Speciality Stainless Steel long products for high end applications

K R Srinivasan, Dominic Savio, Sunil Nair

ISSDA 25th Anniversary, New Delhi
## Stainless Steel Growth in India

<table>
<thead>
<tr>
<th>GROWTH PARAMETER</th>
<th>1980</th>
<th>1985-2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANUFACTURING FACILITIES</td>
<td>Conventional EAF</td>
<td>AOD/VOD, Duplex / Triplex</td>
</tr>
<tr>
<td>GRADES</td>
<td>304, 316, 410, 420</td>
<td>More varieties</td>
</tr>
<tr>
<td>SUPPLY CONDITION</td>
<td>Mainly hot rolled</td>
<td>As per customer spec.</td>
</tr>
<tr>
<td></td>
<td>Annealed incase of</td>
<td>Solution annealed,</td>
</tr>
<tr>
<td></td>
<td>martensitic grades</td>
<td>Hardened and tempered</td>
</tr>
<tr>
<td>APPLICATION COVERAGE</td>
<td>Mainly kitchen utensils</td>
<td>Wide industrial applications</td>
</tr>
<tr>
<td>STAINLESS STEEL FAMILIES</td>
<td>Austenitic with some</td>
<td>All varieties including</td>
</tr>
<tr>
<td></td>
<td>Martensitic</td>
<td>Ferritic, Stabilised, PH and Duplex</td>
</tr>
</tbody>
</table>
## Technological changes in manufacturing

<table>
<thead>
<tr>
<th>THEN</th>
<th>NOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Electric Arc Furnace for melting, decarburisation and chemistry control.</td>
<td>EAF is only for melting.</td>
</tr>
<tr>
<td>Lengthy and expensive process.</td>
<td>VOD/ AOD process for decarburization and chemistry control.</td>
</tr>
<tr>
<td>Low Carbon/ high Chromium as demanded in speciality stainless steels difficult to achieve.</td>
<td>Thermodynamically favorable condition for Carbon removal. Shorter cycle time.</td>
</tr>
<tr>
<td>Conventional continuous casting.</td>
<td>Capability to achieve low carbon/ high chromium and high nitrogen as desired.</td>
</tr>
<tr>
<td>Non-mechanised rolling mills and lack of heat treatment and downstream facilities.</td>
<td>Mechanised rolling mills with heat treatment and downstream facilities</td>
</tr>
</tbody>
</table>
Duplex v/s Triplex Process

**Duplex Process**

- EAF - AOD
  - Short Treatment Time
  - Flexibility w.r.t Ferroalloy-Scrap Ratio

- EAF - VOD
  - Low Argon Consumption
  - Low FeSi Consumption
  - Low Carbon/Gas levels

**Triplex Process**

- EAF - Convertor - VOD
  - Low Argon Consumption
  - Low FeSi Consumption
  - Low Carbon/Gas levels
  - Flexibility in Ratio of Ferroalloy to Scrap
  - High Refractory life of Convertor
  - High Chromium Yield
Milestones In SS Production In India

- More types of grades
- More supply conditions
- More application coverage
- High corrosion resistant steels import substitution.

- Application oriented grades
- Higher exports.
- SS family & supply condition.
- More long products

- Modern facilities installed
- ISSDA formed 1989
- Bulk SS flats
- 201 introduced

Production, 1000 Tons

<table>
<thead>
<tr>
<th>Year</th>
<th>Production, 1000 Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>102</td>
</tr>
<tr>
<td>1990</td>
<td>250</td>
</tr>
<tr>
<td>1995</td>
<td>500</td>
</tr>
<tr>
<td>2000</td>
<td>900</td>
</tr>
<tr>
<td>2005</td>
<td>1500</td>
</tr>
<tr>
<td>2010-11</td>
<td>2600</td>
</tr>
<tr>
<td>2015</td>
<td>3500 (projected)</td>
</tr>
</tbody>
</table>
Stainless steel development phases at Mukand for long products

