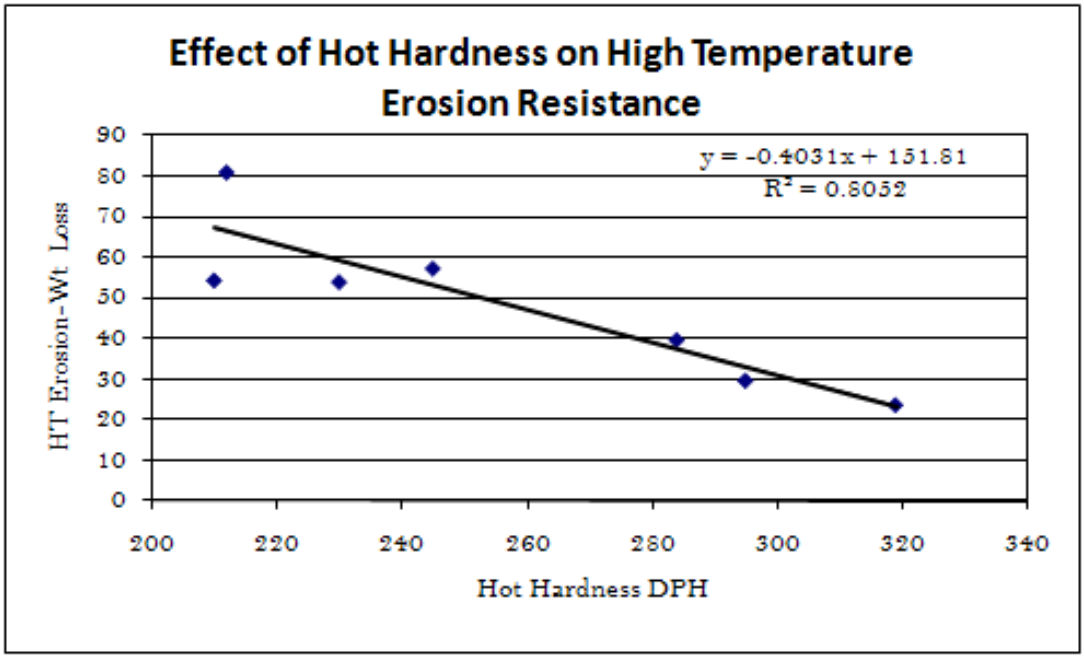


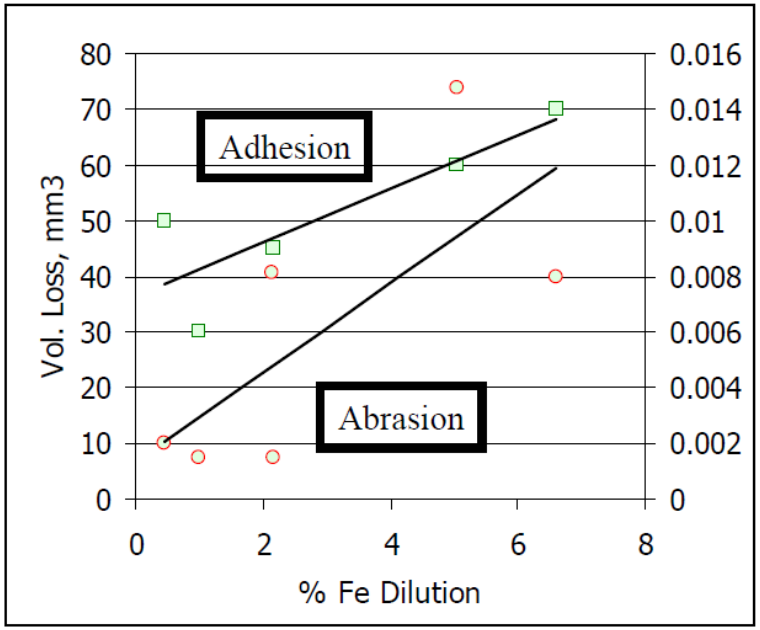


10% dilution

Effect of Dilution on Wear Resistance

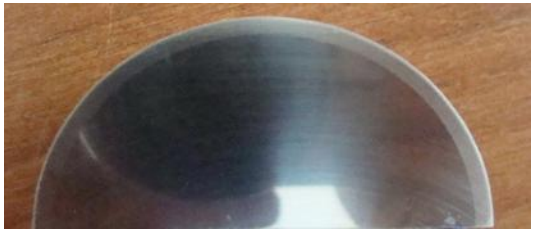
- Erosion doubles when hardness decrease from 320 to 200 DPH
- Abrasion wear increases 6x in Stellite 1 weld overlays as dilution increases to 6% and hot hardness decrease

