# ADVANCES IN SINGLE CRYSTAL SUPERALLOYS – CONTROL OF CRITICAL ELEMENTS

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## Abstract

In the highly competitive world of aero and industrial gas turbine design, manufacture and engine service, the demands imposed on engine performance are continually escalating. In response, fuel efficiency requirements, inlet gas temperatures and component life requirements are all increased commensurately. Component designs for single crystal castings are increasingly complex and high casting yield with excellent quality is essential. To accomplish these goals, development and application of advance single crystal alloys has played a vital role, and control of deleterious elements such as [N], [O], S, P and Si are critical to successful alloy implementation. The ability to accurately and consistently measure these elements is also integral to trace and tramp element control.

On the positive side, the addition of highly reactive elements, La and Y at the ppm level, in conjunction with very low (1 ppm or less) sulfur content has demonstrated improved bare oxidation resistance and thermal barrier coating adherence and life including prime reliant applications. The ability to pre-alloy the ingot with La and Y has provided additional benefit in terms of consistency, control and convenience. This technology has been applied to a number of SX superalloys, including CMSX-4® and CMSX-486® alloys.

In this paper, the role (both positive and negative) and control of critical elements at the ppm level as it applies to many advanced SX superalloys will be examined and discussed.

**Keywords: Superalloys, Critical Elements, Tramps, Traces, VIM**

## Introduction

The superalloys comprise a class of Ni-, Fe- and Co-base materials that are used structurally at operating temperatures of 540°C (1000°F) or higher and maintain high strength at temperatures approaching 85% of melting point. These complex materials are a blend of ten or more alloying elements developed to optimize properties tailored to an application. Superalloys exhibit excellent elevated temperature properties combined with good hot corrosion and oxidation resistance to meet the demanding requirements of aero and industrial gas turbine engines. Investment castings are utilized to produce cost-effective components of complex shapes and/or internal configurations with controlled uniform microstructure.

Single crystal (SX) cast superalloys are used in aero and industrial gas turbine engine applications, such as turbine blades, vanes and combustor components, requiring the hottest temperature/highest stress capability. The benefits of SX castings have been well documented; these alloys offer improved creep-rupture, fatigue, oxidation and coating properties, resulting in superior turbine engine performance and durability [1,2,3,4,5]. Superalloy casting alloy development and manufacturing improvement efforts have benefited from the control of critical elements (both deleterious and beneficial); this paper will examine both aspects of alloy performance.

## Background

Bieber and Decker published the first systematic study of the effect of trace elements and minor alloying additions in nickel [6]. In 1976, Holt and Wallace published a useful classification of impurities and trace elements in nickel-base superalloys, as shown in Table I [7]. As can be seen, the elements are divided into two groups: detrimental and beneficial. Detrimental trace elements include residual gasses, non-metallic impurities and metallic/metalloid impurities; beneficial elements include refining aids and intentional alloying additions. It is important to note that alloying elements which are beneficial at the ppm or low weight percent (wt%) level can become detrimental if present in higher amounts.

Table I. Holt and Wallace Classification of Impurities and Trace Elements in Ni-Base Superalloys [7]

| Type | Examples |
|---|---|
| Detrimental Elements | |
| Residual Gasses | O, H, N, Ar, He |
| Non-Metallic Impurities | S, P |
| Metallic/Metalloid Impurities | Pb, Bi, Sb, As, Se, Ag, Cu, Tl, Te |
| Beneficial Elements | |
| Refining Aids | Ca, Mg, Ce, La |
| Minor/ppm Alloying Additions | B, Zr, Hf, Mg, C |
| Alloying Additons up to 1.5% | Hf, Zr |

A great deal of research has occurred subsequent to this early pioneering work, with alloy complexity and temperature capability dramatically increased due to the development of directionally solidified and single crystal casting alloys and technology. These improvements have optimized trace elements additions and are dependant upon advances in critical element control and measurement.