<table>
<thead>
<tr>
<th>Types of Steel</th>
<th>1990-95</th>
<th>1995-05</th>
<th>2005-08</th>
<th>2008-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic</td>
<td>Martensitic</td>
<td>Ferritic</td>
<td>Martensitic</td>
<td>PH grades; Stabilised</td>
</tr>
<tr>
<td>Martensitic</td>
<td>Austenitic</td>
<td>Ferritic</td>
<td>Martensitic</td>
<td>Ferritic</td>
</tr>
<tr>
<td>PH grades; Stabilised</td>
<td>Martensitic</td>
<td>Austenitic</td>
<td>Martensitic</td>
<td>Martensitic</td>
</tr>
<tr>
<td>Duplex</td>
<td>Duplex</td>
<td>Duplex</td>
<td>Duplex</td>
<td>Duplex</td>
</tr>
</tbody>
</table>

Year
Application change over the years

**Kitchenware%**
- 2011-12, 65%
- 1990-91, 90%
- 2007-08, 70%
- 2000-01, 75%

**Industrial%**
- 2011-12, 35%
- 1990-91, 10%
- 2007-08, 30%
- 2000-01, 25%
Breakup of industrial application

Breakup of industrial application for 35% of Stainless Steel production
2011-12

- Construction, 6%
- Transportation, 6%
- Others, 5%
- Tubes, 8%
- Manufacturing, 10%
Process Metallurgy Of Speciality Stainless Steels
Metallurgical Objectives

- ALLOY LEVEL > 30% (AUSTENITICS)
- PITTNG RESISTANCE EQ.NUMBER AS PER CUSTOMER SPECIFICATION:
  - %Cr + 3.3 % Mo + 16 % N for austenitics
  - % Cr + 3.3% Mo for ferritics
- CONTROL ON S, P & TRAMP LEVELS
- NITROGEN CONTROL AS PER SPECIFICATION
- PROPER STABILISATION RATIOS Nb & Ti
- ALLOY BALANCE FOR MICROSTRUCTURE
- HIGH CLEANLINESS
- SATISFACTORY SURFACE QUALITY
## Chemistry Of Specialty Steels Made At Mukand