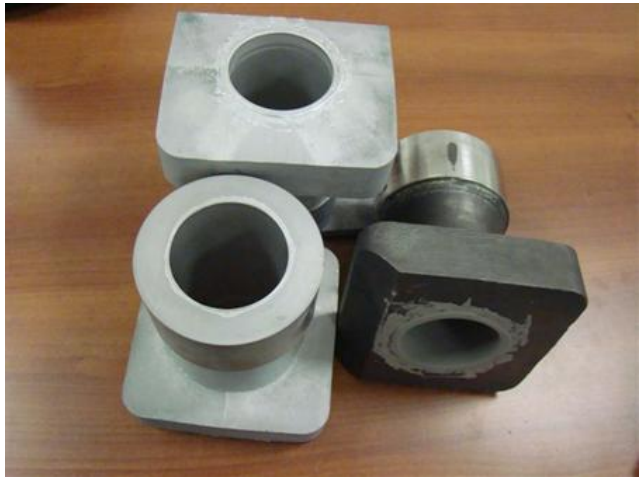




Contents

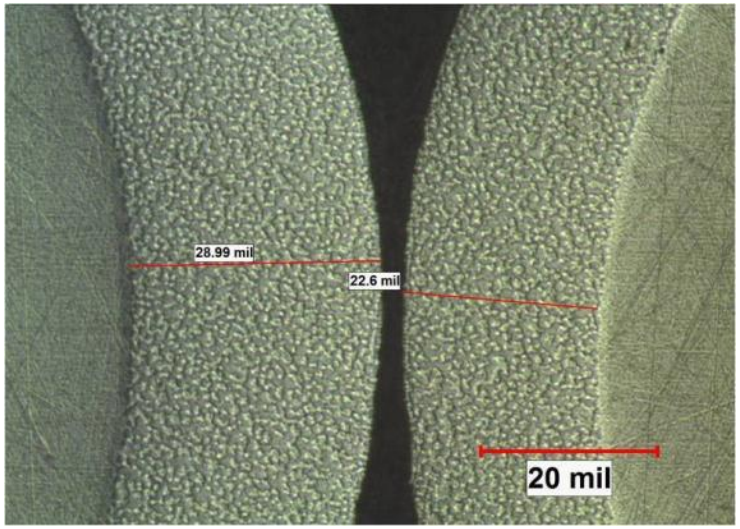
FusionStell™ Coatings





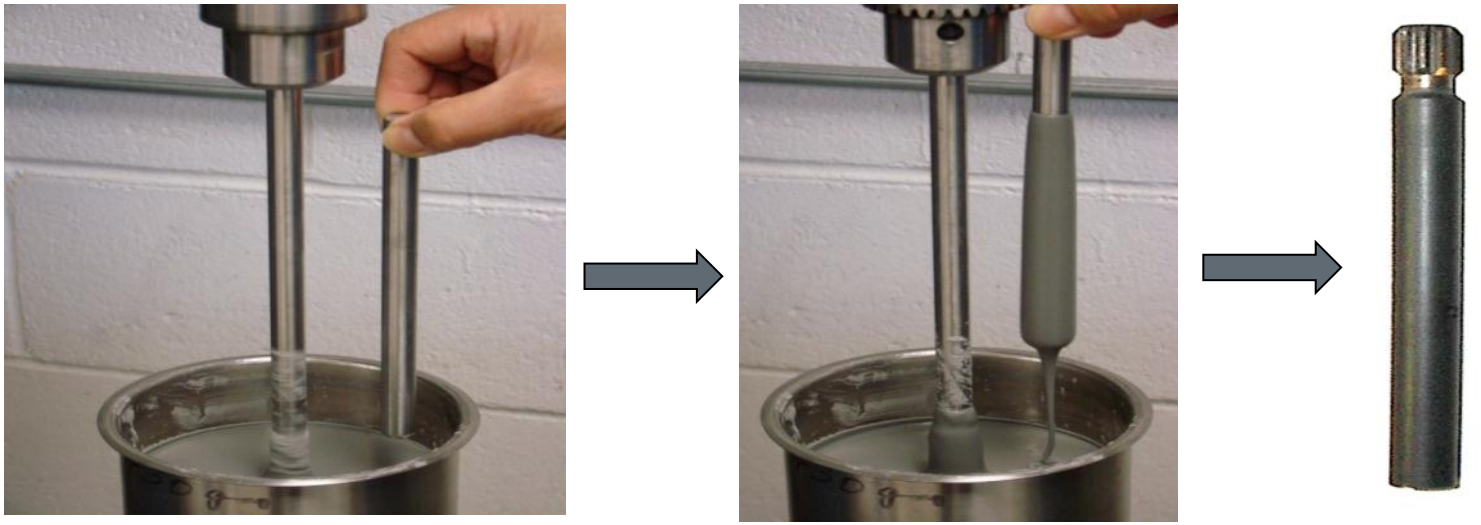
FusionStell™ Process

- A novel technology to metallurgically bond a thin layer of Stellite with full density onto metal substrates
- The coating offers the wear resistance of a cast cobalt component on a non-cobalt substrate, typically steel
- Properties of the FusionStell™ coating the same as cast alloy
  - Chemical composition identical
  - Hardness the same
  - Finish the same as equivalent cast alloys
- No Fe-dilution or heat affected zone as in hardfacing of Stellite
- More consistent coating sintering than spray & fuse coatings



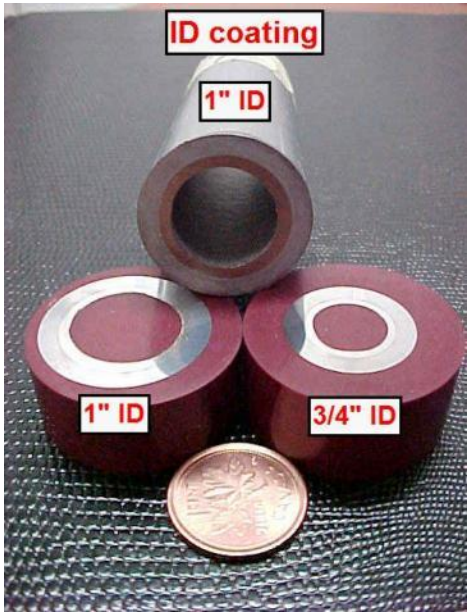
FusionStell™ Process

- Stellite powder is mixed with water, organic binder, and various additives to form a slurry
- Substrate components are dipped into the slurry and the metal coating adheres to the component surface
- The coating is air dried to remove the water, before sintering in a vacuum furnace at temperatures of 1100 – 1300°C



