Investment Cast Cobalt Alloys

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Introduction

Cobalt-based alloys have been used in demanding applications for as long as investment casting has been available as an industrial process. From the introduction of “Stellite®” in the late 1920’s, to the dental alloy “Vitallium®” in the ‘30’s, the turbocharger alloys such as HS 31 and X-40 in the ‘40’s, through to today’s technology, cobalt alloys have contributed significantly to industrial products and processes.

Today, cast cobalt alloys play an important role in the performance of aero and land-based gas turbines. While vacuum cast nickel alloys predominate in the hot sections of modern aero turbine engines, cobalt alloys are routinely specified for particularly demanding applications such as fuel nozzles and vanes for industrial gas turbines. Investment cast Co-Cr-Mo alloys compete directly with titanium and cobalt forgings for medical prosthetic implant devices. The majority of investment castings made from the cobalt superalloys are cast in the open atmosphere as opposed to vacuum investment casting.

This paper examines the castability, casting quality, mechanical properties and applications of this important class of materials. Discussed in detail are production aspects and technical benefits of induction melted AOD refined continuous cast cobalt-based superalloy meltstock for investment casting with applications including gas turbine components, medical implant devices, glass fiber production and other heat, wear and corrosion resistant parts.
Experience Base

Since 1982, Cannon-Muskegon has produced in excess of 40 million pounds of AOD refined continuous cast cobalt-based alloys for the investment casting industry. Essentially all of the production of this alloy has been subsequently cast in air for critical end-use applications. Of the total, about 85% have been produced for medical implant use, 10% for high temperature components and the balance as wear and corrosion resistant castings.

Nominal Compositions

The compositions of representative AOD refined investment cast cobalt alloys are shown in Table 1. While the alloys shown offer a range of mechanical properties, all is similar in that they are based on the Co-Cr binary system. The alloys also have in common the presence of significant amounts of carbon. All of the alloys discussed here are strengthened to some extent by the presence of various carbides. These carbides are based on refractory elements such as tungsten and molybdenum, as well as on chromium. Nickel is included in many of the compositions for austenite stabilization. Reactive elements such as aluminum, titanium and zirconium are usually not included in these airmelt alloy compositions. The strength of these alloys are generally proportional to the carbon and refractory element (carbide forming) content and at low carbon contents, strengthening is provided by solid solution hardening. HS 25 is an example of a low carbon, high refractory element containing alloy strengthened by solid solution hardening. Haynes Ultimet® relies on the low stacking fault energy of the nickel and carbon stabilized cobalt FCC matrix phase to resist cavitation and sliding erosive wear.

AOD processing

The argon-oxygen-decarburization (AOD) process was developed by Union Carbide Corporation and Joslyn Stainless Steel in the late ‘60’s as a means of producing low carbon stainless steels using low cost, high carbon charge materials. Cannon-Muskegon installed the Union Carbide-Linde patented AOD process in 1981. The process was acquired in order to economically produce higher quality steel and stainless steel re-melt ingot than had been possible with simple air induction melting. AOD processing is particularly effective at lowering the levels of carbon, silicon, sulfur and dissolved gases. Once the benefits of AOD processing were realized for ferrous alloys at Cannon-Muskegon, practices were developed for nickel and cobalt alloys as well.

The AOD process consists of chemical oxidation, primarily of carbon, followed by reduction. During AOD processing, a mixture of oxygen and argon are injected near the bottom of a cylindrical converter. Nitrogen and other gases are used when appropriate.
The gas mixture is initially adjusted to be rich in oxygen (relative to the amount of argon) when carbon and silicon are being removed from the melt. As the carbon level decreases, the ratio of oxygen to argon is lowered which thermodynamically favors the further removal of carbon to low levels. Once the oxidation step is complete, aluminum and silicon are added as reductants to recover elements (primarily chromium) which become temporarily tied up as oxides during decarburization. The large volume of gas injected into the AOD vessel during processing and the evolution of carbon monoxide from the decarburization reaction provides an excellent purging action which removes unwanted gasses from the melt. These gases include oxygen, hydrogen, and nitrogen. Low gas contents are important in the foundry performance of casting alloys and result in lower levels of non-metallic inclusions and gas/shrink related porosity. A diagram of the Cannon-Muskegon AIM/AOD/CC process is shown as Figure 1.

