13-15 September / Eylül 2012, Tüyap, İstanbul
6th International Ankiros Foundry Congress
6. Uluslararası Ankiros Döküm Kongresi

Bu bildiri 6. Uluslararası Ankiros Döküm kongresinde sunulmuştur

This paper was presented on 6th Ankiros Foundry Congress

http://kongre.tudoksad.org.tr/

Eylül 2012
September 2012
Tüyap, İstanbul

MgFeSi with La, an effective alternative to standard RE for production of Ductile Irons

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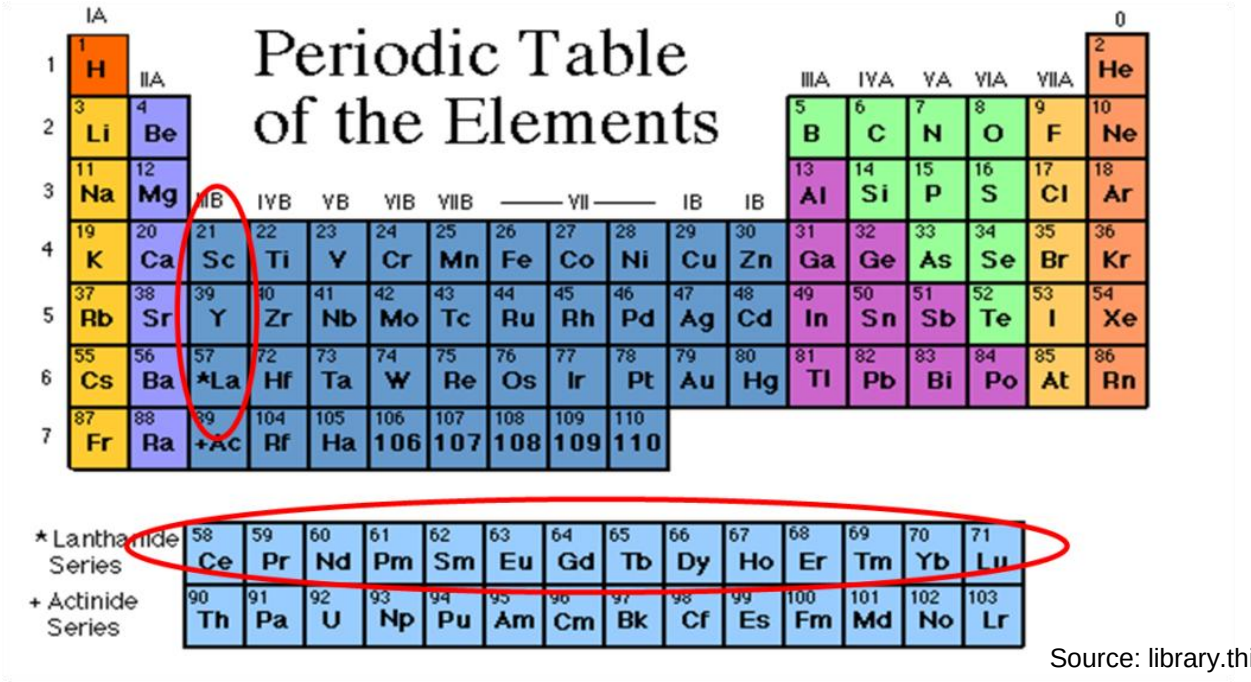
Rare Earth Basics (I)