FusionStell™ samples

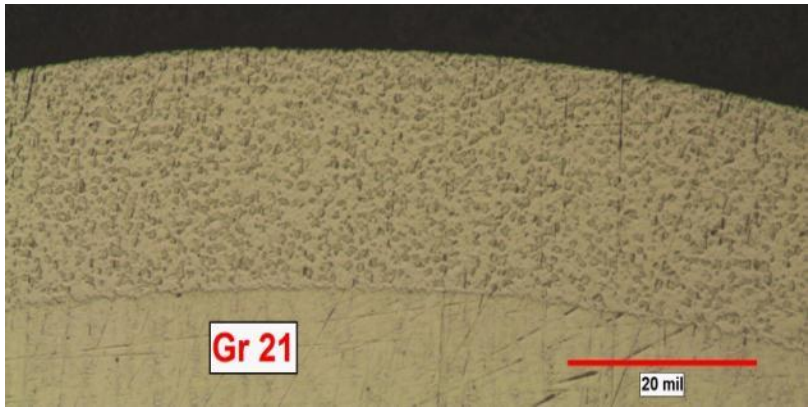
Outside diameters



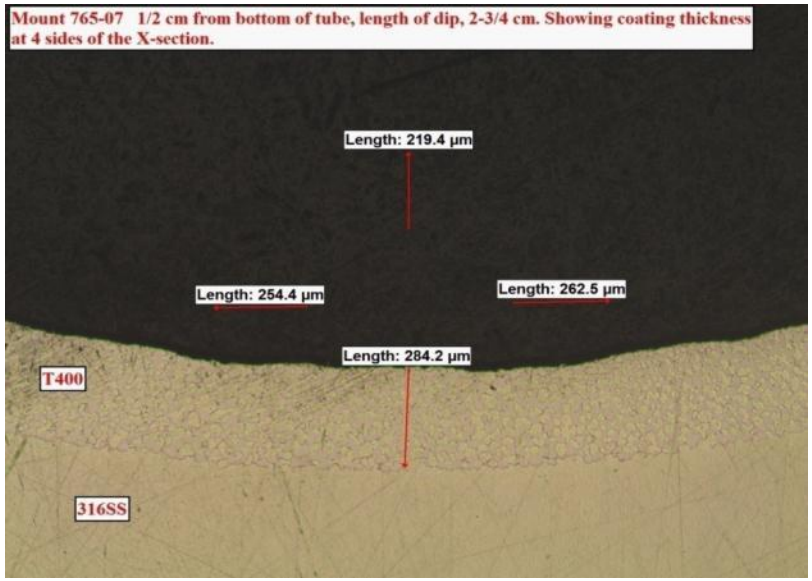
Inside diameters

Complex shapes

Metallurgically bonded coatings

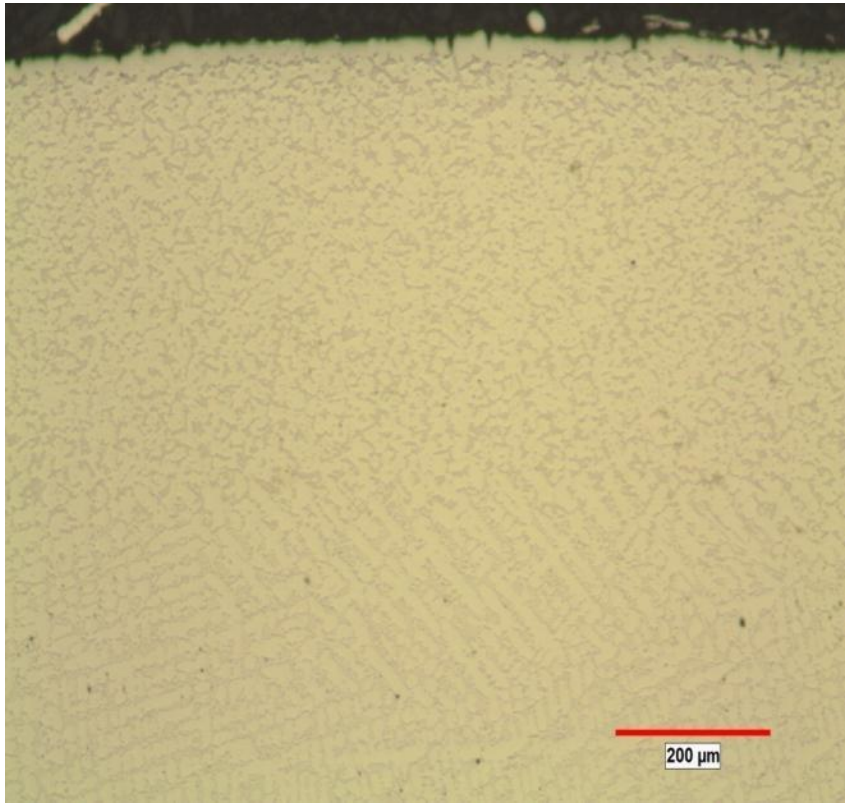


OD



ID

Stellite on steel



Stellite 12 coating on Stellite 12 casting

Substrate Limitations

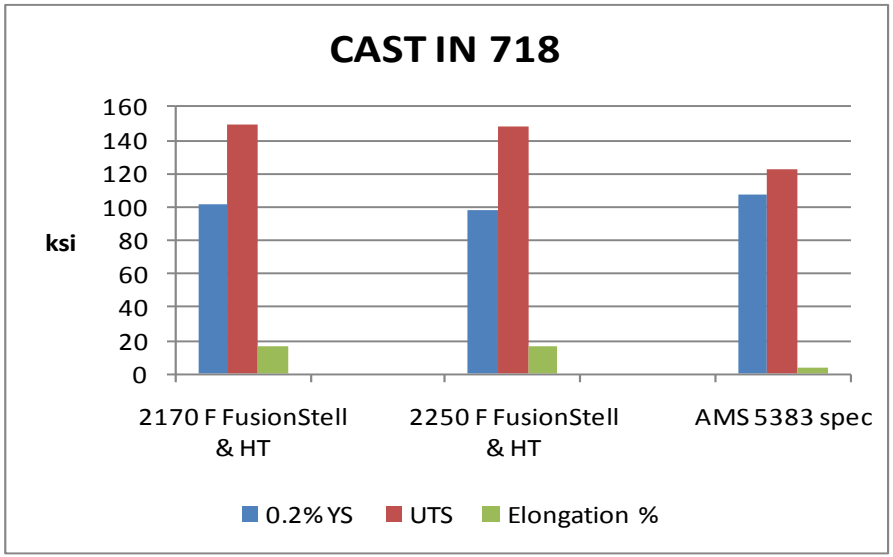
Deloro Stellite

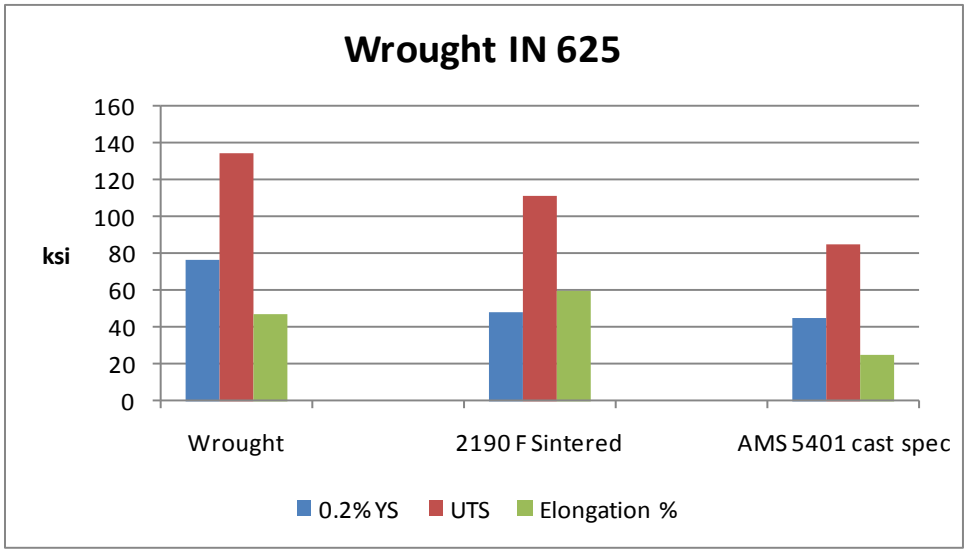
Certain substrates cannot be subjected to high temperature sintering

- **Stress cracking in the coating on some martensitic steels due to the volume change during the phase transformation**
  - **Limit range of coatings to 'more ductile' compositions such as Stellite 6 or 12**
- **Changes in mechanical properties of substrate during high temperature sintering (can sometimes be recovered with HT)**
  - **Increased strength, but decreased ductility of 410 stainless steel**
  - **Grain growth of IN718 after sintering, although tensile strength can be recovered**