## Commercial Production/VIM

Commercial vacuum induction melting (VIM) production began in the 1950's due to the introduction of reactive elements (Al, Ti, Zr) in superalloys. VIM introduced superior control of alloy composition and homogeneity through melt stirring and improved alloy cleanliness and quality through vacuum induction refining. As shown in Figure 1, the vacuum induction refining process involves a carbon boil which removes oxygen from the melt [8,9,10,11], with a small loss of nitrogen and some tramp elements. Carbon monoxide (CO) is favored by decreased melt chamber pressure, elevated bath temperature and increased carbon activity [12]. The reaction $C+O \rightarrow CO$ occurs most readily at or near the melt surface, since the ferrostatic head inhibits deoxidation in the body of the melt. The kinetics is therefore affected by crucible geometry and melt stirring. Melt stirring is controlled by furnace frequency and proper power application with the goal of stirring the melt without eroding the furnace lining. Consequently, key attributes for successful VIM production include optimization of the melt refine temperature and time, melt stirring and carbon boil.

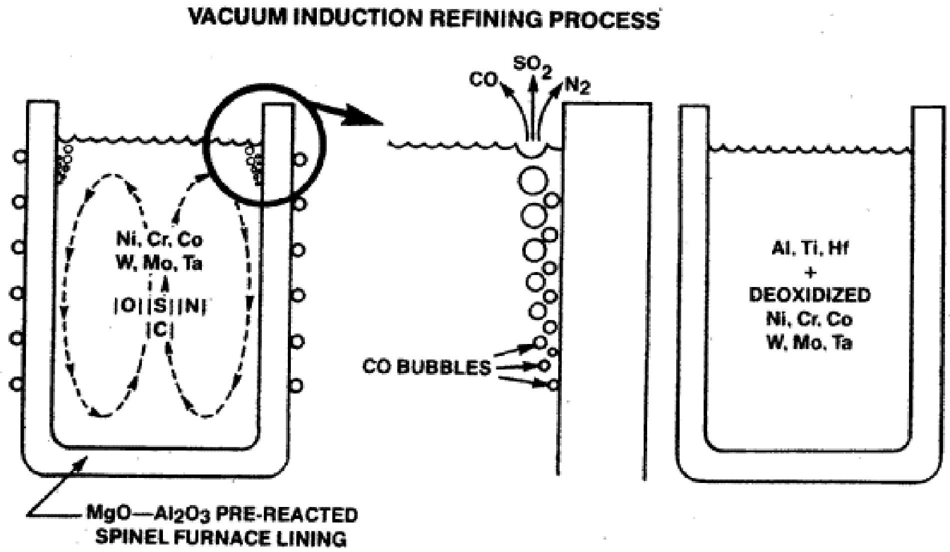
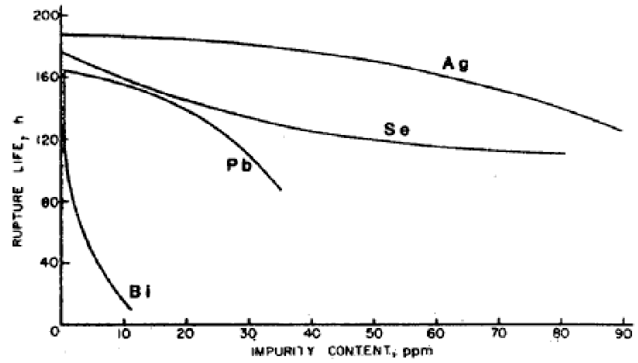