<table>
<thead>
<tr>
<th>Name</th>
<th>Grade</th>
<th>C</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
<th>Others</th>
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</thead>
<tbody>
<tr>
<td><strong>Duplex</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Duplex</strong></td>
<td><strong>2205</strong></td>
<td>0.015</td>
<td>0.002</td>
<td>22.70</td>
<td>5.40</td>
<td>3.15</td>
<td>0.15</td>
<td>0.1700</td>
<td>-</td>
</tr>
<tr>
<td><strong>Lean Duplex</strong></td>
<td><strong>2304</strong></td>
<td>0.015</td>
<td>0.002</td>
<td>22.60</td>
<td>4.40</td>
<td>0.30</td>
<td>0.30</td>
<td>0.1150</td>
<td></td>
</tr>
<tr>
<td><strong>Austenitic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>317LM</strong></td>
<td></td>
<td>0.020</td>
<td>0.008</td>
<td>18.40</td>
<td>12.20</td>
<td>3.10</td>
<td>0.10</td>
<td>0.0900</td>
<td></td>
</tr>
<tr>
<td><strong>904L</strong></td>
<td></td>
<td>0.013</td>
<td>0.002</td>
<td>19.90</td>
<td>24.10</td>
<td>4.20</td>
<td>1.25</td>
<td>0.0350</td>
<td></td>
</tr>
<tr>
<td><strong>Ferritic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>430FSiHMo</strong></td>
<td></td>
<td>0.025</td>
<td>0.290</td>
<td>17.40</td>
<td>-</td>
<td>1.50</td>
<td>-</td>
<td>0.0190</td>
<td>Si = 1.5</td>
</tr>
<tr>
<td><strong>430FR</strong></td>
<td></td>
<td>0.017</td>
<td>0.290</td>
<td>17.40</td>
<td>-</td>
<td>0.20</td>
<td>-</td>
<td>0.0200</td>
<td>Si = 1.25</td>
</tr>
<tr>
<td><strong>409</strong></td>
<td></td>
<td>0.016</td>
<td>0.003</td>
<td>11.20</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>0.0125</td>
<td>Ti - 0.25</td>
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<tr>
<td><strong>Electrode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ER 2209</strong></td>
<td></td>
<td>0.015</td>
<td>0.002</td>
<td>23.20</td>
<td>9.00</td>
<td>3.10</td>
<td>-</td>
<td>0.1350</td>
<td></td>
</tr>
<tr>
<td><strong>ER 312</strong></td>
<td></td>
<td>0.10</td>
<td>0.002</td>
<td>30.00</td>
<td>9.00</td>
<td>-</td>
<td>-</td>
<td>0.0750</td>
<td></td>
</tr>
<tr>
<td><strong>ER347Si</strong></td>
<td></td>
<td>0.018</td>
<td>0.008</td>
<td>19.50</td>
<td>9.40</td>
<td>0.10</td>
<td>0.15</td>
<td>0.0700</td>
<td>Nb - 0.30</td>
</tr>
<tr>
<td><strong>430LNbTi</strong></td>
<td></td>
<td>0.015</td>
<td>0.002</td>
<td>18.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0150</td>
<td>Ti – 0.35, Nb – 0.55</td>
</tr>
<tr>
<td><strong>ER309LSi</strong></td>
<td></td>
<td>0.017</td>
<td>0.007</td>
<td>23.30</td>
<td>12.50</td>
<td>0.15</td>
<td>0.15</td>
<td>0.1400</td>
<td>Si – 0.85</td>
</tr>
<tr>
<td><strong>Precipitation</strong></td>
<td><strong>Hardening</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>17-7PH</strong></td>
<td></td>
<td>0.075</td>
<td>0.002</td>
<td>16.50</td>
<td>7.70</td>
<td>-</td>
<td>-</td>
<td>0.0120</td>
<td>Al – 1.00</td>
</tr>
</tbody>
</table>
Mukand Process Flow

Scrap ➔ Ultra High Power Electric Arc Furnace (40T Capacity)

Ferro Alloys ➔ Converter (40T) (Oxygen Top & Bottom Blown)

Energy ➔ VOD/VD Station (40T)

Oxygen ➔ Trimming of Chemistry under Vacuum

Closed Stream Casting ➔ Bloom Caster with AMLC & EMS (10.5m Radius)

Ferro Alloys ➔ Computerised Process Control

Blooms & Billets

- Ultra High Power - 36 MVA
- Nominal Capacity – 40 MT
- Eccentric Bottom Tapping
- Computerised Process Control
- Bulk Alloy Addition System

- 40 MT Nominal Capacity
- Bulk Alloy Addition System

- Five stage steam ejectors
- Suction capacity
  - 1700 Kgs / hr at 40 mbar
  - 167 Kgs / hr at 0.67 mbar
- Microprocessor controlled alloy addition system
- Inert gas purging – Argon / Nitrogen
- Wire injection for Ti, Ca, C, S

- 250x250 mm$^2$ or 160 x 160 mm$^2$
- Submerged nozzle casting
- Auto Mould Level Control
- Electro Magnetic Stirrers (Mould/Secondary)
- Level II automation for Primary / Secondary cooling
Achieving Desired Chemistry
‘C – Cr’ Relation
Carbon-Chromium relation in VOD for 904L

- Decarburisation
- VCD
- Reduction

Time (min)  | Carbon (wt%)  | Chromium (wt%)
--- | --- | ---
0 | 0.38 | 20.2
50 | 0.015 | 19.45
130 | 0.01 | 19.75
180 | 0.01 | 19.75

