Study on Defect Reduction in Casting of Ni-Cr alloy (UNS N06003)

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Abstract. In modern times, selection criteria of materials are solely based on its utilization. The characteristics of materials like high temperature sustainability with regard to its strength and corrosion resistance is the primary requirement to satisfy its operations. Industries categorised in sectors like energy, manufacturing, electronics etc. greatly rely on input materials and their purity decides their performance. Amongst many developed alloys, nickel-based alloys find their position in applications having temperatures from cryo to nuclear ranges. One of such unique materials, being used from minute components of semiconductor industry to huge components of marine industry is UNS N06003. It is basically Ni-Cr based alloy having greater than three-fourth fraction of nickel. For major applications wrought material is widely used, but cast material marks their positions in selected applications. This paper deals with casting of UNS N06003 and improving its quality. The reasons associated with cast defects and drawbacks of defects in terms of performance have been discussed. To minimize casting defects and produce a sound casting, this research adopts a novel approach of removal of unwanted gaseous elements. In degassing stage, molten metal is introduced with the combination of calcium-based fluxes which mainly remove the entrapped gases and lighter impurities in the form of slag. It has been found that the addition of quicklime (CaO) in combination with calcium carbide (CaC₂) resulted in reduction of gaseous elements like nitrogen, phosphorus and sulphur. Up to 33% reduction of gaseous elements has been detected.

1. Introduction

Nickel based alloys were developed and introduced to industry for providing magnificent corrosion resistance and strength even under high temperatures or adverse environments. UNS N06003 is one of such alloys is potentially very strong candidate for industrial applications in the field of energy, manufacturing, marine, chemicals/petrochemicals, and electronics[1, 2, 3]. It is the combination of hard and ductile nickel, and lustrous and non-oxidizing chromium[4]. Nickel-chromium based UNS N06003 is an alloy with advantage of solid solution strengthening mechanism and precipitation hardening mechanism. This is the primary cause for its high temperature resistance[5, 6]. This alloy is also known as ASTM 80Ni-20Cr, EN NiCr8020 and NICHOME V[7]. It forms a preventive layer of chromium oxides on its surface in severe conditions[8, 9]. Components like casings, discs, turbine blades, stator vane segments, vanes, exhaust systems shafts, blades etc. are used in hot gas path. These components are designed using UNS N06003 to achieve serviceability with high temperature strength[5, 6]. Area of applications of UNS N06003 include...
marine structures, land-based utilities in power generation, vehicular components[6], heating sources in electronic devices[10, 11, 12], aircraft turbine engine parts (equiaxed or single crystal) etc. These are designed based on applicability of desired creep resistance. Ingots used to make wrought turbine disks can successfully be made by casting[13, 14]. For these applications, various exposure conditions exist in the form of mixture of complex chemical compounds. These chemical compounds impact the base material and degrade it adversely. Such degradations also badly influence the lifecycle of material. This demands the necessity of defect-free material production and assembly stage. If defects or entrapped residual gases pre-exist, chances of corrosion-based degradation accelerate. Galvanic corrosion happens in the region of complex phases, resulting in microstructural inhomogeneities at microstructural level. These inhomogeneities also translate to generation of localized stresses[15]. The inhomogeneities are minimized with vacuum induction melting technology over the conventional practice. Reduction of the tensile strength occurs due to the such agglomerated elements on grain boundaries at sub-micron levels[16]. In practical conditions of casting, proficiency of foundry man, quality of raw material and process parameters play vital role to determine quality[17]. Many studies use crucibles having MgO-Al₂O₃ lining, but it forms MgS. Such phenomena shorten the lifespan of lining. Electric arc furnace and Vacuum induction melting are used as alternative methods for casting alloys[18].

In the current study, carbon boil reaction is applicable to enhance melt deoxidation[19]. In real life applications, UNS N06003 shows capabilities of performing at high temperatures (higher than 0.5 times of its melting point) and gives uninterrupted performance. Such capabilities are defined by crystal structure of alloy. For UNS N06003, the equiaxed microstructures are capable of functioning up to 900-950°C whereas single crystal structures can function up to 1100°C[13, 20]. It is essential to remove deleterious phases causing poor mechanical properties, that are formed as a result segregation under non-equilibrium conditions [14, 18]. This research involves experiments in an economical manner for producing cast components from Ni-Cr based alloy.