Figure 1. Schematic of VIM Process

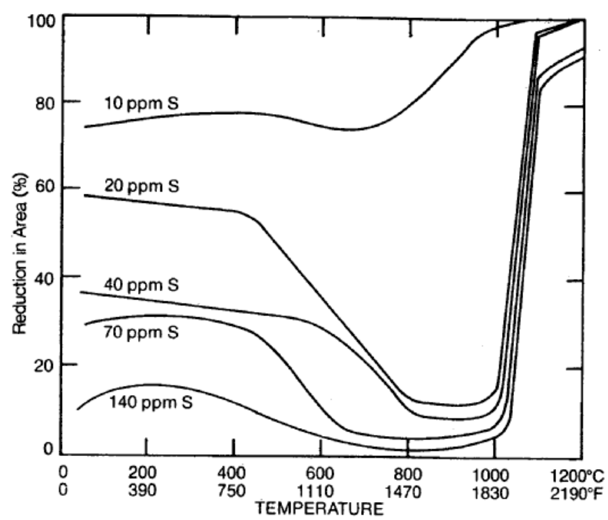
**Detrimental Trace Elements**

As previously mentioned, detrimental trace elements include residual gasses, such as N, O and H, non-metallic impurities (S and P) and metallic and metalloid impurities (Ag, Bi, Pb, Se, Te, Tl, Sb, As, Cu, Si, U & Th). Detrimental trace elements can affect mechanical properties, alloy performance, castability and weldability. Residual oxygen results in non-metallic oxides (dross inclusions) which reduce mechanical properties and weldability and can initiate fatigue cracking. Residual nitrogen produces microporosity, alloy/crucible wetting, and formation of carbonitrides, which also can serve as fatigue initiation sites. N and O can affect DS casting columnar grain control and initiate grain defects in SX castings. Non-metallic impurities, such as S and P, reduce grain boundary ductility resulting in DS grain boundary cracking and weld solidification cracking. Sulfur also increases alloy/crucible wetting and reduces oxidation resistance and coating/TBC adherence. Metallic/metalloid impurities reduce mechanical properties, cause hot short/hot tears and cracking. Figures 2 and 3 [13, 8] are representative examples of the impact of tramp and trace elements on alloy mechanical properties. Note that for elements like Bi, a few ppm can reduce rupture life by 50% or more.




Effect of Various Trace Elements on the 1200°F/100 ksi Stress-Rupture of IN-718 (Ref. 20).

Figure 2. Typical Effect of Detrimental Trace Elements [13]




Tensile ductility of Ni-S alloys between 120°F and 2190°F.
Source: Lozinskiy, et al.

Figure 3. Typical Effect of Non-Metallic Impurities

Control of gasses is accomplished by a combination of removal during the VIM refining process and the use of high purity raw materials. Similarly, deleterious trace and tramp elements are controlled by either evaporation during VIM (Figure 4 [14]) and/or raw material purity. Elements such as Pb, Bi, Se and Te can be reduced in the melt during VIM due to vaporization over time; however, high vapor pressure elements, such as As, Sn and Sb can only be reduced through dilution and are best controlled through careful selection of charge materials. As a result, the analytical capability of the controlling laboratory and industry-wide advances in analytical techniques are key factors for trace element control.

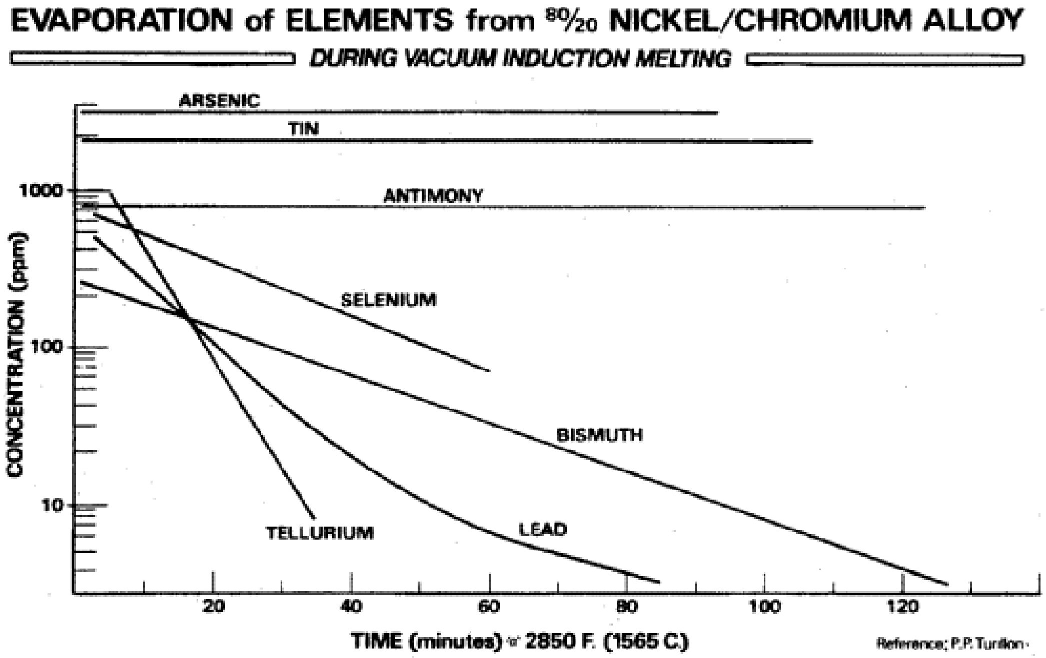



Figure 4. Evaporation of Detrimental Trace Elements during VIM

Detection of critical trace elements at the ppm level and below have enabled more exacting control of alloy chemistry and improved understanding of the impact of these elements on alloy castability and performance. Some of these advanced analytical techniques include atomic absorption (AA), inductively coupled plasma (ICP) and ICP mass spectroscopy (ICPMS) for trace and tramp element detection; very low sulfur analysis by glow discharge mass spectroscopy (GDMS) and low sulfur cell LECO fluxed oxygen fusion analysis; and N and O by LECO inert gas fusion analysis.