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Sulphur, Phosphorus and Nitrogen in VOD for 904L

- Desulphurization
- Trimming additions

- Decarburisation
- VOD
- Reduction

Sulphur, Phosphorus and Nitrogen in VOD for 904L
Carbon-Chromium Relation in VOD for 2205

- Decarburisation
- VCD
- Reduction

- Nitrogen pickup

Carbon (wt%)
0.00 0.045 0.024 0.024 0.025
0.0 0.1 0.2 0.3 0.4 0.5 0.6

Chromium (wt%)
21.0 0.024 0.024 0.025 21.2 0.0 1 1.8 2 2.2 2.4 2.6 2.8

Time (mins)
0 50 70 130 180

. Carbon-Chromium Relation in VOD for 2205
Sulphur, Phosphorus and Nitrogen relation in VOD for 2205
Properties and Applications
Duplex Stainless Steel applications
Applications covered

- Round billets for manufacture of seamless tubes through hot extrusion. User industries Oil and Gas Exploration, Petrochemical & Refineries, Fertilizer plants, Food and Dairy, Desalination plants.

- Bars for bowl forging for separator application in crude oil refineries.

- Wires for well screen for use in desalination plants.

- Paper and pulp industry.

- Ribbed bars for use in concrete reinforcement for construction in coastal regions.

- Wires for welding electrodes for welding of duplex and dissimilar metals.
Quality requirements

- Chemistry balance
- Microstructure
- Mechanical properties
- Corrosion resistance property
<table>
<thead>
<tr>
<th>Duplex Grade</th>
<th>Major alloying elements, wt%</th>
<th>Product forms</th>
<th>Mechanical property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>2205</td>
<td>0.015</td>
<td>22.70</td>
<td>5.40</td>
</tr>
<tr>
<td>2304</td>
<td>0.015</td>
<td>22.60</td>
<td>4.40</td>
</tr>
<tr>
<td>312</td>
<td>0.10</td>
<td>30</td>
<td>9.0</td>
</tr>
<tr>
<td>ER2209</td>
<td>0.015</td>
<td>23.20</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Corrosion Properties

• Pitting Resistance : PRE No. >35

• Absence of detrimental Phases : ASTM A923, Practice C

• Pitting Potential
  – Microstructure free from chromium rich or Molybdenum rich phases like sigma / alpha prime
  – Cleanliness with respect to non-metallic inclusion
## Typical corrosion test results for 2205

<table>
<thead>
<tr>
<th>Test method</th>
<th>Corrosion medium and condition</th>
<th>Max. limit or Desired result</th>
<th>Actual results</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A-923 Method C</td>
<td>6% ferric chloride solution: 24hrs at 25°C</td>
<td>No visual signs of pits. Corrosion rate: 0.0001g/sq.cm (max)</td>
<td>No visual signs of pits. Corrosion rate: 0.000003 - 0.00001 g/sq.cm</td>
</tr>
<tr>
<td>Pitting Potential, potentiometric test</td>
<td>0.1N, NaCl at 80°C</td>
<td>Minimum potential = 250 mV</td>
<td>&gt;350 mV</td>
</tr>
</tbody>
</table>
Pitting Potential Curves for OK and NOT OK Samples

0.1N NaCl, 80°C
Minimum required Potential = 250mV

Breakdown of passive film (NOT OK Heat)
Breakdown of passive film (OK Heat)
Corrosion resistance as a function of temperature and Chloride concentration
Well screen making process:

- 8mm, HRAP → Drawn to 6.00mm → Solution Annealed

Properties obtained:
- TS = 780 MPa
- %E (100mm GL) = 25%

It is extremely important to avoid surface contamination on the wire rods.
<table>
<thead>
<tr>
<th>Process</th>
<th>Operating Condition</th>
<th>Material Choice</th>
</tr>
</thead>
</table>
| Digester                      | Temp : 150 – 180 °C  
Pressure : 10 – 12 Bar  
Acidic Sulphate : pH 2 -4  
Chloride : No                   | 316L or 2205 : The strength at 180 °C is higher for 2205. 316L is OK but maintenance cost is higher. Since Chloride is absent, best choice can be lean duplex with low Mo, ie, 2101. |
| Blow tank, washing and screening | Pulp suspension injected at high Velocity, alkaline/organic vapor phase.  
Erosion from hard particles such as sand. | Optimum choice lean duplex, 2101 or 2304 due to high strength and better erosion corrosion properties as compared to 316L. |
Petroleum Industry Application

Forged Bowls/Machined Shafts for High Speed Separator Assembly

Process steps for forged bowls

- HR Bars
- Forging
- Solution Annealing
- Machining
- Grinding and Polishing

Process for Machined Shafts

- Solution Annealed Bars
- Machining to finish shafts
- Meeting requirement of impact at -10°C of 100 J min. (Test value = 280 J)
Ribbed Bars for construction industry

- High yield strength of Duplex Stainless Steels make them suitable for use in bridges, and other concrete structures in coastal areas.
- Their resistance to general corrosion and SCC make them the best choice material.
- Mechanical properties specified for duplex ribbed bars:
  - 0.2 PS > 500 MPa
  - Tensile strength > 650 N/mm²
  - Elongation > 14 %
  - Surface geometry as per specification

- The properties are achieved by controlling chemistry, roll pass design, and rolling temperature.
Nuclear applications

- Grade 304LN for shafts in Reactor (CRDM)
- Welding wires 308L, 316L with Low Cobalt (<0.05%)
## Quality requirements for CRDM Shaft

### CHEMISTRY
- Minimum specified value for C & N.
- Sulphur, Phosphorus & Silicon level restricted.
- Control on tramp elements.
- Chromium 18.5% min.

### MECHANICAL PROPERTIES
- 0.2PS & UTS higher than ASTM standards.
- Properties to be certified at room temperature as well as at 450°C.
- Impact strength at room temperature.
Carbon & Nitrogen control

- % C
- % N2

Heat No: H3698, H3699, H4182, H4183, H5296

Spec: 0.03 max, 0.024 min
C%: 0.024 min
N2 %: 0.06 min, 0.08 max
Mechanical properties
Special Ferritic Stainless Steel Applications
Special Ferritic Stainless Steels - Applications

- High Silicon, High Mo grade for use in Solenoid Valve

- Titanium stabilised grade for Auto Exhaust Hanger

- Ti & Nb stabilised grades for welding electrodes
Quality requirements

- Soft magnetic properties for solenoid valves
- Cold formability characteristics
- Proper stabilisation ratios & surface quality
- Improved machinability
Solenoid quality steel for valves

- 430FR /430FSiHMo grade steel in solenoid part

**Typical Process Sequence:**
- Mill annealed rods → Surface treatment → Cold Drawn → Special heat treatment condition to obtain optimum metallurgical structure to achieve special magnetic properties.
- Saturation of magnetisation
- Coercive Force as specified in ASTM A 838

**Uses**
- Moderately chlorinated aqueous environment. (e.g Beverage industry)
Cold formed Exhaust hangers

- 409 Ti / Nb grade steel

**Typical Process Sequence**

- Mill annealed rods
- Surface treatment
- Cold Drawn
- Cold bending and Heading

Hanger
904L High Alloy Austenitic
Application Areas for 904L grade

1. Processing plant for sulphuric, phosphoric & acetic acids
2. Pulp and paper processing
3. Components in gas scrubbing plants
4. Seawater cooling equipment
5. Oil refinery components
6. Wire mesh in electrostatic precipitators.
## Corrosion Data

