From Light Metals 1987, R.D. Zabreznik, Editor =

HAZARDS IN ADDING SCRAP COPPER TO MOLTEN ALUMINUM

Warren S. Peterson

Consultant 2113 East 7th Avenue Spokane, WA 99203

Two case histories are presented in which a major explosion took place following addition of scrap copper to molten aluminum. In both cases, some of the copper had not dissolved and was removed from the furnace along with adhering molten aluminum and some "skim." In both cases, the explosion took place outside the melting furnace, and a worker nearby received fatal burns.

INTRODUCTION

The addition of scrap metals to molten aluminum can result in thermite reactions with serious consequences. This paper calls attention to the dangers of using finely divided scrap copper products such as wire and turnings as alloying agents for molten aluminum.

In present-day sheet and plate operations, master aluminum alloys containing high concentrations of elements such as copper and iron are usually used to prepare wrought aluminum alloys, and thermite reactions are avoided.

However, purchased scrap may be used and potentially dangerous pops and flashes can take place at the surface of the melt during charging if the scrap is contaminated with oxidized copper and rusty iron materials.

In some extrusion melt shops, and in most aluminum foundries, use of large amounts of scrap is a way of life. Scrap can be cheaper than prime metal, and aluminum casting alloys can tolerate high levels of impurity elements. Under these conditions, the opportunity to cut cost by using cheap forms of scrap metals as alloying agents is hard to resist.

ALUMINOTHERMIC REACTIONS

Thermite reactions using aluminum as the reducing agent have been known and used industrially since the turn of the century. In these reactions, aluminum reacts with a metal oxide to give a large amount of heat.

2 Al + 3 metal oxide ---> Al₂O₃ + 3 metal + heat

Table 1 gives thermal outputs of some of these reactions. Thermal outputs from the reaction of aluminum with cupric oxide (CuO) and ferric oxide (Fe $_{2}O_{3}$) are similar, 0.98 and 0.95 kilocalories per gram, respectively.

To put these numbers in perspective, these thermal outputs are about the same as the heat of explosion of trinitrotoluene (TNT) of 1.08 kilocalories per gram.

Table I. Thermal Output of Some Aluminothermic Reactions(1)

	Kcal/cm3
0.98 0.95 0.87 1.15 0.73 0.63	5.0 4.0 3.7 4.6 5.1 2.6
	0.95 0.87 1.15 0.73

Note--as comparison the energy release of common explosives is in the range of 0.75-1.3 Kcal/g. The heat of explosion of TNT is about 1.1 Kcal/gm.

EXPLOSIONS RESULTING FROM ADDITIONS OF SCRAP COPPER TO MOLTEN ALUMINUM

Two instances are described in which a major explosion took place following addition of scrap copper to molten aluminum.

-Light Metals

From *Light Metals 1987*, R.D. Zabreznik, Editor =

Case 1--Explosion in a Foundry

The explosion took place just outside the charging end of a melting furnace that was being dredged^{*} manually. Insoluble material which had sunk to the bottom of the furnace had been raked to the charging well end of the furnace.

Worker A was removing pieces of insoluble material from the furnace with a large skimming tool. The furnace was nearly full: the melt was alloy 319^{**} at a temperature of about 1400° F.

Worker A had just removed a piece of insoluble material from the furnace and was in the act of placing it in a sludge pan when the explosion took place. Worker B, standing 10 to 15 feet behind Worker A, reported that the chunk of insoluble material was about 6 to 8 inches in diameter, shiny, with "holes" in it.

The explosion was accompanied by a flash of bright white light, a very loud noise (bang rather than boom), a fire ball, flying particles, and dense white smoke. The explosion shook the building, and dust filled the area.

Worker A was engulfed by the explosion and reaction products. It is reported that virtually all of his outer clothing was burned off. He suffered burns (mostly third degree) over 90% of his body and died later.

Worker B was blown over by the explosion. His shirt was burned extensively. He received mostly first- and second-degree burns to his body.

Deposits of a reddish-white powder were found on surfaces of all equipment, walls, and floor in a wide area around where the explosion had occurred.

Figure 1 shows the relative location of equipment and workers in the area.

Energy dispersive X-Ray (EDX) analysis of samples of these deposits showed the two Major elements present to be copper and aluminum, where Major is above 10% of elements present.

The galvanized fire wall about 24 feet from the charging end of the furnace had particles of aluminum metal embedded in the wall surface as well as deposits of reddish-white powder. Particles of metal were also found on remnants of Worker A's faceshield and safety glasses. Again, the two Major elements in the metal particles were copper and aluminum. Copper content was far in excess of that in 319 alloy.

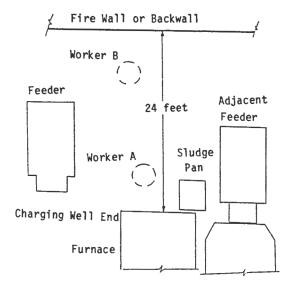


Figure 1 - Plan view showing the relative position of major pieces of equipment at the time of the explosion.

Cause of the Explosion

A number of possibilities were examined, but all confirmed information and evidence including laboratory analyses showed that the explosion was initiated by and resulted from a chemical reaction between finely divided copper oxide particles and molten aluminum.

It was determined that finely divided chopped copper wire bits about 0.025 inch in diameter and 0.25 inch long had been used regularly as one of the sources of copper for the 319 alloy.

Worker B reported that the additions of the chopped copper wire to the metal in the furnace were usually made by throwing the finely divided material from a container onto the surface of the molten metal with no attempt at that time to submerge it below the surface. He said the chopped copper wire "burned" and tended to ball up and turn black. In order to put the copper mass into solution, the use of a rake was required to break up the mass and stir the aluminum.