2. Casting of UNS N06003

Cast alloys are preferred over wrought alloys from hot workability point of view. Major preference of cast alloy as controlling the composition is easier by casting route. Such tailored composition maylead to higher applicability of material owing to its high temperature strength. Cast microstructures generate coarser grains over other manufacturing methods. Hence, even the development of new alternative of UNS N06003 may take a decade or two[21]. Vacuum induction melting is introduced to industries since 1950s[20]. In this study, casting of UNS N06003 has been performed with induction melting furnace. This approach attempts the elimination of impurities and entrapped gases within molten metal[13].

Sound castings are dependent upon the considerations such as neglection of steep temperature or stress variations[22], controlled quality of surface [23], appropriate design of air vent, flow stability[24], proper modelling of runner and riser [25] etc. Poor degassing of molten metal leads to residual impurities, mainly entrapment of gaseous form of elements like phosphorous, sulphur, hydrogen, oxygen and nitrogen. These residual elements are chemically unstable by nature and these ultimately form some compounds to gaining stable structure such as nitrides, phosphides, sulphiodes, carbides etc. The formation of compounds is followed by solidification stage in casting. During solidification, such compounds reside on the grain boundaries due to their limited solubility in matrix[26]. Proper selection and addition of charging materials can resolve such issues [17, 27].

Three dimensional clusters of defects are formed by accumulation and association of tiny individual defects. These defects are created as isolated entities and stay in agglomerated or isolated form based on either operating condition. The presence of non-metallic inclusions, inconsistency in geometry[26], blow holes [28, 29], deviations generated within crystallographic orientations[30], pores [31]etc. greatly cause defects. Failure of casting can be eliminated by taking precautions which minimize such
defects. like manipulation of elemental composition, process parameters and geometry of casting. It’s difficult to exercise control geometry as is based on its functionality. Thus, the former two parameters need consideration for the generation of sound casting [32].

3. Degassing

Appropriate melting practices must be followed to eliminate elements like sulphur, phosphorus, silicon, oxygen and nitrogen which cause deleterious impacts [33, 18]. Degassing of molten alloys in is a crucial required for minimizing the generation of defects caused due to the presence of gaseous elements. Killing process is performed in the steel-making process for the removal of H, N, O, P and S from the alloy melt [34]. Need of similar mechanism is necessary for UNS N06003. Complex role of carbides is observed in superalloys. Carbon is beneficial upto a certain defined range as it provides rupture strength at elevated temperature conditions. If the fraction of carbon elevates beyond a defined limit, it becomes a reason for crack formation due to transformation in nature from ductile to brittle. By removal of such reactive elements, ductility improvement and chemical stability can be achieved. Major types of carbides that are found in superalloys are MC, M6C and M23C6. Cr7C3 is also observed in minor amount. This formation of carbides is beneficial from the perspective of grain boundary precipitation [35, 36, 37].

Mechanical properties such as ductility, toughness, resistance to wear/erosion and friction coefficient are enhanced by optimal addition of phosphorous [38]. Ideally in an alloy, phosphorus content should be below 0.005 wt.% for imparting corrosion/erosion resistance. For many alloys, to maintain their toughness, maximum allowable phosphorous content is 0.020 wt.%. If it exceeds the mentioned amount, intergranular corrosion can be seen which makes it non-useable in applications requiring low temperature or high strength [39, 40].

Considering the metallurgy of alloys, if the content of sulphur does not fall in the range of 0.013-0.078 wt.%, reduction in the solidification temperature can occur [41]. Sulphur causes higher cracking than phosphorus. Increase in brittleness and red-shortness under high temperature conditions is also noticed. Thus, desulphurisation during manufacturing is the need for prolonged life of
components[42]. But when the components have high pressure and low temperature application, the content of sulphur should be maintained in the range of 0.0005-0.001 wt.% [43].