## Beneficial Trace Elements

Beneficial trace elements include refining and deoxidation aids (Ca, Mg, Ce, La Y) and intentional alloying additions (C, B, Zr, Hf). Elements such as Ca & Mg are added to combine with and reduce/eliminate deleterious elements in the molten bath. The elements are highly reactive with a high vapor pressure and any excess (non-combined) quantity tends to come off in the gaseous vapor or during subsequent remelting, rather than remaining in the melt. Rare earth elements, such as Ce, La and Y are effective in combining with S and P to prevent the detrimental effect on alloy properties and oxidation performance[15]; the impact on SX alloy performance will be discussed further.

C, B, Zr and Hf are unique elements, which are intentionally added at the ppm to low wt% level for property improvement, but can be detrimental at higher levels. These elements (at low levels) are beneficial to equiax (EQ) and DS alloy grain boundary strength and ductility; however, they are minimized/eliminated in SX alloys due to negative effects: carbides act as fatigue initiation sites in SX alloys; boron results in incipient melting. High Zr levels can cause DS grain boundary cracking, hot tears and cracking in EQ alloys, and weld solidification cracking. Similarly, elevated

B can result in weld solidification cracking, as shown in Figure 5 [16]. Alloy development has focused on optimum use of these elements and tight control is key to consistent alloy properties.

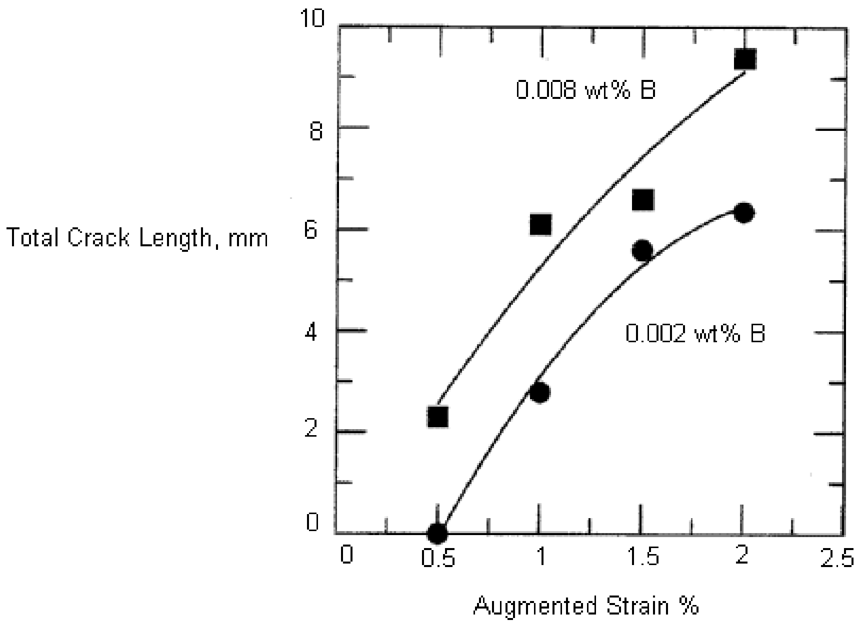



Figure 5. Influence of boron content on solidification cracking resistance of 230 alloy, as indicated by the varestraint test. Courtesy: Haynes International Inc.

## SX Alloy Advances

CMSX-4® is a second generation, Re-bearing nickel-base SX superalloy which has been extensively investigated and documented [3, 4, 17, 18, 19]. The nominal chemistry is provided in Table II. CMSX-4 alloy has been successfully used in numerous aero and industrial gas turbine applications since 1991. Close to seven million pounds (900 heats) of CMSX-4 alloy have been manufactured to date.