<table>
<thead>
<tr>
<th>Test method</th>
<th>Corrosion medium and condition</th>
<th>Max. limit or Desired result</th>
<th>Actual results</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM G-48 Method A</td>
<td>6% ferric chloride solution: 24 hrs at 25°C</td>
<td>Corrosion rate: 0.0001 g/sq.cm (max)</td>
<td>Corrosion rate: 0.000012 g/sq.cm</td>
</tr>
<tr>
<td>ASTM A-262 Practice C</td>
<td>65% Nitric acid: 48hrs * 5 boils</td>
<td>Rate of corrosion: 10 mpy (max)</td>
<td>Rate of corrosion: 5 mpy (average)</td>
</tr>
<tr>
<td>ASTM A-262 Practice E</td>
<td>Copper-copper sulphate solution + 16% sulphuric acid boiled for 15 hrs</td>
<td>No appearance of fissures or cracks</td>
<td>No appearance of fissures or cracks</td>
</tr>
</tbody>
</table>
Application in Electrostatic precipitator thermal power plants

Process Route

1. HR wire rod
2. Annealing
3. Pickling
4. Wire drawing
5. Eddy Current Testing
6. Mesh forming

Diagram:
- Smoke particles are attracted to the collecting plates.
- Smoke particles pick up a negative charge.
- Smoke particles are knocked to remove the smoke particles.
- Positively charged collecting plate.
- Negatively charged metal grid.
- Waste gases containing smoke particles.
- Waste gases without smoke particles.

Mesh
Stainless Steel Welding Electrodes
Quality Requirements

✓ Chemical composition
✓ Drawability for MIG and TIG wire
✓ Surface quality of wire rods
Welding Electores

Austenite 308L

- 309Si (0.65/1.0)
  - High ‘Si’ Arc stability & better humidity.
  - Improve the usability of filler in Gas metal arc welding
  - Enables high M/G welding speed & better S/c finish
  - Less spatter & porosity
- 312
  - High ferrite more crack resistant than 309.
- 347 12°C Nb
  - 347 Si
  - Prevent Carbide Precipitation. High IGC Resistance material with partial
- 904L
  - H₂S/ Severe corrosion condition

Ferritic

- 430Ti
  - Good oxidation resistance in thermal cycles. (Exhaust)
  - Grain growth prevention.
  - Improved IGC
  - Better toughness of Weld material.
  - Mechanical Properties
- 430LNbTi
- 430LNb
- ER410 NiMo
  - To overlay on casting of 410/410NiMo.
  - To combat erosion corrosion in hydro power industries (Turbine wall, power generator)

Duplex 2209

- Weld 2205
  - The weld metal gives a austenitic/ferritic weldment. ; offers very good strength and resistance to stress corrosion and pitting.
## Typical Chemistry & Properties

<table>
<thead>
<tr>
<th>Grade</th>
<th>Typical Chemistry, wt%</th>
<th>Typical Mech. Properties (Annealed)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>ER 309LSi</td>
<td>0.017</td>
<td>23.3</td>
<td>1.5</td>
</tr>
<tr>
<td>ER 312</td>
<td>0.100</td>
<td>30.0</td>
<td>9.0</td>
</tr>
<tr>
<td>ER347Si</td>
<td>0.018</td>
<td>19.5</td>
<td>9.4</td>
</tr>
<tr>
<td>904L</td>
<td>0.013</td>
<td>19.9</td>
<td>24.1</td>
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Product Forms

1. Straight electrodes
2. Coated electrodes
3. Drawn wire in spools as MIG or SAW wire

MiG welding wire spools

TIG welding Electrodes
CONCLUSIONS

✓ Long standing process improvements and adoption of Triplex process route could lead to development of speciality stainless steel grades for high end applications. These steels were hitherto imported for meeting the domestic demands of wire and tube manufacturers.

✓ India, as a fast developing nation, is expected to post a higher GDP growth in the coming years; this can lead to widening the application areas for stainless steels.

✓ In a changing global scenario, acquiring greater capability in tune with customers changing pattern of application plays a vital role. Mukand has the vision to radically transform itself in meeting these objectives.
THANK YOU