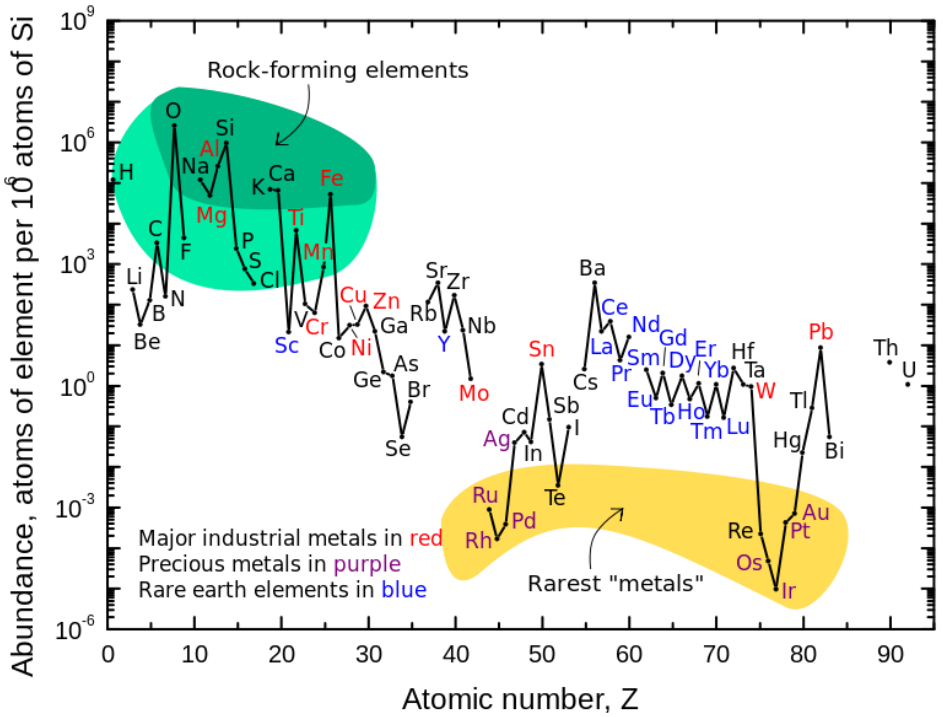
- Rare Earth elements (RE) is a collective term for seventeen chemical elements, specifically the fifteen lanthanides plus scandium (Sc) and yttrium (Y)
- Exhibit similar chemical properties.



Source: library.thinkquest.org

Rare Earth Basics (II)

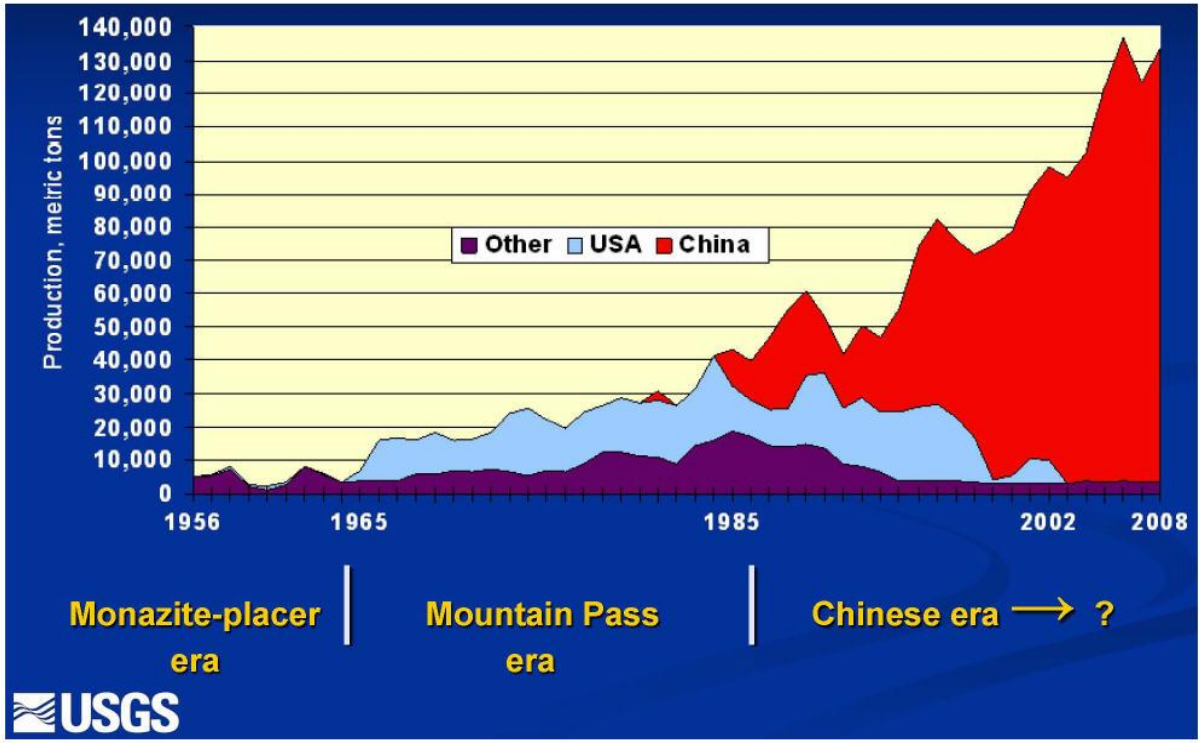
- RE are not that particularly scarce, their abundance is comparable with common metals such as nickel, copper and cobalt.
- Unlike the common metals, which form fairly concentrated natural deposits, RE occur widely distributed in low concentrations, at most at 6 – 7% RE oxides.
- Added to their mineralization and especially the complex extraction processes, the “nickname” may nevertheless be justified