Table II. CMSX-4 Alloy Nominal Composition

| Element | Wt% | Element | Wt% |
|---|---|---|---|
| Cr | 6.5 | Al | 5.6 |
| Co | 9.6 | Ti | 1.0 |
| W | 6.4 | Ta | 6.5 |
| Re | 3 | Hf | 0.1 |
| Mo | 0.6 | Ni | Balance |

As discussed, rare earth element additions, such as La and Y are beneficial to alloy oxidation performance. CMSX-4 [La+Y] alloy was introduced to meet ever-increasing engine design requirements for hot section turbine components. Of particular interest was improvement in bare alloy oxidation behavior to minimize blade tip and internal degradation and improve thermal barrier coating (TBC) adherence. As shown in Figure 6, the addition of rare earth elements dramatically improves the dynamic cyclic oxidation behavior of CMSX-4 [15].

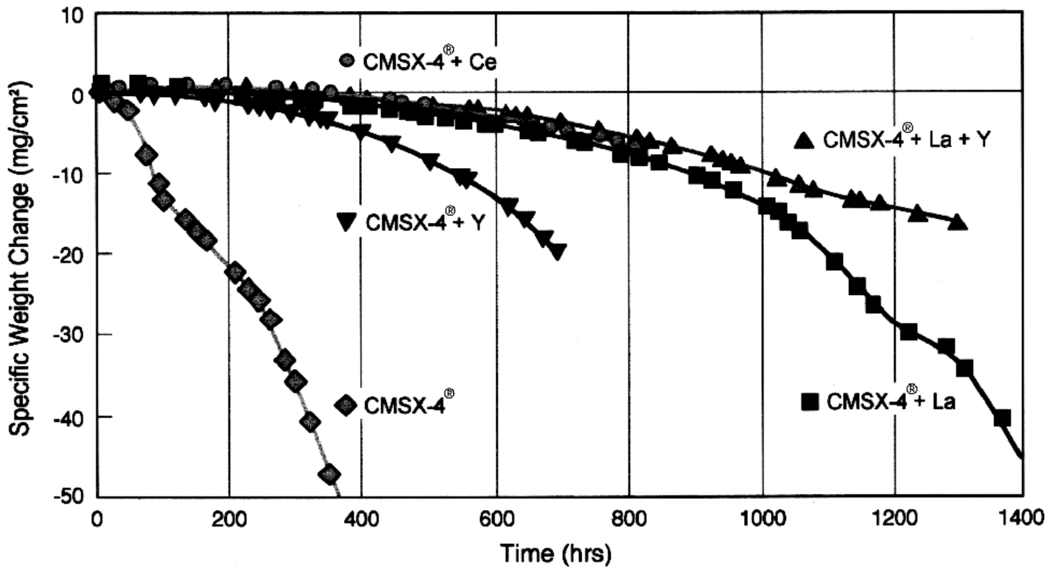



Figure 6. 1093°C (2000°F) Dynamic Cyclic Oxidation Test Results for Bare CMSX-4 Alloy with and without Reactive Element Additions

CMSX-4 (SLS)[La+Y] alloy is an improved version of CMSX-4 which is pre-alloyed with La and Y and has consistent low sulfur content of 1 ppm. Initial development work included production of R&D-size (V5) heats to demonstrate 1 ppm sulfur content capability and La + Y control. Subsequently, the manufacturing technology was scaled to 4000 lb. and 5000 lb. (V6) heats without negative impact on critical heat chemistry (Table III). CMSX-4 (SLS)[La+Y] has excellent alloy cleanliness in terms of stable oxide inclusions, as represented by 1-2 ppm oxygen content over multiple heats.

Table III. CMSX-4 (SLS) [La+Y] Production Heats – Critical Chemistry

| Heat | La ppm | Y ppm | S ppm | Mg ppm | Zr ppm | Si | [N] ppm | [O] ppm |
|---|---|---|---|---|---|---|---|---|
| 5V0114 | 363 | 339 | 1 | <180 | <10 | <.01 | 1 | 2 |
| 5V0115 | 500 | 490 | 1 | <180 | <10 | .01 | 1 | 2 |
| 5V0128 | 430 | 410 | 1 | <180 | <10 | <.01 | 1 | 2 |
| | | | | | | | | |
| 6V2451 | 142 | 142 | 1 | <180 | <10 | <.01 | 1 | 1 |
| 6V2461 | 747 | 620 | 1 | <180 | 14 | .01 | 1 | 2 |
| 6V3647 | 1100 | 850 | 1 | <180 | <100 | <.01 | 4 | 2 |
| 6V3665 | 822 | 564 | <1 | <200 | <50 | <.01 | 3 | 2 |