When moderate to high carbon contents (relative to stainless steels) are desired, as is typical in cobalt alloys, AOD processing consists of modest oxidation and reduction steps combined with a pure argon stir or purge. Artificial slags rich in lime (CaO) other basic oxides are used to control sulfur to extremely low levels. Sulfur levels of 10 ppm or less are common and 2 ppm or less is achievable. Sulfur is detrimental in cast grades because it can contribute to hot tearing tendencies and also promotes undesirable wetting between the alloys and refractories during subsequent melting and casting.

Trace element control in cobalt alloys is accomplished through the refining action of the AOD as well as through careful raw material selection. Many of the trace elements, which are controlled to low levels in nickel-based superalloys, are also of concern in cobalt alloys. These elements include Pb, Sn, Sb, TI, Te, Zn, Bi, etc. In the AOD, elements with high vapor pressures at steel making temperatures are volatilized and effectively removed as a gas. The elements tin and antimony have relatively low vapor pressures and are kept low through careful control of revert, select and raw materials. Table #2 shows typical trace element concentrations in AOD refined cobalt master alloy heats.

Cobalt master alloys are often produced in controlled closed-loop reverting arrangements although nearly any combination of virgin, revert and select material sources can be accommodated. A typical charge might include 60% customer owned revert combined with 40% virgin cobalt, chromium, tungsten or molybdenum and nickel. Virgin/revert ratios are specified by individual foundries to manage revert pools effectively. While the optimum ratio would appear to be equal to the overall foundry casting yield, ratios are occasionally used to maximize economic gain in light of cobalt price volatility.

Secondly, machining chips are routinely found to contain iron-based contaminants, usually stainless steel, that cannot be effectively removed. For this reason, machining chips are often pre-melted to determine their exact composition before being incorporated into production heats. A third source of iron contamination (as well as other elements) is mixed casting revert. Approximately 2% of the foundry revert material received at Cannon-Muskegon is found to be mixed. The effect is most apparent with cobalt alloys with the lowest iron tolerances, sometimes as low as 0.4%. Some iron also comes into cobalt alloys from shot blast media and from iron-containing refractories.
In many cases, iron tends to be the single element that limits the use of cobalt-based foundry revert or select materials. Iron finds its way into these alloys by several routes.

First, raw cobalt may contain some iron depending on source. The best available high-grade cobalt contains less than 10 ppm iron whereas some alternate grades can have .01%-.30% Fe. Secondly, machining chips are routinely found to contain iron-based contaminants, usually stainless steel, that cannot be effectively removed. For this reason, machining chips are often pre-melted to determine their exact composition before being incorporated into production heats. A third source of iron contamination (as well as other elements) is mixed casting revert. Approximately 2% of the foundry revert material received at Cannon-Muskegon is found to be mixed. The effect is most apparent with cobalt alloys with the lowest iron tolerances, sometimes as low as 0.4%. Some iron also comes into cobalt alloys from shot blast media and from iron-containing refractories.

**Continuous Cast Ingot**

Cannon-Muskegon employs horizontal continuous casting (HCC) to produce metallurgically clean re-melt ingot. Following AOD refining, 5 ton cobalt heats are tapped into a bottom pour ladle for transfer to the continuous casting machine. The HCC caster consists of a refractory lined tundish and a two component horizontally arranged cylindrical permanent mold. The alloy forms an initial skin against a water-cooled beryllium-copper mold segment. Subsequent cooling is provided by a water-cooled graphite mold section. Casting proceeds by the incremental withdrawal of the product, accomplished under computer control by electric servomotors driving hydraulically clamped withdrawal rolls. This incremental withdrawal consists of a forward stroke followed by a brief pause, a short backstroke and another pause. The process repeats 60-130 times per minute and exit speeds of 70-140 inches per minute are common. Final centerline solidification occurs well outside the permanent mold. With appropriate controls over casting temperatures and speeds, a nearly sound ingot is produced. Some centerline shrink may be present in the ingot. The use of bottom pour ladles in conjunction with a deep, bottom-feeding tundish provides sufficient residence time for inclusion flotation and removal. Argon tap stream shrouding is used to protect the molten alloy as it enters the tundish. Extraneous refractory inclusions are avoided through the use of the permanent mold (as opposed to sand cast ingots).