Source: wikipedia.org

History of RE Supplies

- From the 1960-ies Mountain Pass (USA) leading producer.
- Since the 1990-ies China more or less the sole producer. Strategic move of the Chinese government? Former leader Deng Xiaoping in 1992: "The Middle East has oil, but China has rare earth“.



Source: USGS

Use of Rare Earth Metals

- RE used in a wide range of modern and “green” products.
  - Metallurgy (incl. foundries) only about 9%.
- A modern car contains approx. 15 kg RE metals.

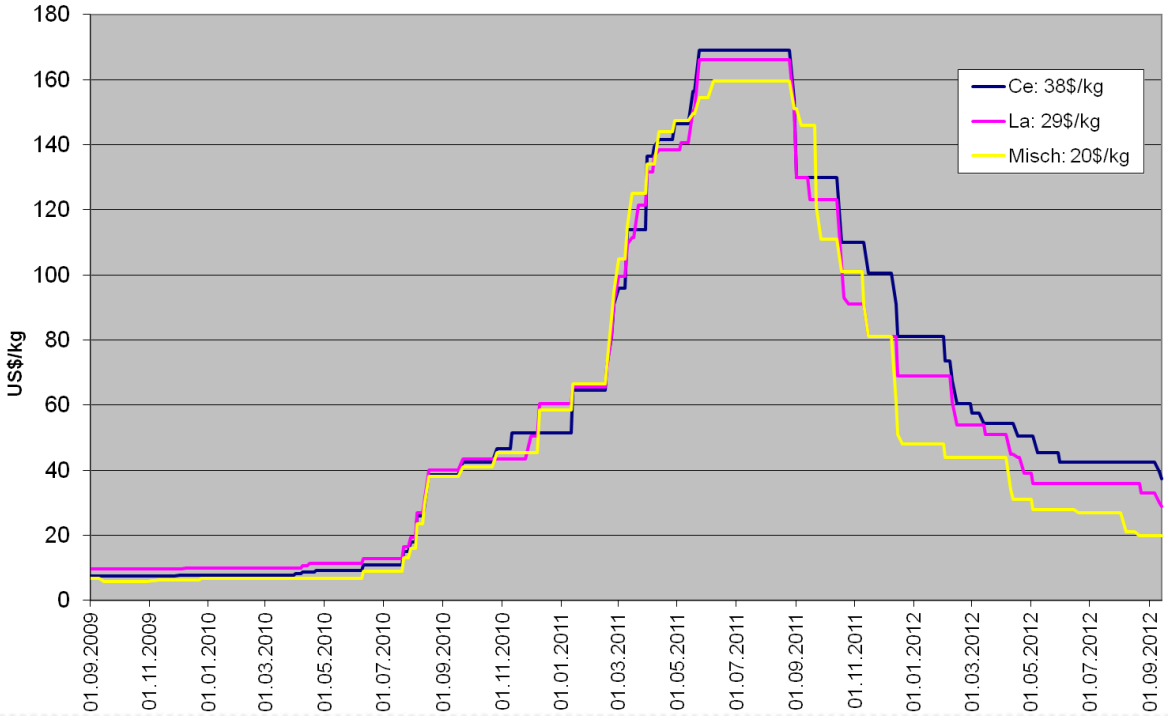
Application area	%
Magnets	25
Catalyst – Cracking	15
Batteries	14
Polish	14
Metallurgy	**9**
Catalyst – Cars	7
Glass additives	6
Luminiscens	6
Other	4

