How It’s Made:
Premium Grade Virginia Mullite™

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Purpose of the Presentation

1. Explain the steps involved in making Premium Grade Virginia Mullite™
2. Explain how mullite made from kyanite differs from other mullites
3. Show that reducing iron oxide in aluminosilicate raw materials positively impacts the high temperature properties of the shell, leading to better dimensional stability
Outline

Introduction
The Deposit
Mining and Comminution
Wet and Dry Processing
Calcination
Grinding and Sizing
Why it Matters
Refractory Raw Materials

There are many types of refractory materials used in investment casting flours and stuccos

• Zircon, fused silica, alumina, aluminosilicates, etc.

The origin of these materials is very important as no two deposits are the same

• Naturally occurring purity
• Amount of the impurities
• Mining processing
• Mineral processing techniques
Aluminosilicates

Aluminosilicates are a mixture of alumina and silica

Very desirable because they contain mullite

Mullite: $\text{3Al}_2\text{O}_3\cdot\text{2SiO}_2$

- Very refractory with a high melting point
- Excellent thermal shock resistance
- Stoichiometric mullite is 72 weight% alumina
Aluminosilicates

Pure stoichiometric mullite is very rare in nature
• Not enough to be mined commercially
Mullite aggregates are instead created by one of three ways:
• Mixing, extruding, and sintering clay minerals
  • Vast majority of aluminosilicates
• Fusion of silica and alumina to make fused mullite
• Calcining one of the sillimanite group of minerals, such as kyanite
Aluminosilicates are discussed in terms of alumina content
• Really means how much mullite is present
  • Remainder is silica and other impurities
Oxide Impurities

Oxides

• Fe$_2$O$_3$, Na$_2$O, MgO, K$_2$O, CaO, etc.

These react with the excess silica in aluminosilicates to form glass

• The oxides reduce the melting point of the silica

Since aluminosilicates are typically used in backups, the major negative of the oxides is in creep resistance

• Glass becomes molten and can flow, causing deformation

• This affects dimensional stability of the castings and leads to lower yield

Removal of problematic oxides is very important in order to gain better hot properties for the shell

• Kyanite Mining Corporation has decided to make a new Premium Grade Virginia Mullite$^\text{TM}$ with a lower iron oxide content (<0.19%) than standard (avg 0.5%) to improve performance of the shell
In order to make Premium Grade Virginia Mullite™, we must first mine and beneficiate its precursor material, Virginia Kyanite™.
Kyanite: The precursor to Virginia Mullite™

Kyanite is one of the sillimanite group minerals
• Sillimanite and andalusite

All three have the same chemical composition of \(3 \text{ (Al}_2\text{O}_3 \cdot \text{SiO}_2)\)

Pressure and temperature of formation determine the crystal structure and thus the mineral formed

Blade shaped crystal (high aspect ratio) due to different hardness along and across the crystal

Can be calcined to form mullite
• Kyanite has requires the lowest calcination temperature of the three sillimanite minerals to convert to mullite
The Deposits

2 Deposits in Central Virginia

• Willis Mountain
• East Ridge

100,000-120,000 tons of combined annual demand for Virginia Kyanite™ and Virginia Mullite™

• Each deposit contains between 20-25% kyanite in the ore
  • Quartz, iron oxides, pyrite, micas, clays, rutile, etc.

• Roughly 650,000-700,000 tons of ore are mined per year

At current production rates, the mine will last several generations
Blasting

Blasting
• Once or twice a month
• Liquid explosive in pre-drilled holes
• Any rocks that are still too large after blasting are broken down by a rock breaker
Mining

Done on a single daylight shift, 5 days a week

Fleet of haul trucks work in multiple areas of each deposit at all times

• This ensures mixing of the different areas of the deposits

• No two areas in the mine are the same

KMC does not follow a vein

• Take the whole mountain/ridge

• Very careful not to use up the best material all at once
Comminution

Rocks from the quarries come first to a jaw crusher
• Reduces rocks from several tons to only a few dozen pounds

From here, the ore goes through several further stages of crushing and screening
• Mainly gyratory
• Reduce rocks from a few dozen pounds to one inch by down in size
Wet Processing (The Float)

More than 20 steps in this part of the process alone
• Rod and ball mills, hydro-sizers, hydro-cyclones, screens, floatation cells, spirals, extractors, etc.

Very water intensive
• 7,000-8,000 gallons per minute

Runs 24 hours a day, 5 days a week

Size of the product is 40 mesh (400 µm) and finer
• Must be ground down to this size to remove the quartz and other impurities
Typical Mineralogy after Wet Processing

80-85% Kyanite
5-10% Quartz
5-10% Iron Oxides
1-2% Titania
<0.05% Alkali/Alkaline Earth oxides
Dry Processing: The Dryer

Damp material from the float is dewatered in several steps
This material then goes to a fluid bed dryer
• Top chamber is very similar to a fluid bed used for applying stucco
Material is heated to over 1000°F (540°C)
Material then goes through a rotary cooler where the iron oxide is converted to a magnetic form
Runs 24 hours a day for a campaign of days
Dry Processing: The Magnet House