After continuous casting, the strand is hot sheared to the increment lengths ordered by the customer. Cobalt alloys are produced in nominal diameters of 2½", 3" and 4". Recently, 2" diameter capabilities have been added. A typical re-melt ingot measures 3"f x 18" weighing about 36 pounds. The increments are water quenched, shot blast with stainless steel shot, ink jet marked with an alloy and heat number, inspected and packed. The time required from casting to packaging is about 30 minutes. The total processing time including induction melting and AOD refining is about 6 hours.
Foundry Performance

The castability of all the airmelt cobalt alloys is considered good to excellent, especially compared with nickel alloys and stainless steels. The compositions are characterized by high carbon contents with appreciable silicon, both providing fluidity. Shown in Table 3 are average solidus, liquidus and melting range temperatures obtained by differential scanning calorimetry (DTA). This table shows that most of the commonly cast cobalt alloys have fairly narrow melting ranges indicating good fluidity. The alloys possess good hot strength (which is often the basis for their use in the first place) and are quite resistant to hot tearing. Some cracking may be experienced in the high carbon wear resistant alloys when rough treatment or severely restrictive gating arrangements are encountered. The nitrogen containing alloys such as F-75 and Ultimet are stable in terms of nitrogen pick-up or loss.

Foundry deoxidation of AOD refined cobalt alloys is usually neither required nor recommended. With ingot oxygen contents typically less than 100 ppm, deoxidation additions rarely result in oxygen decreases and may actually increase the oxygen content of castings. The alloys are quite able to hold nitrogen in solution. The solubility of nitrogen in cobalt alloys is a function of alloy content, especially chromium. The upper limit of nitrogen solubility in F-75 (29% Cr) is about 0.22% [N]. Carbon appears to lower nitrogen solubility. While high carbon contents combined with moderate chromium levels can make some alloys prone to soluble gas defects, AOD refining effectively lowers the nitrogen below the level where it is troublesome.

Argon melt protection is recommended and often employed when making critical cobalt castings. The use of argon is almost always beneficial, regardless of the alloy being cast. In the case of cobalt alloys, the higher cost of the alloys and the critical nature of the component usually justify the use of argon. Several commercially available protection schemes are available using gaseous or liquid argon. Additionally, many foundries have engineered their own systems for argon delivery to the furnace. In any case, argon protection systems should be checked periodically for performance. Portable, hand held oxygen meters are available and easily used. Oxygen contents above the melt should be less than 1%.

In any airmelt operation, mechanical removal of the small amount of dross present on the melt surface before casting is crucial. While AOD refined ingot melts often appear clean enough to omit any attempt at slag removal; this step should not be skipped. However, in all cases, furnace power should be turned off before tap to allow dross to rise to the melt surface. This dross should be carefully removed with a slag stick. The use of argon melt protection will reduce the amount of dross formation but will not eliminate the need to remove this small amount of dross.
Many cobalt alloys respond well to grain size control through shell inoculation. Incorporation of 2-6% cobalt aluminate, cobalt metasilicate or cobalt oxide yields substantial grain size reductions near casting surfaces with careful control of casting temperatures. The amount of grain size reduction is proportional to the amount of inoculant used. Inoculants also shorten slurry life so the amount used in practice is a compromise.

The use of filters for casting airmelt cobalt alloys is a point of debate. While the best practice will always be to start with clean alloy and keep it clean, filters can be useful. Filters can reduce fill rates, acting as chokes to reduce turbulence and entrapped air if placed in the ingates. Acting as a restriction however, the use of filters may require additional superheat to maintain the ability to feed thin sections or long distances. In any case, filters should be viewed as the "last line of defense" against non-metallic inclusions rather than the primary means by which clean casting are produced.

