Production of Cu–Cr Alloys by In-situ Reduction of Chromium Oxide during Air Induction Melting

V. V. Satya PRASAD, Y. Satish BABU and Ujjwal. PRAKASH

Defence Metallurgical Research Laboratory, Hyderabad-500 058, India.
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1. Introduction

Recently we have reported on a technique for production of copper–chromium alloys using electro slag crucible melting.1) Copper containing up to 1% chromium is a precipitation hardening alloy which exhibits good room temperature strength, ductility and high electrical and thermal conductivities.2) The electroslag crucible melting process uses chromium metal and copper scrap for producing Cu–Cr alloy, thereby obviating the need for using expensive and proprietary master alloys containing up to 10% chromium. The process was subsequently modified to allow chromium to copper by in-situ reduction of chromium oxide added to the slag.3)

The electroslag crucible melting process is a specialized melting process and is not practised universally. In the present work, a more conventional melting process, namely Air Induction Melting (AIM) process is described to produce Cu–Cr alloys using fine copper scrap as a raw material. AIM is normally not used for melting light scrap due to difficulty in electro magnetic coupling with the charge. Extensive surface oxidation of the charge is also a problem. The process described here uses a modified charging schedule and melting under slag cover to overcome these problems. The chromium is alloyed to copper by in-situ reduction of chromium oxide.

2. Experimental

Fine copper scrap (turnings and borings) was subjected to magnetic separation and cleaned. The scrap was compacted into solid blocks measuring approximately 55 mm diameter and 75 mm height. A medium frequency 125 kW Inductotherm furnace was used for melting alloy from the scrap. A thick walled graphite crucible of 160 mm OD, 85 mm ID and 300 mm height was inserted in the 50 kg Alumina lined melting coil provided with the furnace.

The compacted copper scrap was charged in the crucible. Melting of the scrap was carried out at a power level of 35 kW. As the charge was heated up graphite powder was sprinkled from top to avoid excessive oxidation of the charge. The hot scrap was rammed from the top using a graphite rod to ensure better packing of the crucible. Fresh scrap compacts were added once the previous charge was rammed down sufficiently. The process was continued until all the scrap (4 kg) was charged into the crucible. Graphite powder was sprinkled after each charge.

600 g of a slag comprising 20%CaF2–30%CaO–30%SiO2–20%NaF (all composition in mass%) was mixed with 90 g of chromium oxide (Cr2O3). The slag mixture was then preheated in a resistance furnace at 800°C for 2 h. The preheated slag was charged into the crucible after charging of copper scrap. The slag was rammed after charging and formed a sintered cake on top of copper charge. A schematic of the melting set up used is shown in Fig. 1. The remaining was continued until melting of copper was observed. The melt was held until copper as well as slag had melted. Aluminium pieces weighing in total 32 g and measuring 5 mm×5 mm×5 mm were added to the slag for in-situ reduction of chromium oxide present in the slag. The melt was then held for 10 min following which the power was switched off. The melt (Melt No. 1) was allowed to solidify in the crucible. After cooling, the Cu–Cr ingot of 85 mm diameter and 75 mm height was removed from the crucible. In one experiment (Melt No. 2) the melt was also stirred periodically with a graphite rod after aluminium addition.

For understanding reaction mechanisms, a third 'melt' (Melt No. 3) was conducted in a resistance furnace. A charge of compacted copper scrap weighing 2600 g was placed in a graphite crucible. On top of the copper scrap, 1140 g of slag mixture was then added. The crucible was placed in a resistance furnace. The furnace was heated to 1 473 K and aluminium pieces weighing 20 g and measuring 5 mm×5 mm×5 mm were added to the top of the melt. The furnace was held at 1 473 K for 30 min. It was then switching off and allowed to cool to room temperature. The cast alloy discs of 115 mm diameter and 30 mm height were removed from the crucible.

The ingots were tested for their soundness in a radiography unit using a 5 curie Co60 gamma radiation source. For determination of chromium and aluminium contents, samples by drilling were taken from top and bottom of the cast ingots. The chromium and aluminium were determined by using atomic absorption spectroscopy (AAS) technique. The ingot was then sectioned in the longitudinal direction. To examine the macrostructure, the ingot section was sur-
face machined, ground and etched with a fresh solution of silver nitrate in nitric acid. For metallographic studies, samples of 10 mm × 10 mm were mounted in bakelite, polished to a 1 micron finish and subsequently etched with potassium dichromate solution.

3. Results and Discussion

The cast AIM ingot weighed approximately 4 kg and possessed good surface finish. Surface defects normally present in castings such as fins and ripples were not observed. This may be because the liquid metal was not poured but was allowed to solidify in a graphite crucible. Radiography test confirmed that the AIM ingots were sound. This may be explained by noting that the liquid metal was left to solidify in a hot graphite crucible and was also protected by a liquid slag layer on the top of the metal.

Excessive surface oxidation of the light scrap during heating can be a serious problem because of large surface area available. In the present work excessive oxidation was avoided due to several reasons. Initially graphite powder was used to minimize oxidation. Subsequently the heated scrap at bottom was protected from exposure to atmosphere by the fresh charge being added from the top. Finally the presence of slag at the top prevents further oxidation. Intermittent ramming of the scrap during charging helps in increasing packing of charge which also minimizes oxidation.