Source: sgu.se

Source: usgs.com

Recent Price Development of RE

- Until Aug. 2010: Stable below $10/kg.
- Aug. 2010 – May 2011: Steep increase, peaked at $160-170/kg.
- Since May 2012: Rapid decrease, current price at $20-40/kg.
- *Sept. 2012: Has the market found the balance? Are prices stabilized?*



Source: metal-pages.com

MgFeSi Overview (I)

- MgFeSi treatment alloys are commonly used for production of ductile irons (DI)
- Generally, 50% Si based ferroalloys with defined levels of the active elements Mg, Ca, Al and RE metals
- Si and Fe mainly act as the carrier that ensures consistent and high yield of the active elements.
- Mg is the principal nodularising element of MgFeSi.
- Ca reduces the reactivity of Mg, is a strong nodularising element and the resulting sulfide and silicate inclusions are excellent nuclei for graphite formation.
- Al improves inoculation and increases ferrite content.

MgFeSi Overview (II)

- RE metals are commonly added to MgFeSi due to:
  - Ability to neutralize detrimental tramp elements like antimony, lead, bismuth and arsenic.
  - Strong deoxidizing and desulphurising elements.
  - Form stable and dense oxides and sulfides that are less prone to fading.
  - High melting points and low volatility give less violent reaction and fume formation compared to Mg.
  - Inoculation effect that gives increased nodule count.
- The principal RE metals to DI are Ce and La:
  - Commonly introduced as a premixed blend denoted mischmetal (MM), which typically is ½ - ⅔ Ce and ¼ - ⅓ La + minor amounts of Nd and other RE metals.
  - Typical levels: approx. 1% total RE.

Typical levels of RE in DI and alloys

- Ductile irons:
  - Base iron (for DI): 0.005 – 0.008% Ce,
    0.001 – 0.003% La
  - Final DI: 0.007 – 0.012% Ce,
    0.004 – 0.006% La

- Alloys:
  - MgFeSi w/RE: 0.5 – 2.5% RE
  - Inoculants w/RE: 1.5 – 2.0% Ce/RE

RE Cost Impact on Ductile Iron

July 2010	August 2011	September 2012
Misch metal price	**Misch metal price**	**Misch metal price**
7 $/kg	160 $/kg	20 $/kg
MgFeSi	**MgFeSi**	**MgFeSi**
0.08 $/kg	1.92 $/kg	0.24 $/kg
Treated Iron	**Treated Iron**	**Treated Iron**
1.26 $/ton	28.80 $/ton	3.60 $/ton

Assuming 1% RE in MgFeSi, 1.5% MgFeSi addition

Optimizing RE-level in DI production

4 step strategy by Elkem in 2010:

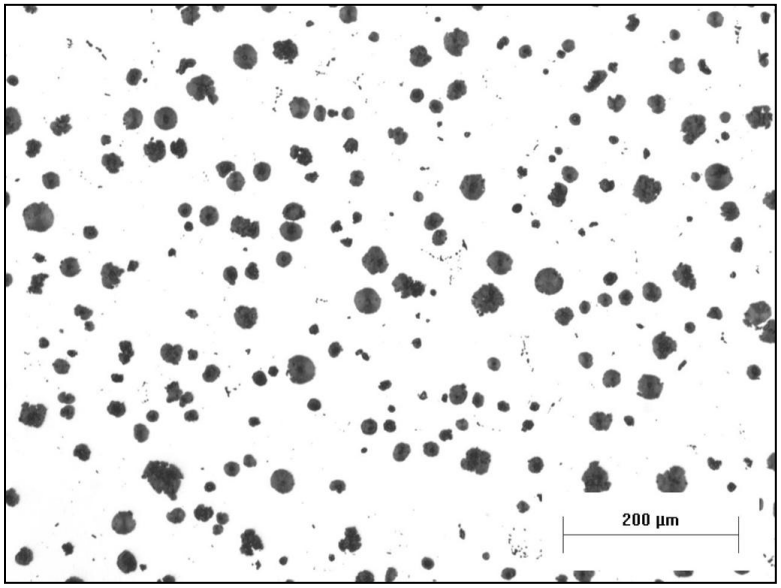
1. Optimize the treatment process.
2. Optimize RE-content in treatment alloys.
3. Replace MM-based MgFeSi with La-based MgFeSi.
4. Use a RE-containing inoculant with a low or RE free type MgFeSi.