Casting revert generated from AOD refined master alloy can be recycled in-house within reason and where permitted by specification. Silicon and manganese levels should be monitored and corrected if needed.

Casting Quality

Freedom from non-metallic inclusions is a critical aspect of casting quality. With appropriate foundry practices, cobalt alloys can be cast in air to be very clean. Oxygen contents of 100 ppm or less in AOD refined meltstock contribute to this cleanliness. One of the more demanding applications in terms of non-metallic defects is the use of highly polished medical implants. Wear surfaces are often polished to a .03-.05mm finish, inspected visually at 10-20x and must be inclusion free. Inclusions on the order of 30 microns diameter are not acceptable. Using effective argon melt protection and good practices in general, the oxygen increase from ingot to casting can be 20 ppm or less.

Thin sections and fine detail are readily filled with all of the commonly cast cobalt alloys. The fluidity of the alloys is a function of carbon and silicon contents as well as superheat. With melting ranges somewhat lower than the stainless steels, pouring temperatures rarely exceed 3,000°F. Using a fixed superheat over liquidus approach (+250°F, for example) suggests that pouring temperatures of 2,850°F or less are reasonable.

Applications

Aero and Land Turbines

Cobalt alloys are well suited to high temperature creep and fatigue resistant non-rotating applications where stress levels are lower than for rotating components. For this reason, turbine vanes and other static components are frequently designed in cobalt alloys.

A somewhat lower coefficient of thermal expansion and better thermal conductivity than the nickel alloys make cobalt alloys good candidates for applications where thermal fatigue is a critical design issue.
As in the case of aero-turbines, cobalt alloys are employed in non-rotating roles. Due to long service life requirements, land based casting specifications are becoming progressively more stringent (more rigorous than for similar aero counterparts in some cases). For example, one aircraft vane specification allows a maximum size of .035" whereas land based shroud casting specification has .015" maximum defect size limitation.

**Implants**

The use of artificial orthopedic implants has been practiced for many years. Advances in medical technology have allowed the use of quality-of-life improving implants for an ever-increasing range of patients. Two materials have dominated in terms of structural implants: titanium and cobalt alloys. While titanium offers an advantage in weight, Co-Cr-Mo is unparalleled in its acceptance and widespread use.

In the late 1920's, Austenal Laboratories searched for an alternative to gold for fabricating denture supports. That alternative was found in a derivative of Haynes Stellite, which was subsequently known as Vitallium® and used from the '30's. Today, this alloy is used for orthopedic implants, most notably as artificial hips and knees. The alloy is generically referred to by its ASTM designation F-75 and contains 29% chromium and 6% molybdenum (also by ISO 5832 part 4). While the ASTM specification limits carbon to 0.35%, implant manufacturers have opted for lower levels of carbon and an intentional addition of nitrogen.

The addition of nitrogen as an intentional alloying element has allowed Co-Cr-Mo to achieve high levels of strength with good ductility and without sacrificing corrosion resistance and biocompatibility. This addition is easily and economically accomplished in the AOD through the direct injection of nitrogen gas. In APM or VIM melting, nitrogen additions are made using nitrogenated chromium. Iron, nickel and trace elements are kept to low levels through AOD refining and through careful selection of raw materials.

Highly polished components include femoral stems for replacement hips and knee condyles. Other cobalt medical castings include acetabular cups and tibial trays. In all cases, but especially in hip components, casting quality is imperative, as parts are heavily loaded and subject to fatigue. Castings are given multi-step heat treatments including solution annealing, hot isostatic pressing and sintering of bone-ingrowth materials. Final polishing is one of the last operations to precede inspection. The rejection of a casting at this late stage is very expensive. AOD refined alloy is relied upon to produce sound, inclusion free medical castings.

**Glass Fiber**

One of the methods for making glass fiber for residential and commercial thermal building insulation is by a melt spinning process in which molten glasses based on oxides of silicon, sodium, potassium and others are centrifugally forced through the perforated rim of a rapidly rotating disk. The process takes place near the melting point of the glass (typically 1,700-2,100°F). External heating sources are used to maintain process temperatures.
Solidification of the glass occurs within the wall of the “spinner”.