- **Ti alloys cannot be coated due to chemical reaction and formation of low melting point eutectic between Ti alloys and Stellite**

Substrate Mechanical Properties

- Mechanical properties of steels recovered with post-coating heat treatment
  - Austenitic steels unaffected
  - Precipitation hardened and martensitic steels fully recovered
- Cast IN 718 properties fairly well recovered after heat treatment
  - Slight reduction in yield strength
- Wrought IN 625 properties reduced around 25% due to grain growth
  - Yield strength mostly affected





Substrate compatibility

	Carbon & Alloy steels (1026, 4130, 1018)	**Austenitic stainless steels** (316, 304, 308, 303, 347)	**Precipitation hardened steels** (17-4 PH)	**Martensitic steels** (410, 420, 440C, 9Cr1Mo, F9, F91)	**Ni-based alloys** (Hast C276, IN718)
Common Stellite Stellite 6 & 12 (hardness range 40 – 48 HRc)	✓	✓	✓	✓	✓
Very hard Stellite Stellite 720, Star J (hardness range 53 - 58 HRC)	✓	✓	✓	440C ✓ 9Cr1Mo* ✓	✓
Tribaloy alloys T400, T800 (hardness range 53 - 56 HRC)	✓	✓	✓	440C ✓ 9Cr1Mo ✗	C276 ✓ IN718 ✗