Use of La in the production of DI

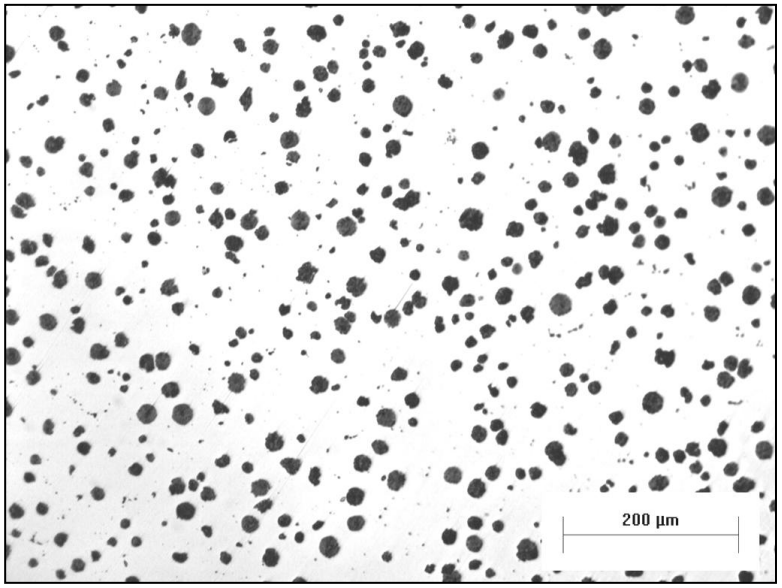
- Research development:
  - Research of the influence of RE elements in the DI treatment process Has shown that La has a lower optimum content in the iron and gives more fine sized nodules that are formed at a late stage of the iron solidification process, compared to other RE.
  - Consequently, the benefits from La are higher nodule count, increased nodularity and reduced pearlite content, chilling tendency and shrinkage porosity.
  - This lead to the introduction of a new range of MgFeSi grades with La from Elkem AS, namely the Lamet® nodularisers.
  - They generally have a La content of about 0.5%, which is about half the amount of total RE in common MgFeSi grades.
- Five case studies of Lamet® nodularisers follows…

1. Replacing 0.5% MM-based with 0.5% La-based MgFeSi

- Graphite structure greatly improved;
- Alternatively, if the old structure was regarded as adequate, the foundry could have reduced the La level.