An example of the benefit of La + Y additions is shown in the surface microstructure observed following creep-rupture testing at 1050°C (1922°F) (Figure 7) [20]. After 1389 hours there was an 8 micron thick, 2-layer oxide film and no evidence of gamma prime depletion at all. Without the La+Y addition, significant γ' depletion would be expected from extended exposure at this temperature. This behavior translates to substantial improvement to EB-PVD TBC life, as demonstrated in (Figure 8) [21].

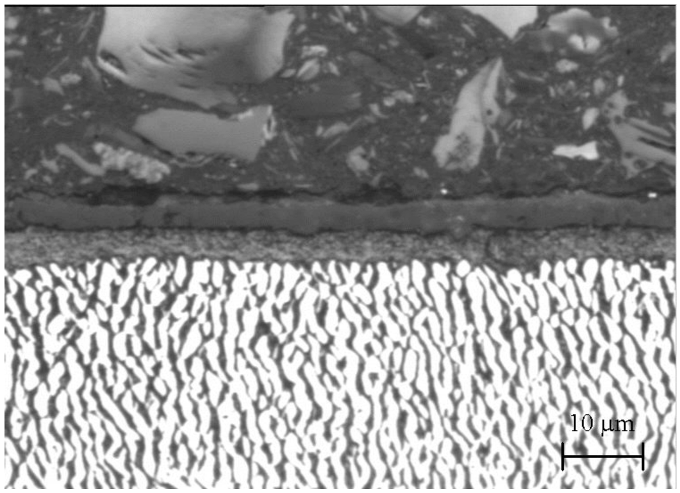



Figure 7. Surface Microstructure on CMSX-4 (~39 ppm La+Y) following 1389 hours creep-rupture testing at 1050°C/125 MPa (1922°F/18 ksi) [Courtesy Rolls-Royce plc]

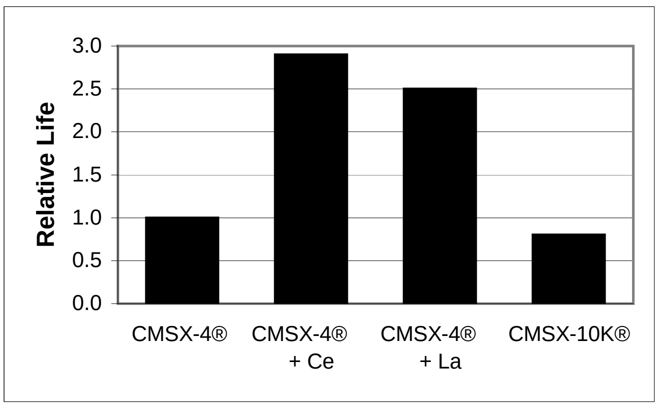



Figure 8. Reactive Element Effects on EB-PVD TBC Life
1093°C (2000°F)/10 hr Thermal Exposure Cycles
[Courtesy Solar® Turbines]

These successful improvements to CMSX-4 alloy are currently under evaluation for CMSX-486® (SLS)[La+Y] alloy. Initial development work has included production of an R&D-size heat to demonstrate 1 ppm sulfur content capability and La + Y control. As shown in Table IV, heat 5V0176 has excellent alloy cleanliness in terms of stable oxide inclusions ([O] content), [N], Si and S contents. It is also postulated that the 1.2% Hf content of CMSX-486 (SLS)[La+Y] alloy will protect the melt from excessive La and Y loss during remelt, resulting in improved control of retained La+Y content.

Table IV. CMSX-486 (SLS)[La+Y] Heat – Critical Chemistry

| Heat | La ppm | Y ppm | S ppm | Si | [N] ppm | [O] ppm |
|---|---|---|---|---|---|---|
| 5V0176 | 890 | 760 | 1 | .03 | 2 | 2 |

## Keys to Alloy Quality

There are many aspects to producing high quality VIM alloy. From a manufacturing standpoint, furnace design, lining/tundish technology, melt practices and processing parameters, and filtration are key factors. As mentioned earlier, charge materials, both elemental raw materials and reverted alloy, have significant impact on alloy quality. Finishing and inspection techniques, including chemical analysis provide the last opportunity to ensure that only conforming product reaches the casting furnaces.

