ALLIED METAL
COMPANY
Aluminum Alloys ■ Zinc Alloys ■ Metal Trading

TECHNICAL PAPER

(Sludge, Hydrogen Adsorption, Oxides and Fluxing)

SLUDGE

1 x FE + 2 x Mn + 3 x Cr = sludge
Typical sludge from an A380.1 heat: Fe (.97), Mn (.24), Cr (.08)
(.97 + .48 + .24) = 1.69 sludge

The causes of High values of sludge

Time and Temperature. One of the primary factors contributing to the increase of sludge for die casters is the change in temperature at holding pots or charge furnaces. When “cold” metal in introduced into molten, sludge elements immediately have the propensity to “fall out” of solution. Maintaining consistent temperature to keep the alloy composition in solution is extremely important. Periodic removal of sludge from the bottom of charge pots is recommended to keep from building up. Another factor that increases the likelihood of high sludge comes from remelting gates and runners and cold ingot into the holding furnaces at the die cast machine. The best melting practices would utilize central melt furnaces with transfer of molten to the die casting station.

The effects of high sludge values on castings

Negative impact is the production of “hard spots”, thus effecting secondary machining operations.

How can sludge values be controlled?

- At the order specification level – Common sludge level to the smelter producer specification is 1.80% max., although some production heats run as low as 1.50 – 1.70
- At the furnace - Recommended procedures?
    - Control Temperature to keep sludge elements in solution
    - Skim out sludge build up in pots routinely
    - Use a central melt furnace for charging scrap and ingot and transfer molten metal to die casting stations rather than remelting cold ingot or gates and runners.

Melting and Metal Treatment

Aluminum and aluminum alloys can be melted in a variety of ways. Coreless and channel induction furnaces, crucible and open-hearth reverberatory furnaces fired by natural gas or fuel oil, and electric resistance and electric radiation furnaces are all in routine use. The nature of the furnace charge is as varied and important as the choice of furnace type for metal casting operations. The furnace charge may range from pre-alloyed ingot of high quality to charges made up exclusively from low-grade scrap. Even under optimum melting and melt-holding conditions, molten aluminum is susceptible to three types of degradation:

- With time at temperature, adsorption of hydrogen results in increased dissolved hydrogen content up to an equilibrium value for the specific composition and temperature.
- With time at temperature, oxidation of the melt occurs; in alloys containing magnesium, oxidation losses and the formation of complex oxides may not be self-limiting.

Transient elements characterized by low vapor pressure and high reactivity are reduced as a function of time at temperature; magnesium, sodium, calcium, and strontium, upon which mechanical properties directly or indirectly rely, are examples of elements that display transient characteristics. Turbulence or agitation of the melt and increased holding temperature significantly increase the rate of hydrogen solution, oxidation, and transient element loss. The mechanical properties of aluminum alloys depend on casting soundness, which is strongly influenced by hydrogen porosity and entrained nonmetallic inclusions.

Hydrogen influence on aluminum

Aluminum alloys are very susceptible to hydrogen absorption in the molten state. Hydrogen is the only gas that is appreciably soluble in aluminum and its alloys. Its solubility varies directly with temperature and the square root of pressure. During the cooling and solidification of molten aluminum, dissolved hydrogen in excess of the extremely low solid solubility may precipitate in molecular form, resulting in the formation of primary and/or secondary voids. Because of the affinity of the metal for oxygen, the principal source of hydrogen absorption comes from the reduction of water vapor from the atmosphere in contact with the melt:

$$3H_2O + 2AL \rightarrow 6H + Al_2O_3$$

Drossing fluxes are designed to promote separation of the aluminum oxide (Al2O3) dross layer that forms on the surface of the melt from the molten metal. Drosses and liquid or solid metal are usually intermingled in the dross layer. The drossing fluxes are designed to react with Al2O3 in the slag or dross layer and to recover metal. The fluorides wet and dissolve thin oxide films according to the general reaction.

Hydrogen Sources. There are numerous sources of hydrogen in aluminum. Moisture in the atmosphere dissociates at the molten metal surface, offering a concentration of atomic hydrogen capable of diffusing into the melt. The barrier oxide of aluminum resists hydrogen solution by this mechanism, but disturbances of the melt surface that break the oxide barrier result in rapid hydrogen dissolution. Alloying elements, especially magnesium, may also affect hydrogen absorption by forming oxidation reaction products that offer reduced resistance to the diffusion of hydrogen into the melt and by altering liquid solubility.

Hydrogen Porosity. Two types or forms of hydrogen porosity may occur in cast aluminum. Of greater importance is inter-dendritic porosity, which is encountered when hydrogen contents are sufficiently high that hydrogen rejected at the solidification front results in solution pressures above atmospheric. Secondary (micron-size) porosity occurs when dissolved hydrogen contents are low, and void formation is characteristically subcritical.

Finely distributed hydrogen porosity may not always be undesirable. Hydrogen precipitation may alter the form and distribution of shrinkage porosity in poorly fed parts or part sections. Shrinkage is generally more harmful to casting properties. In isolated cases, hydrogen may actually be intentionally introduced and controlled in specific concentrations compatible with the application requirements of the casting in order to promote superficial soundness.