Incoloy 800H

Engineered Solutions for Severe Service Valves

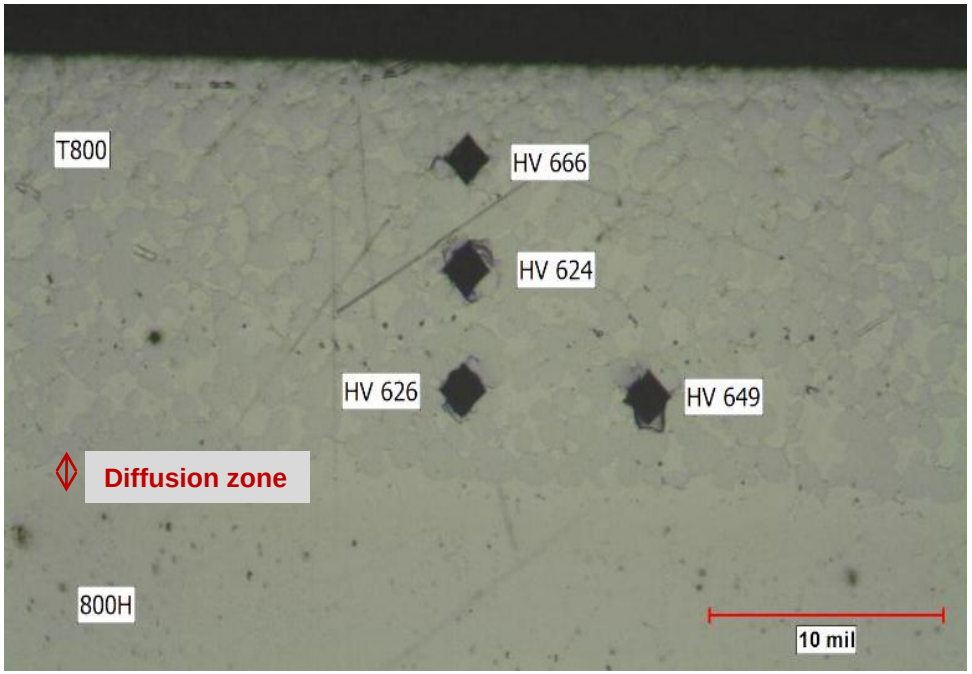
- Hardfacing material choice often compromised by manufacturability
  - Stellite 1 has high wear resistance, but prone to cracking during weld overlay
  - Tribaloy alloys have exceptional corrosion and wear resistance, but nearly impossible to hardface

- The FusionStell™ process is ideal to produce coatings from alloys that cannot be hardfaced ➡ best material for a specific application

Alloy Family	Hot hardness	Abrasion	Erosion	Cavitation	Galling	Corrosion
Stellite alloys	H	M - H	H	H	H	M – H
Tribaloy alloys	H	H	M – H	M – H	H	H
Deloro alloys (Ni-base spray & fuse)	M - H	M - H	M	M	M	L - M

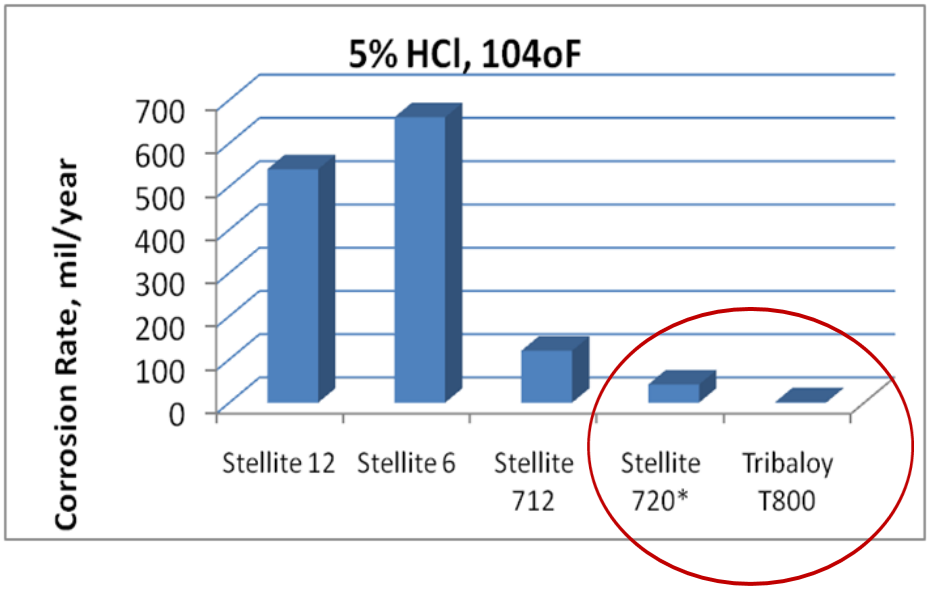
FusionStell™ T800 coating on Ni-base alloy

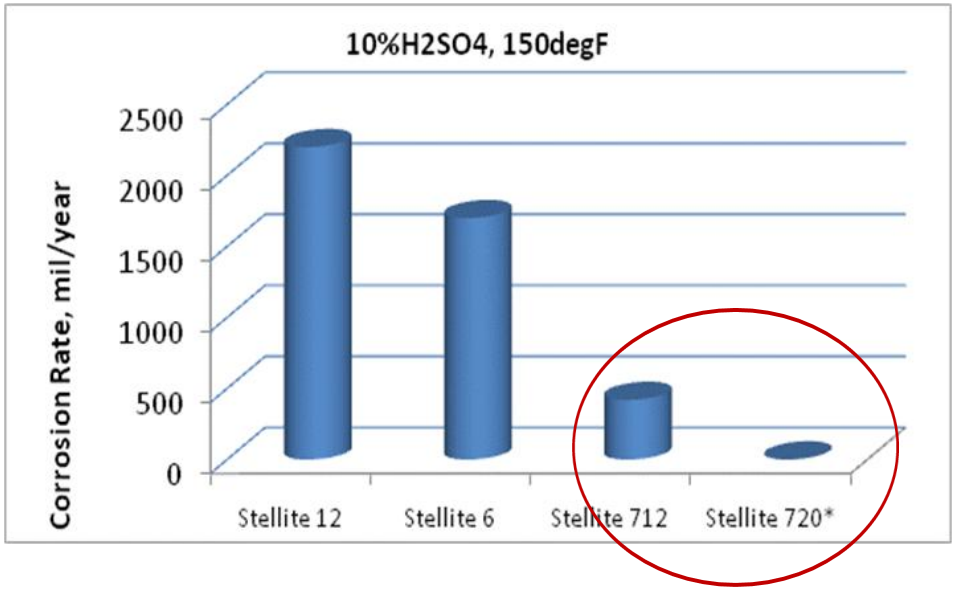
- The FusionStell™ process produce a ‘pure’ Stellite coating
- Dilution only occurs in the diffusion zone for metallurgical bond
- Diffusion zone is typically 0.001” thick