As such, the small diameter holes, which directly form the outside diameter of the glass fiber, are subject to the combined deteriorating effects of chemical corrosion, abrasion and oxidation. Product performance of thermalinsulation is directly related to fiber diameter and the rate of growth of the fiber-forming holes governs the useful life of the spinner. Creep deformation plays a secondary role in determining the useful life of a spinner.

The composition of the alloys used for glass fiber spinners varies by manufacturer. Most manufacturers guard the composition of their alloys as trade secrets. These alloys tend to be based on industry standard materials such as X-40 with modifications appropriate to the application. The compositions of the glasses used may be oxidizing or reducing and dictate the alloys which must be used to produce fibers. In the case of higher melting point glasses, chemical corrosion is the primary cause of wear. For lower temperature glass, erosion plays a stronger role in hole degradation. Because of the high temperatures employed, alloy oxidation is always a factor in spinner life. The corrosive effect of the glass on the cobalt alloy spinners is related to the general composition of the glass as well as the amount of impurities in the glass and to operating temperature. Impurities can result from efforts to recycle post-consumer glass products such as beverage and food containers.

Spinner diameters can be in the range of 12-25" with castings weighing between 5 and 15 pounds. Wall thickness dimensions are on the order of 0.10-0.15". Between 10,000 and 40,000 closely spaced, small diameter holes are laser drilled in the rim of each spinner. Fiberglass spinners are remelted as foundry revert once their useful life has been exhausted. AOD refined master heats are made using 80-100% expired spinners and revert. The refining action of the AOD can limit impurities contained in the glass. Only an insignificant amount of alloy is actually lost through oxidation and corrosion in use.

**Wear Resistant Applications**

The history of the use of cobalt alloys for wear resistant applications begins with the 1907 patents by Elwood Haynes for his “Stellite” alloys based on cobalt and chromium. Since that time, cobalt alloys have served in extremely harsh conditions as castings, wrought fabrications and as hardfacing deposits applied as welded or flame sprayed coatings. Carbon (and occasionally boron) is used in conjunction with chromium and one or more refractory elements to produce a high hardness, carbide rich material. Hardness values ranging from Rc 30-70 are obtainable.

The melting range for these high carbon alloys is a typically lower and narrower than of the high temperature and medical alloy. As such, the wear resistant alloys possess very good casting fluidity.
Investment Cast Cobalt Alloys

Stellite® 6 is the most common cobalt wear resistant alloy. It's ability to withstand sliding and abrasive wear comes from the high volume fraction of carbide formed form the alloy's 1.2% carbon, 5% tungsten and 30% chromium. The alloy has a Rockwell hardness of about 43 Rc but very limited tensile ductility.

Other alloys in the family include Co #3, #12, #19, Star J and 98M2. Alloys such as these approximate cast equivalents of cemented carbides produced by powder metallurgy methods.

An alternative approach to wear resistance is offered by Haynes Ultimet®. This alloy contains rather low carbon content (and thus a low volume fraction of carbide). By careful control of alloy balance to achieve a low stacking fault FCC matrix and subsequently high work hardening rate, Ultimet achieves excellent wear resistance combined with a high degree of corrosion resistance. This combination of resistance to environmental degradation is unique. The alloy also shows good tensile ductility and weldability due to lower levels of carbon. The alloy features an intentional nitrogen content and good foundry performance.

Conclusion

Cobalt-based casting alloys continue to be an important part of industrial processes and products. While some cobalt alloys contain reactive elements and must be vacuum cast, many of the most industrially useful alloys are cast in airmelt foundries. AOD refined continuous cast remelt ingot provides metallurgical cleanliness, low gas content and controlled chemistry for the production of critical investment cast components. The castability of these alloys allows the production of complex highly detailed castings. The productivity of an airmelt operation can be an asset to foundries currently pouring cobalt alloy in vacuum furnaces.

References

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3. The Superalloys, Sims and Hagel, John Wiley & Sons, New York, 1972

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Table 3- Cobalt alloy melting data by DTA

Figure 3  A diagram of the Cannon-Muskegon AIM/AOD/CC Process