After cooling, the kyanite goes to the magnet house

A mixture of low and high intensity permanent magnets and rare earth magnets are used to remove the iron

• Typical iron oxide content after this process is 0.5%
Premium Grade Virginia Kyanite™

Extra magnetic removal steps are used to create Premium Grade Virginia Kyanite™

• Iron content of 0.19% or less

This lower iron oxide content is important in high temperature applications
Calcination: Kyanite to Mullite

Premium Grade Virginia Kyanite™ is taken to one of 3 rotary kilns
• Kyanite is exposed to temperatures in excess of 2700°F (1480°C)
Runs 24 hours a day for a campaign of days
Kyanite undergoes a phase transformation to make mullite

\[ 3(Al_2SiO_5) \xrightarrow{heat} 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \]

The chemistry remains unchanged
Calcination: Kyanite to Mullite

Kyanite undergoes an irreversible 17 vol% expansion when converted to mullite

• Not an issue when using Virginia Mullite™ as the expansion has already happened in the calcination process

• This does mean that the largest particles of mullite can be slightly larger than the 40 mesh (400µ) kyanite, allowing for the production of 20x50
  • Can’t get any larger due to the size of the starting kyanite

The resulting mullite also retains the same high aspect ratio of the kyanite
Grinding and Sizing

Flour
• -200m and -325m
• Ground in a special ball mill with alumina media

Stucco
• 20x50 and 50x100
• Multi-deck vibratory screening
What is Unique About Mullite Made from Kyanite?

Particle Shape

• Because kyanite has a different hardness along two axes, it has a high aspect ratio, even when ground
• This is maintained through the calcination process
• High aspect ratio particles with green strength in the shell
  • Has been used to reduce the number of backup coats required
Premium Grade Virginia Mullite™ 20x50
*scale lines are 1mm
What is Unique About Mullite Made from Kyanite?

Location of Impurities

• Mullite made from clay particles is highly homogenized as the clays are mixed before extrusion and firing
  • Impurities are very evenly distributed throughout the aggregate

• Mullite made from kyanite has very localized impurities
  • The impurities (ex. quartz) are still attached to the kyanite crystal, not in the kyanite crystal itself
    • Would have to grind finer to remove, but loose the ability to make coarse product
  • This aids in creep resistance as the impurity will only cause localized creep instead of throughout the entire mullite grain

Localized TiO2 impurity
Creep

Creep means deformation under load
A shell that creeps loses its dimensional stability
• Increased scrap rate
• Increased finishing labor costs

Factors influencing creep in aluminosilicates:
• Overall alumina content
• Amount of oxide impurities
  • React with the excess silica to form glass
  • Glass will flow, causing the shell to change shape
Creep Resistance

Tested several aluminosilicates on a dilatometer to examine movement under load, aka creep

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<th>Name</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
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<td>43.8</td>
<td>0.18</td>
<td>0.05</td>
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<td>Temperature °F (°C)</td>
<td>Dwell Time (min)</td>
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<td>36 (20)</td>
<td>2550 (1400)</td>
<td>60</td>
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<td>3</td>
<td>36 (20)</td>
<td>77 (25)</td>
<td>100</td>
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</tbody>
</table>

**Premium Grade Virginia Mullite Al2O3=55.08 Fe2O3=0.18**

- M1: Al2O3=66.74 Fe2O3=1.23
- Virginia Mullite Al2O3=57.6 Fe2O3=0.48
- M2: Al2O3=61.92 Fe2O3=1.27
- M3: Al2O3=52.38 Fe2O3=0.94
- M4: Al2O3=48.1 Fe2O=0.77

**Material ▲ L**

- PGVM 9
- M1 23
- VM 25
- M2 33
- M3 51
- M4 63

Heating Profile

Aticus Evaluation V1.0.1:
Creep Resistance

**Premium Grade Virginia Mullite™**

- Showed the least amount of creep
  - Due to the least amount of iron oxide
- Even better creep resistance than the 66.7% alumina sample, M1
  - Shows that while alumina content is important, impurity amount is even more crucial
- Better in creep resistance than standard Virginia Mullite™
  - Shows the influence of reducing iron oxide and explains the purpose of this new product
Creep Resistance

M2
- Most similar sample to the Virginia Mullite™ products in terms of alumina content
- Lower creep resistance than either Virginia Mullite™ due to higher level of impurities

M4
- Exhibited the highest amount of creep
- Had the third lowest iron, but had the lowest amount of alumina
- Important to remember that alumina content is still crucial to high temperature properties
Conclusions

There is more than one way to make mullite-one of which is to calcine kyanite
• Very complex and lengthy process involving more than 25 steps
Calcining kyanite to make mullite creates a raw material with several unique characteristics
• Blade shaped particles
• Non-homogenous impurity location which aids in creep
Reducing the amount of iron oxide in the shell materials increases resistance to creep
• Improves dimensional stability of the shell, improved yields, and can reduce finishing labor costs
• Impurity level can play a more important role in creep resistance than alumina content
• New Premium Grade Virginia Mullite™ exhibited the highest creep resistance of the aluminosilicate materials tested due to the low level of iron oxide
Thank you for your time and attention!

Questions?