Hydrogen in Solid Solution. The disposition of hydrogen in a solidified structure depends on the dissolved hydrogen level and the conditions under which solidification occurs. Because the presence of hydrogen porosity is a result of diffusion-controlled nucleation and growth, decreasing the hydrogen concentration and increasing the rate of solidification act to suppress void formation and growth. For this reason, castings made in expendable mold processes are more susceptible to hydrogen-related defects than parts produced by permanent mold or pressure die casting.

Hydrogen Removal. Dissolved hydrogen levels can be reduced by a number of methods, the most important of which is fluxing with dry, chemically pure nitrogen, argon, chlorine, and freon. Compounds such as hexachloroethane are in common use; these compounds dissociate at molten metal temperatures to provide the generation of fluxing gas.

Gas fluxing reduces the dissolved hydrogen content of molten aluminum by partial pressure diffusion. The use of reactive gases such as chlorine improves the rate of degassing by altering the gas/metal interface to improve diffusion kinetics. Holding the melt undisturbed for long periods of time at or near the liquidus also reduces hydrogen content to a level no greater than that defined for the alloy as the temperature-dependent liquid solubility.

Oxidation

Aluminum and its alloys oxidize readily in both the solid and molten states to provide a continuous self-limiting film. The rate of oxidation increases with temperature and is substantially greater in molten than in solid aluminum. The reactive elements contained in alloys such as magnesium, strontium, sodium, calcium, beryllium, and titanium are also factors in oxide formation. In both the molten and solid states, oxide formed at the surface offers benefits in self-limitation and as a barrier to hydrogen diffusion and solution. Induced turbulence, however, results in the entrainment of oxide particles, which resist gravity separation because their density is similar to that of molten aluminum.

Oxides are formed by direct oxidation in air, by reaction with water vapor, or by aluminothermic reaction with oxides of other metals, such as iron or silicon, contained in tools and refractories. Aluminum oxide is polymorphic, but at molten metal temperature the common forms of oxide encountered are crystalline and of a variety of types depending on exposure, temperature, and time. Some crystallographic oxide forms affect the appearance and coloration of castings, without other significant effects.

Oxide Separation and Removal. It is usually necessary to treat melts of aluminum and its alloys to remove suspended nonmetallics. This is normally accomplished by using either solid or chemically active gaseous fluxes containing chlorine, fluorine, chlorides, and/or fluorides. In each case, the objective is the dewetting of the oxide/melt interface to provide effective separation of oxides and other included matter and the flotation of these nonmetallics by attachment to either solid or gaseous elements or compounds introduced or formed during flux treatment.

Fluxes can also be used to minimize oxide formation. For this reason, melts containing magnesium are often protected by the use of salts that form liquid layers, most often of magnesium chloride, on the melt surface. These fluxes, termed covering fluxes, must be periodically removed and replaced. Carbon, graphite, and boron powder also effectively retard oxidation when applied to the melt surface.

The addition of a covering flux to the molten aluminum melt forms a barrier for gas absorption and oxidation of the metal. The flux also reacts with nonmetallics, residues from burned coating, and dirt in the scrap, collects such impurities and allows physical separation from the molten aluminum. The exact composition flux cover used varies from smelter to smelter, but is generally some combination containing one or more of the following: sodium chloride, potassium chloride, calcium chloride, calcium fluoride, aluminum fluoride, and cryolite. A common flux mixture is 47.5 percent NaCl, 47.5 percent KCl, and 5 percent cryolite. At the melting point of aluminum, the fluxes usually range from a tacky semisolid to a liquid depending on the composition of the mixture and the technique used to remove it from the melt.

The amount of flux used depends primarily on the material charged. Scrap containing a relatively large surface area creates large amounts of oxides and requires proportionally larger amounts of flux. The flux generally is added along with the aluminum scrap in amounts from less that 10 percent to 33 percent by weight of the material charged. This EPA Effluent Guideline for secondary aluminum smelting discusses reactive flux in some detail, primarily chlorine gas, which is mixed into the molten bed to remove unwanted magnesium, a process called “demagging”. The Effluent Guideline document explains “skimming” in which spent flux is removed from the surface of the molten metal using a metal scrapper, which is pulled over the surface of molten aluminum.

Effects of Inclusions. In addition to oxides, a number of additional compounds can be considered inclusions in cast structures. All aluminum contains aluminum carbide (Al4C3) formed during reduction. Borides may also be present. By agglomeration, borides can assume sufficient size to represent a significant factor in the metal structure, with especially adverse effects in machining.

Under all conditions, inclusions whether in film or particle form are damaging to mechanical properties. The gross effect of inclusions is to reduce the effective cross section of metal under load. The more devastating effect on properties is that of stress concentration when inclusions appear at or near the surface of parts or specimens. Fatigue performance is reduced under the latter condition by the notch effect. Ultimate and yield strengths are typically lower, and ductility may be substantially reduced when inclusions are present.

Hard particle inclusions are frequently found in association with film-type oxides. Borides, carbides, oxides, and nonmetallic particles in the melt are scavenged and then concentrated in localized regions within the cast structure.

References

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