Nitrogen is another gaseous element which impacts the properties of alloys. In low temperature conditions, higher content of nitrogen makes the material prone to pitting as well as intergranular corrosion phenomena as the material loses toughness up to some extent. It may also cause health hazards as it causes removal of nickel[44, 45]. During solidification of cast alloys, nitrogen causes nitrogen bubble porosity[46]. Also, dislocated nitrogen atoms interact with the atomic lattices of other major constituting elements creating strain-age embrittlement. This causes diffusion of nitrogen to multiple sites, thereby raising the activation energies and formation of solidification cracks. For materials which are going to be welded, nitrogen content should be less than 0.045wt.% to avoid weld porosities[47].

Researches have shown that better methods of ventilation, control over the curing time or addition of optimum content of resin/clay in sand have been successful methods for degasification [48]. Also, for methods such as inert gas fluxing, oxidation-reduction reactions, zinc flaring, vacuum degassing, a solid degassing flux can be used for degassing during casting of alloys. In molten alloys at high temperatures, the addition of solid degassing fluxes is widely exercised in the foundries. It is also a cost-effective way. Limestone (CaCO$_3$), dolomite ((Ca, Mg) CO$_3$), calcium carbide (CaC$_2$), fluorspar (CaF$_2$) and sodium carbonate (Na$_2$CO$_3$) are commonly used fluxes for removal of N, P and S during casting of alloys. Limestone liberates CO$_2$ gas when it is added during the casting of nickel-based alloys and elimination of carbon occurs [49, 50, 51]. Thus, by using fluxes based on calcium and/or carbon, such unwanted elements along with slag can be done. The current study investigates the advantages of the same.

4. Materials and Methods

For casting of UNS N06003, sand casting method has been used. A sand standard American Foundry Society has been followed throughout the entire process and sand of size ‘48’ number was used. Mould has been prepared with mixture of silica sand and silica binder. Mixture of fresh and reclaimed sand has been used in the ratio of 40:60. Environment friendly binder was employed for binding the mould, which burns off during pouring stage and does not produce any noxious gases. Carbon dioxide gas was blown over mould cavity for hardening. Proper ramming of sand in mould box was ensured, which avoids inappropriate densification of particles. Probability of happening a damage is high if temperature gradient is introduced to mould in pouring stage. Hence as a precaution, defined range of compaction was applied to the mould sand. Ladle and mould-box were subjected to flame heating before introducing to molten metal to avoid steep temperature difference. Once the temperature of 1550ºC was achieved, melt refining and flux treatment was performed. Flux mixture of CaO and CaC$_2$ in equal proportion was added to the molten metal. Properly lined ladle was used to avoid sand erosion and moisture entrainment.

From the large cast component of UNS N06003 material, to be used for marine industry, three small samples of different castings were been taken for this study. During casting of the components, mixture of powders of preheated quicklime (CaO) and calcium carbide (CaC$_2$) was added to the molten alloy as flux material. Considering the volume of casting, flux mixture was added in ratio of around 10kg/ton. Commonly observed composition of the Ni-Cr alloy (UNS N06003) is as shown in table 1.

| Table 1. Percentage of elements in UNS N06003[7]. |
|---------------------|------|------|------|------|------|------|------|------|------|
| Element       | Ni   | Cr   | Mn   | Si   | Cu   | Al   | P    | S    | C    |
| Wt.%          | Bal. | 19.0 | 1.0  | 0.5  | 0.3  | 0.02 | 0.015| 0.15 | 0.15 |
| (~75%)        | (max.) | (max.) | (max.) | (max.) | (max.) | (max.) | (max.) | (max.) | (max.) |
All the samples had cylindrical geometry and dimensions in D × H are approximately 35mm × 25mm. The image of one of the samples is as shown in the Figure 2.