There are many important design features in a VIM production furnace. Crucible geometry, furnace frequency and power application contribute to effective refining without lining erosion. Appropriate vacuum pumping capacity and effective, maintainable seals are required to obtain and maintain proper vacuum levels throughout the process. In-process melt addition capability and monitoring of vacuum levels and melt temperatures are also critical to process control. Smooth controlled pouring processes are required to successfully transfer the alloy into the bar molds without introducing gas, defects or inclusions.

Advanced lining and tundish technology is also required to minimize reactivity and impurities from the ceramic materials. Cannon-Muskegon utilizes a high bond-strength, high purity $MgO\text{-}Al_2O_3$ spinel rammed lining, with optimized lining installation, fritting, alloy sequencing and furnace parameters to prevent lining erosion. A multi-compartment tundish is also utilized to control flow and allow flotation and filtration of any impurities prior to pouring.

Key melt practices for high quality VIM alloy include proper sequencing of the base charge and the addition of alloying elements. This allows the primary purification during the carbon boil with optimized parameters including time, temperature, stirring and chamber pressure. Subsequently, the reactive elements (Al, Ti, Hf, Zr) are added with appropriate solutioning and homogenization holds. Tight chemistry control with proper aims are critical for both optimum properties and castability and consistency heat to heat. Key melt processing parameters include good vacuum control and monitoring, slow heat up to close any lining cracks, detailed procedures to ensure product consistency and consistent, controlled pour rate. The practices of hot topping versus backfill and filtration methods can also have a key impact on product quality. Filtration improves alloy quality when implemented correctly and reduces turbulence in the pour stream from the tundish. At the same time, filtration adds potential risk due to breakage, freeze off and leakage and can affect oxygen content and chromium loss during pour for certain alloys with high Ti, Ta and/or Hf content.

Raw material trace/tramp element requirements should be established commensurate with the casting application. The highest temperature/stress components, including single crystal castings, demand premium quality raw materials. The quality of raw materials in terms of detrimental tramp elements are affected by both the ore deposit and refining processes used. In general, electrolytic, EB processes produce the highest quality raw materials. It is a fact that all “virgin” materials are not created equal. Examples of this include EBCb, NiCb and FeCb, and electrolytic versus aluminothermic chromium. As shown in Table V, NiCb and FeCb have significantly higher gas content compared to EB Cb, and FeCb has much higher S content. Similarly, aluminothermic chromium contains aluminum oxide, which essentially introduces dross inclusions into the alloy. For these reasons, even though they are considered “virgin” raw materials, FeCb and aluminothermic Cr are not used in any CM vacuum alloys. Similarly, careful evaluation and control of all charge materials has a significant impact on subsequent alloy quality.

Table V. Comparison of Typical Impurities (ppm) in Cb Materials

| Impurity | EB Cb | NiCb | FeCb |
|---|---|---|---|
| [N] | 25 | 50 | 60 |
| [O] | 50 | 500 | 500 |
| S | <5 | 20 | 40 |
| Si | 35 | 800 | 800 |

Blend heats are an effective way to utilize casting foundry scraps and reduce alloy costs. However, casting foundry materials and processes can affect the revert cleanliness. Si, Zr and S are often picked up during the remelting/casting process and are dependant upon the purity and reactivity of the foundry ceramics, the metal and mold temperatures and the use of exothermic hot top materials and/or exposure of the hot mold to atmosphere. For the most critical application, such as SX alloys, it is recommended to premelt the foundry revert for definitive chemistry on key elements (Si, Zr, S, P, N, O and Pt).

The final opportunity to ensure a high quality alloy product is during finishing and inspection. This step involves detection of surface imperfections, complete chemical analysis with industry leading techniques, equipment and accuracy and provides data for continuous process improvement.

## Conclusions/Summary

Trace elements can have a significant impact (both detrimental and beneficial) on the performance of cast Ni-base superalloys. Control of critical elements is key to optimizing alloy castability and properties, and involves many aspects of alloy manufacturing, raw material selection and analytical chemistry capability. The success of advanced SX superalloys in aero and industrial gas turbine engines depends upon consistent, diligent measurement and control of critical elements throughout the alloy manufacturing process.

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