Better Corrosion Resistance than Hardfacing

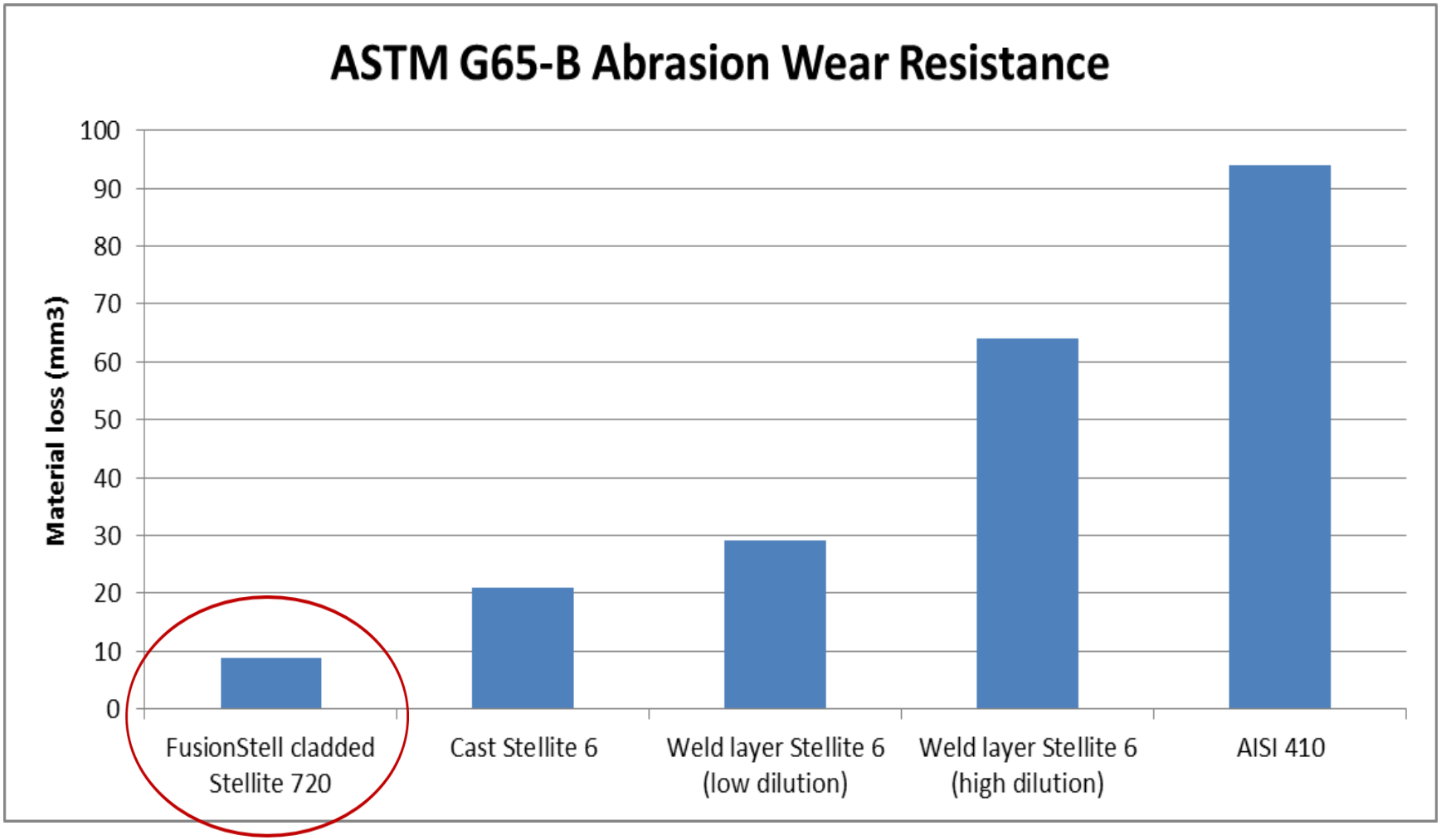
- Tribaloy T800 for acetic acid & chlorosilane environments
- Stellite 720 for sulfidation environments