![Figure 2. Image of one of the samples in top-view and side-view.](image)

For measuring the compositional details of the samples, optical emission spectroscopy technique was used. The advantage of using this technique is that it requires minimal sample preparation but the results given are accurate with precision up to 0.0001 wt.%. This technique employs a sparking phenomenon on the application of electrical charge on the sample. As a result, small amount of material is vaporized and composition is known[52]. An optical emission spectrometer (Make: GNR, Model: S5 SOLARIS CCD Plus) was used for this testing.

5. Results and Discussions

The composition of samples was tested for the samples casted without addition of flux and after the addition of flux. It can be clearly observed that percentage of C, P, S and N has lessened. The results indicate a strong possibility of reduction of porosities and cracks in the produced casting. Also, the effectiveness of produced casting is enhanced by proper mixing of flux with the molten alloy. Degasification is thus achieved within a short span of time with higher reaction rate.

| Sample | State | Elements (in wt.%) |
|--------|-------|--------------------|
|        |       | C  | P     | S  | N   |
| S1     | Initial| 0.230 | 0.012 | 0.023 | 0.034 |
|        | Final  | 0.223 | 0.010 | 0.021 | 0.033 |
| S2     | Initial| 0.160 | 0.014 | 0.025 | 0.037 |
|        | Final  | 0.150 | 0.011 | 0.022 | 0.034 |
| S3     | Initial| 0.110 | 0.013 | 0.016 | 0.031 |
|        | Final  | 0.017 | 0.005 | 0.010 | 0.030 |
| Average% Reduction | 31.28 | 33.21 | 19.40 | 4.76 |
Table 2 shows the values of elements before and after degassing treatments for samples. On degasification, the average content of C, P, S and N reduces by 31.28%, 33.21%, 19.40% and 4.76% respectively. The individual percentage reduction of samples has been presented in Figure 3. This degassing technique, by decreasing the proportion of C, P, S and N also diminishes the possibility of creating a porosity. The microstructure of the cast alloy shows nickel-based solid solution of Cr and Fe in Ni matrix having austenitic structure.

Carbon, which was initially appearing in higher amount within the alloy appears under the controllable limits by addition of fluxes. This carbon is seen in the form of carbides along the inter-dendritic spacing. The microstructure also shows inter-dendritic porosity.

In any casting process, proportion of minor elements is difficult to be controlled. Shrinkage-based pores are found near the solidified regions whereas gas-based pores are of distributed nature found throughout the cast material. This may also pose variations of compositions up to 10% within the same casting. Such occurrences cause uncontrolled diffusion and affects the hermiticity of castings[53, 54]. The percentage decrease of gaseous elements indicate that the adopted technique has great influence on the quality of casting.

Holappa et al. [55]and Sanyal et al. [56]had also performed similar study and found that usage of using lime with calcium carbide affected the final composition of cast alloy. Si and Al as minor elements.
alloying elements in UNS N06003 and may be externally added as degassing agents[57]. By using calcium-based fluxes, reduction metallic-degassing materials is also possible. Minor amount of Al can provide better results if used with calcium-based fluxes[20, 51].

6. Conclusions and Prospects

Analysis of the data obtained from optical emission spectroscopy revealed that the importance of addition of fluxes play a pivotal role in the casting of UNS N06003. The percentage reduction of gaseous impurities was found up to 61.53%. Carbon, which is present in higher amount than allowable limit has also reduced up to 84.54% and its content can be observed adhering to ideal chemical composition of alloy. This study asserts that the addition of appropriate fluxes eliminates the impurities/gaseous elements and consequently produces sound castings. This technique attractively upgrades the quality of cast UNS N06003 through induction melting system. In the absence of vacuum technology, better quality castings, devoid of Nitrogen, phosphorous, sulphur and carbon are achieved by degassing. This also reduces the possibility of crack formation, hot shortness, cold shortness and strain-age embrittlement. This method establishes an inexpensive way to fabricate good quality nickel based solid solution strengthened alloys.

This study uses only few samples for research on degasification using CaO with CaC\textsubscript{2} casting. It can be further extended for more number of samples varying the proportion of mixture of fluxes and changing the process parameters of casting to understand the respective behaviours. A development of a permanent degassing system can also be explored. Effects of different fluxes on casting of UNS N06003 require further investigations.

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