AIM is generally not used for melting light scrap due to difficulty in electro magnetic coupling with the charge. In the present work the improved packing due to ramming may improve the electro magnetic coupling of the charge. Also it greatly improves the heat transfer in the charge. Copper is a soft material and it loses its strength rapidly with increasing temperature. This greatly facilitates further densification of the heated scrap compact by ramming. It was observed that the level of the charge significantly decreased on ramming once the compact has been heated. This then allowed charging of fresh scrap which could not have been charged in the beginning. Thus the low initial charge packing was significantly improved by repeated ramming. This was an important factor contributing towards successful melting of light copper scrap by AIM.

The melting of the scrap started from the bottom of the crucible where the packing density was also very high. Once melting was initiated, the entire metal charge melted quickly. Subsequently the slag at the top was melted due to transfer of heat from the hot metal. The quantity of slag that can be melted in this fashion is very limited. Since the slag cannot couple electro magnetically it is important that the amount of slag used is just enough to provide a continuous protective cover at the top of the melt. For this reason the quantity of slag used was considerably less than that used for electro slag crucible melting. Slag ingredients used in electro slag processes include fluorides (for improved fluidity and electrical conductivity) which attack furnace linings and are generally not suitable for melting in induction furnaces. The slag used in the present work was similar to that used for electro slag crucible melting. This was possible because melting was carried out in a graphite crucible thus protecting the (alumina) furnace lining.

| Melt No. | Cr (mass%) Top | Al (mass%) Top | Cr alimed (mass%) | %Cr Recovery during the melt |
|---------|---------------|---------------|------------------|-----------------------------|
| 1       | 1.23          | 0.038         | 1.5              | 81                          |
| 2       | 1.50          | 0.039         | 1.5              | 100                         |
| 3       | 2.30          | 0.038         | 1.5              | --                          |
| 4*      | 0.84          | <0.01         | 2.0              | 41                          |

* Electroslag crucible melted alloy (3)

The chromium picked up by the metal is due to reduction of chromium oxide in the slag by aluminium:

\[ \text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3 \]

It was observed that aluminium added to the melt floated on top of the slag until it had melted. After melting, the liquid aluminium does not join the metal pool below. This may be because the density of liquid aluminium (−2.5 g/cm³) is less than that of the liquid slag (2.6–2.8 g/cm³) and significantly less than that of liquid copper. Hence, the reaction above occurs in the bulk slag phase and the chromium generated in the slag phase joins the metal below thereby to copper–chromium alloy formation.

The efficiency of chromium pick up depends significantly on the stirring of the metal bath. Greater stirring of the liquid metal can be achieved during air induction melting as compared to electroslag crucible melting. It may be seen from Table 1 that Cr recovery during AIM is more efficient (81 %) as compared to electroslag crucible melting (41 %). 100 % Cr recovery was achieved on stirring of the melt by graphite rod during AIM. The amount of chromium alloyed with copper using AIM is more than the levels previously reported in literature. In the absence of stirring (Melt No. 3) the chromium produced by direct reduction is accumulated at the slag–metal interface which also results in inhomogeneous ingot (Table 1). Increased stirring ensures transfer of chromium from the interface to the liquid metal which also helps in driving the reduction reaction forward. Best results were obtained when slag as well as metal were stirred (Melt No. 2).

Because of stirring of metal during AIM some aluminium pick up (upto 0.04 mass%) was observed in the AIM ingots. The thickness of slag layer in ESCM (Electro slag Crucible Melting) is larger than that in AIM. Also, during ESCM the liquid metal experiences very little stirring. Both these factors lead to a lower Al pick up (<0.01 %) in ESCM ingot. Though the aluminium content in AIM ingots is higher than that observed in ESCM ingots, overall aluminium levels remain very low.

The macrostructure of the longitudinal section of the ingot (Fig. 2) revealed columnar grains free from defects, namely, pipe, shrinkage cavity, and microporosities which are commonly observed in conventional castings. The grain growth appears to have taken place from side walls towards the center of the ingot and from bottom upwards yielding a
casting with a dense and directionally oriented columnar grain structure. The as-cast microstructure of the alloy is shown in Fig. 3 and exhibits a dendritic structure consisting of large alpha grains with chromium particles dispersed at the interdendritic boundaries.

In summary, light copper scrap was successfully melted by AIM. The technique described, however, is critically dependent on achieving densification of the scrap prior to melting. For this reason, not all types of metals may be amenable for recycling using this technique. Cu–Cr alloys are generally melted using proprietary master alloys containing up to 10 mass% Cr. The direct reduction route described for production of copper–chromium eliminates the need for using master alloys, further bringing down the production cost.

4. Conclusions

Light copper scrap can be successfully melted by AIM. Repeated ramming of the solid scrap from the top ensures adequate densification of the charge. The use of the graphite powder during ramming and a slag cover at the time of final melting prevent oxidation and contribute to successful melting of the scrap. In-situ reduction of chromium oxide by aluminium is then used to alloy chromium to the molten copper. Sound and homogeneous Cu–1.5%Cr alloy ingots with good surface finish were successfully produced using the modified air induction melting technique. The use of AIM to melt fine copper scrap and in-situ reduction of Cr$_2$O$_3$ significantly reduces the cost of production of Cu–Cr alloys.

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