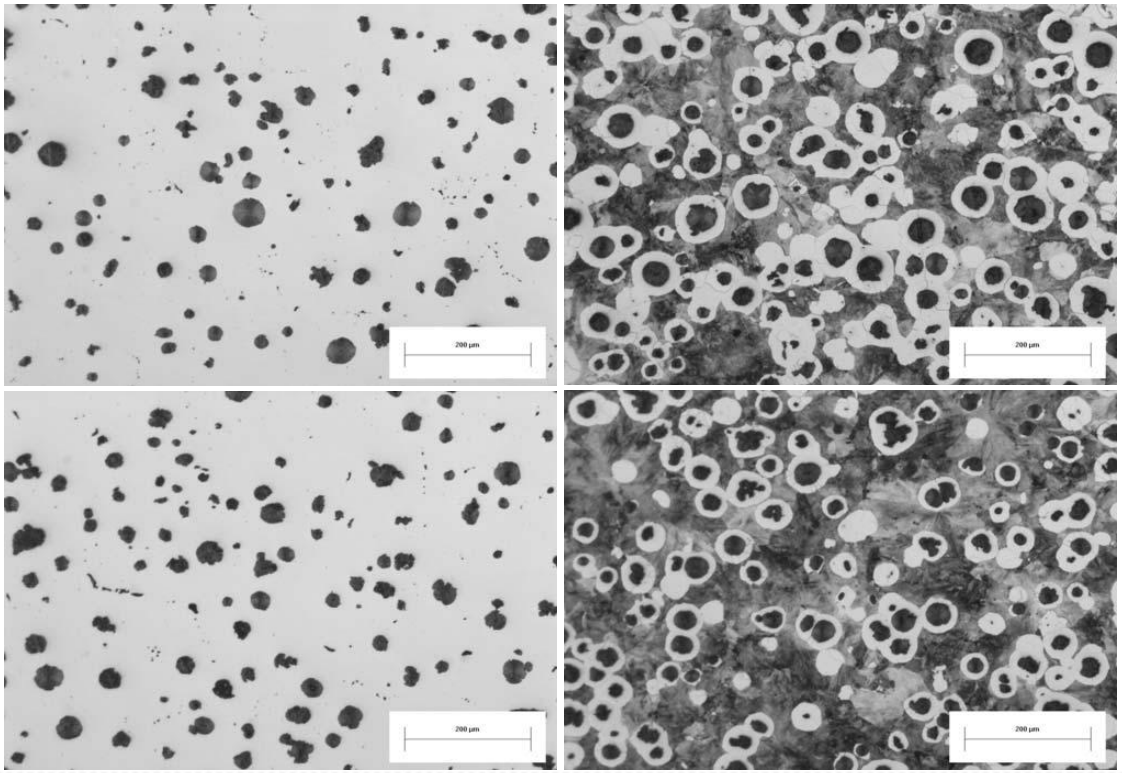
MM-based MgFeSi w/0.5% RE



La-based MgFeSi w/0.5% La

2. Replacing 2% MM-based with 0.5% La-based MgFeSi

- Addition rate reduced from 1.5% to 1.25% with La-based MgFeSi.
- Increase in final Mg (0.039% vs. 0.045%), same Mg yield (76 vs. 78%).
- Small decrease in nodule count (174 vs. 152), same nodularity (88 vs. 87%).

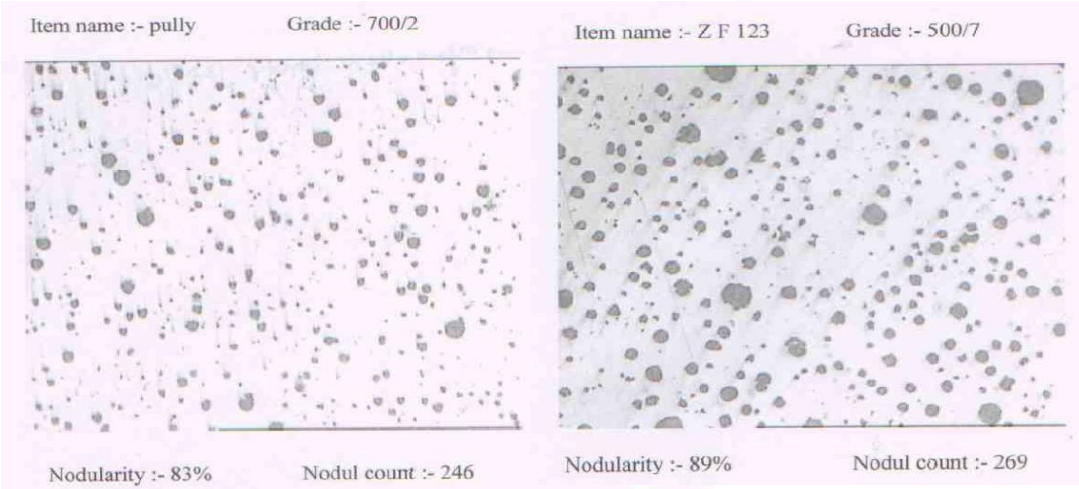


MM-based MgFeSi
w/ 3%Mg/2% RE

La-based MgFeSi
w/4.6%Mg/0.5% La

3. Replacing 2-2.5% RE-based with 0.5% La-based MgFeSi

- Automotive parts for small cars. Porosity defect revealed after machining.
- Trial with La-based MgFeSi found porosity defect almost nil.
- Also got increased nodule count and nodularity.
- Similarly trial on “ZF steering system” (case differential), where porosity was totally eliminated.