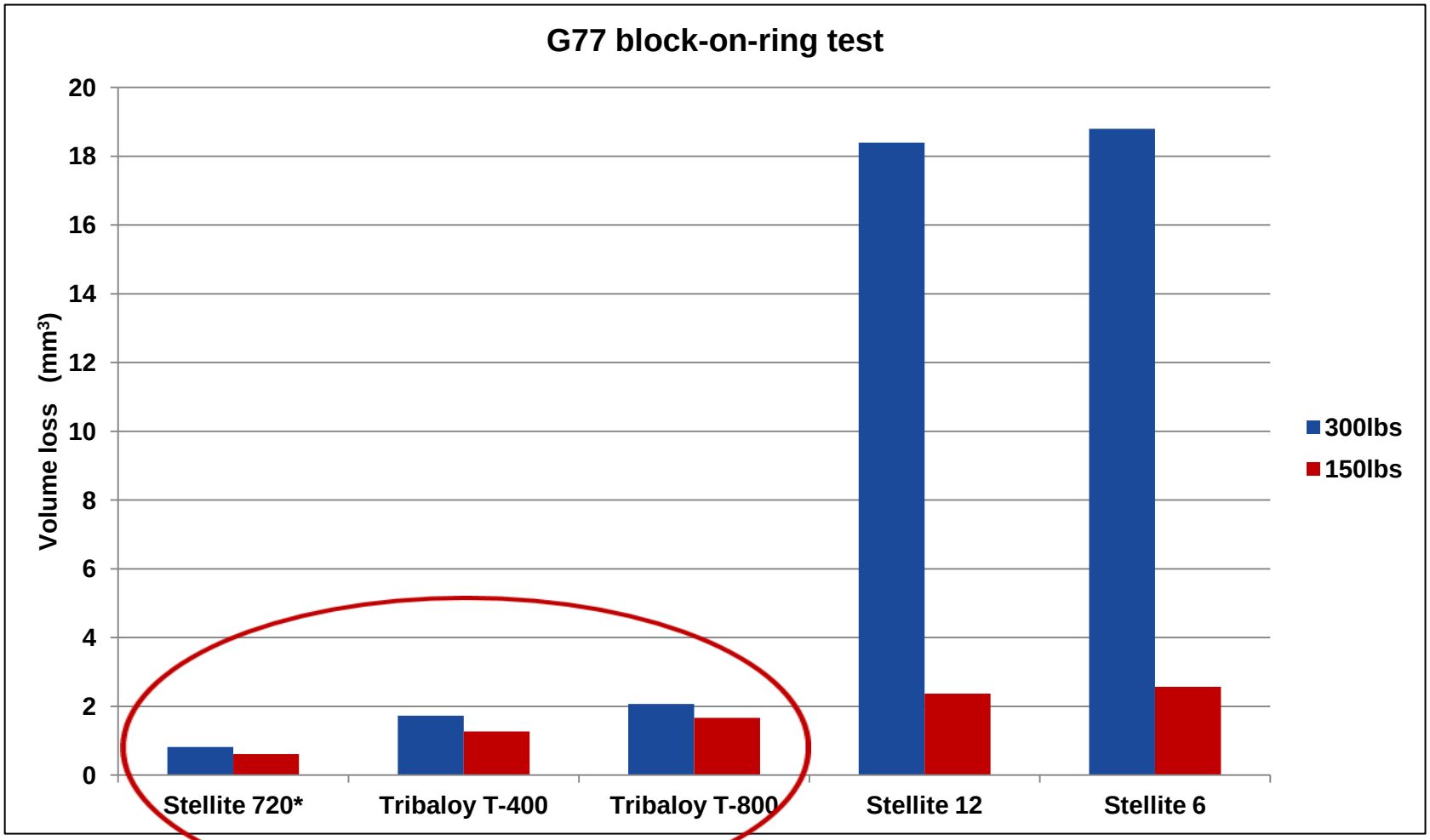


Tribaloy T800 and Stellite 720 have substantial higher corrosion and wear resistance than Stellite 6 or spray & fuse alloys