In this scenario, the lump of material on the skimmer was a mass of heavily oxidized, chopped copper wire bits which had balled up and sunk to the bottom of the furnace without dissolving. When this mass was removed from the melt in the furnace into the air, the copper oxide-aluminum reaction not only was initiated but allowed to continue because of the very high local temperatures developed by oxidation (burning) of thin films of freshly exposed molten aluminum.

The instantaneous release of large amounts of energy as heat caused expansion of the air in holes in the burning mass (and possible gaseous reaction products). The resulting explosion with the accompanying flash of light and sharp bang had the characteristics of a "chemical" explosion as opposed to the more common vapor explosion resulting from water trapped in molten aluminum.

Worker B said that Worker A seemed to be enveloped by the ball of flame. The heat generated

^{*} Dredging is a term used for the operation in which solid materials which have not dissolved in the molten aluminum alloy are removed from the furnace. The workman uses a rake to move the insoluble materials to the charging well end of the furnace where they are removed by a skimming tool and placed in a steel container.

^{**} Aluminum alloy 319 has a nominal composition of 5.5-6.5% Si, 3.0-4.0% Cu, .5% Mn, 1% Zn.

Light Metals

in the explosion and the impingement of the cloud of metal particles and reaction products caused instant burning and melting of his polyester clothing and burns to his body.

Case 2--Explosion in a Cast Shop

This explosion took place in the Cast Shop of a plant which makes aluminum sheet and plate. Scrap copper wire had been added to the molten aluminum in an effort to produce an aluminum-copper alloy.

Fewer details are available, but the nature and results of the explosion are similar to that described in Case 1.

The furnace was a large, fuel-fired melter of about 60,000 lbs. capacity. It was nearly full, and adjustments were being made to bring a 2000 series alloy to composition in respect to copper content. Temperature of the melt was reported to be normal for plant practice.

A large bundle of tangled scrap copper wire had been added to the melt.

When it was determined that solution of the bundle had not occurred, even though a considerable period of time had elapsed, a worker proceeded to remove it from the furnace.

The mass of copper wire and adhering molten aluminum and skim and dross were dragged from the furnace onto the floor in front of the furnace.

Reports are conflicting, but there was indication that some skim was burning. Also, it was said that the worker who had removed the mass appeared to poke the mass with a tool.

In any event, an extremely violent explosion took place accompanied by a blast of heat, a bright flash of light, and a loud sharp bang.

The workman who had removed the mass from the furnace was knocked down by the blast with all of his clothing afire. He died shortly after of burns over most of his body.

The group that investigated the explosion concluded that the explosion was caused by a copper oxide-aluminum thermite reaction. Further use of scrap copper wire as an alloying agent was banned.

DISCUSSION

Why do we not have more explosions when we add large pieces of copper and iron to make up alloy hardeners? Also, in charging purchased scrap, when in some instances, pieces of these metals may be present in various sizes and degrees of surface oxidation?

A look at the chemistry of the thermite reaction provides the answer to this question.

2 Al + 3 CuO ---> 3 Cu + Al₂O₃

Although the reaction between aluminum and copper oxide can start to take place at temperatures where aluminum is molten, the reaction will stop unless the temperature at the interface of the reaction rises high enough to melt the aluminum oxide formed at the contact areas between copper oxide and aluminum. The formation of solid aluminum oxide over the copper oxide surfaces and particles stops further reaction.

This information is the key to understanding how and when reactions and explosions can take place between oxidized copper pieces and molten aluminum.

Reaction takes place much more rapidly, of course, when the oxidized copper pieces are very small in size. However, even with finely divided oxidized copper bits, rapid reaction and explosion cannot take place when the oxidized copper pieces are submerged below the surface of the molten aluminum.

In this situation, although chemical reaction may be initiated, the reaction will immediately stop, because the excellent thermal conductivity of aluminum will prevent temperatures at point of contact from reaching the point where the formation of solid aluminum oxide layer no longer is a barrier to continued chemical reaction.

The times we do see evidence of continued thermite reaction between pieces of oxidized copper and iron and molten aluminum is when these pieces somehow become entangled with skim and dross on the surface of the melt. At these times, we can have pops and small explosions at the melt surface. Oxidation (burning) of the dross produces temperatures in excess of the melting point of alumina (2045°C).

CONCLUSION

Although explosions occur only rarely when elemental copper scrap is added to molten aluminum, this paper shows that violent death-dealing explosions can take place.

As stated in <u>Guidelines for Handling Molten</u> <u>Aluminum</u>,(2) "Light gauge copper scrap, when heavily oxidized, can be particularly dangerous because it is difficult to dissolve and may be dragged from the furnace when skimming; this may result in a thermite explosion outside the furnace."

All alloying materials should be clean and dry when added to the melt. If heavy sections of copper are added to molten aluminum, portions of the surfaces should be abraded to remove oxides and ensure rapid alloying with the aluminum.

The possibility of explosive thermite reactions and disastrous effect on personnel, equipment, and production puts the economic benefits of using cheap materials in question. Copper-aluminum hardeners of excellent quality are readily available commercially. These hardeners dissolve quickly and pose no thermite problems.

REFERENCES

- Haws, L.D., Kelley, M.D., and Mohler, J.H., "Consolidated Al/Cu₂O Thermites," Monsanto Research Corp., Report MLM-2531 (OP), Sept. 28, 1978.
- <u>Guidelines for Handling Molten Aluminum</u>, The Aluminum Association, Washington, DC 20006, October 1982.

Recommended Reading

Richter, R.T., D.D. Leon, and T.L. Levendusky. Investigations of coatings which prevent molten aluminum/water explosions-progress report (1997, pp. 899–904).