La-based MgFeSi w/5.8%Mg/0.5% La. Pully (right), ZF123 (right)

4. Replacing 1.1% RE-based with 0.5% La-based MgFeSi

- Mg in treatment alloy reduced from 6.25% to 4%.
- Final Mg was identical, thus recovery was 55% higher with new alloy.
- Acceptable nodularity and nodule count with RE-based MgFeSi, but also at least 5% carbides.
- With La-based MgFeSi: at least 50% higher nodule count, increased nodularity and no carbides.

(No images due to customer discretion.)

5. Replacing 0.5-1% RE-based with 0.5% La-based MgFeSi.

- With RE-based MgFeSi: problems with micro porosity in crank shafts after machinin, rejection varying from 20-60% in same type of casting!
- Trial with La-based MgFeSi made 75 crank shafts and dispatched to customer. After machining they found castings to be porosity free. Foundry is waiting for final feedback from their customer.

(No images due to customer discretion.)

Critical factors when changing RE-level

- Do not change too many variables at once.
  - Ideally: Change only one factor at once.
- Know your typical tramp and RE-level in your iron.
- Mix your way to the optimum RE-level in the MgFeSi.
- Change in RE-level in MgFeSi may require change in inoculation.

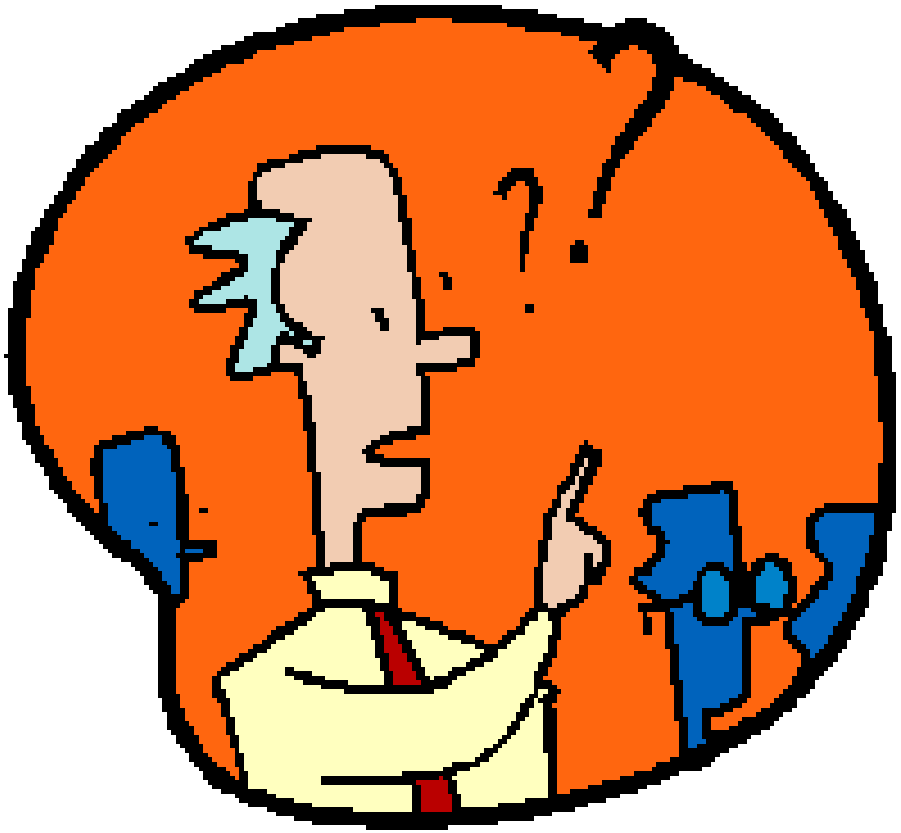
Finally:

- Patience is key – it will take time to see the full effect of changes and until residual levels have stabilized.

Summary

- RE situation is seemingly back to normal, but the last two years have given the whole world strong warnings not to rely on China for supplies of crucial materials. *New surprises may lie ahead of us!*
- There is currently no viable substitute for RE in DI.
- Change to La-based nodularisers have been successful in reducing cost and giving increased benefits of the alloy.
- Change your DI process step by step.

Questions and Comments?



Thank You for Your Attention!

For further information….

Please take a look at:

www.elkem.com/foundry