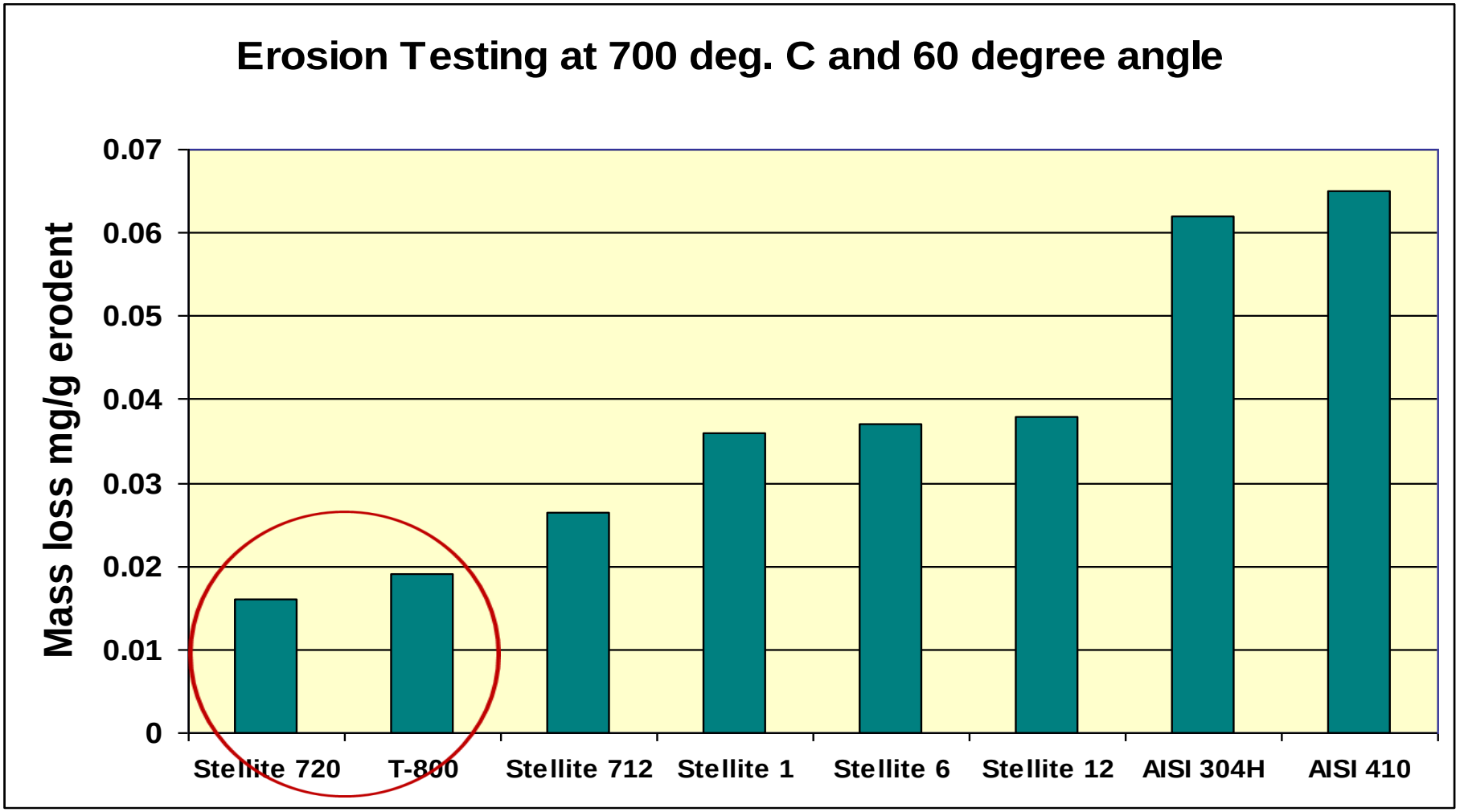
Better Wear Resistance than Hardfacing



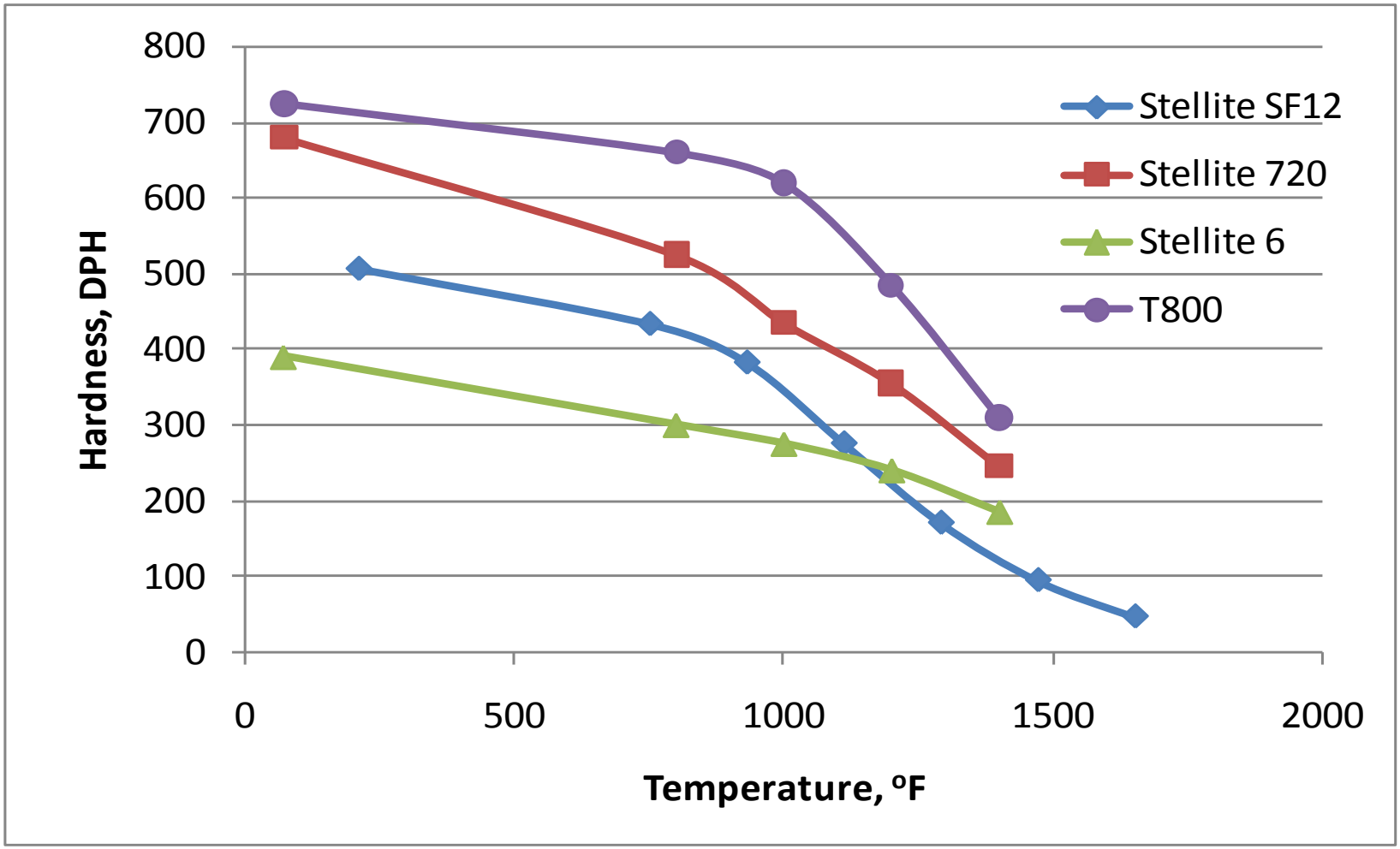
Better metal-on-metal Wear than Hardfacing



Better High Temperature Erosion Resistance



Better Hot Hardness than Spray & Fuse



Benefits of FusionStell™ Technology

- Process can produce coated solutions not possible with any other technology
- Metallurgically bonded coatings with superior wear and corrosion resistance relative to spray & fuse coatings or Stellite hardfacing
- Coating of inside diameters not possible with any other coating technology
- No need for a “one coating fits all” approach
- Engineered materials solutions for severe service environments
  - Select optimum coating compositions for a specific application

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