Note

Effect of Process Variables on Electroslag Crucible Melting of Copper–Chromium Alloys

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1. Introduction

Recently we have reported the feasibility of recycling high purity copper scrap by a modified crucible melting technique.¹⁾ It was established that slag purity as well as purity of the graphite used for making the crucible and electrode plays an important role in determining the purity of crucible melted copper ingot. However, commercially available slag and graphite may be used for melting copper scrap through this technique when very high purity is not a consideration. In the process reported, the copper scrap is gradually added to the graphite crucible as the melting progresses. This may also allow addition of alloying elements to enable production of copper alloys using a charge of copper scrap.

Copper containing upto 1% chromium is a precipitation hardening alloy which exhibits good room temperature strength, ductility and high electrical and thermal conductivities.²⁾ Alloys of copper and chromium are particularly suitable for applications where considerably higher strength than that achievable with copper is required, in conjunction with high electrical and thermal conductivities. Important applications of Cu–Cr alloys also include spot and seam welding electrodes, electronic connectors and lead frames.^{3,4)} Very little published data is available in the literature on melting of copper–chromium alloys. Alloying of chromium with copper during melting is difficult due to the large difference in (a) melting points (copper–1083°C, chromium–1875°C) and (b) density (copper–8.95 g/cm³, chromium–7.19 g/cm³) as well as the limited solid solubility (maximum solid solubility 0.65 wt% at 1070°C) of Cr in copper. Because of these difficulties, copper–chromium alloys are usually melted using expensive and proprietary master alloys containing upto 10% Cr.^{2,5)}

The purpose of the present communication is to report an electroslag crucible melting technique (ESCM) for production of copper–chromium alloys using chromium metal and copper scrap. The role of process variables such as charging practice, power input and holding time on the chromium content of the alloy is also described.

Fig. 1. Showing schematic of electroslag crucible melting.

Table 1. Process parameters in ESCM for production of Cu–Cr melts.

Melt No.	Amount of charged Cr (%)	Size of Cr pieces	Holding time (min)	Power during holding (kW)
1	1.5	4–5 mm	5	38
2	1.5	<1 mm	10	45
3	1.5	<1 mm	20	30
4	1.5	<1 mm	20	45
5	1.5	2–3 mm	20	38
6	1.5	2–3 mm	30	38
7	2.5	<1 mm	30	38
8	1	<1 mm	30	38

2. Experimental

An AC ESR furnace of 350 kVA capacity comprising a graphite electrode (80 mm diameter) and a graphite melting crucible (150 mm internal diameter) were used in the present work. An arc was struck between the graphite electrode and the base of the graphite crucible to start the process (Fig. 1). Slag was then added to the crucible. After some slag had melted, the molten slag itself served as the ohmic source of heat due to its resistance. A slag comprising 20%CaF₂–30%CaO–30%SiO₂–20%NaF (all compositions in wt%) was used in the present work.

Typically 2 kg of slag was initially charged into the crucible. Once all the slag had melted, about 5 kg of copper scrap (turnings and borings) was charged through annular gap between the electrode and the crucible. Due to its large volume-to-weight ratio, the copper scrap floats on top of the slag until it melts. The melt rate used was 1 kg/min. The charging was resumed once the previously added scrap had completely melted. After all the copper was charged, chromium pieces were added to the melt. The melt was held at high temperature before transferring to a graphite mould. The molten metal, together with the liquid slag, was poured in the mould and was allowed to solidify. The slag cover was thus maintained during crucible melting as well as subsequent solidification to protect the metal from atmospheric oxidation. A range of process parameters (power input, time of holding and size and quantity of chromium charged) were used and are given in Table 1.

Ingot of 50 mm in diameter and 300 mm long were

Table 2. Chromium distribution in ingot obtained by ESCM.

Sample location (distance from ingot bottom)	Melt-1	Melt-2	Melt-3	Melt-4	Melt-5	Melt-6	Melt-7	Melt-8
50 mm	—	0.6	0.59	0.59	0.44	0.65	0.7	0.66
100 mm	—	0.7	—	0.61	0.44	0.65	—	—
150 mm	0.15	0.74	—	0.63	0.45	0.68	—	—
200 mm	—	0.85	—	1.2	0.44	0.69	—	—
250 mm	—	0.96	0.57	—	0.44	0.69	0.72	0.64

Fig. 2. Flash photograph showing crucible melted Cu-Cr ingots (ingot diameter 50 mm).

Fig. 3. Top section of a Cu-Cr ingot (50 mm diameter) showing unmelted chromium pieces embedded in the alloy.

obtained by the ESCM technique described above. The ingots were tested for their soundness in a radiography unit using a 5 curie Co_{60} Gamma-ray source. For determination of chromium content, drillings were taken from different locations in the cast ingots as given in **Table 2**. The chromium content was determined by using atomic absorption spectroscopy (AAS) technique. The chromium content in slag was determined by using AAS dissolving the slag samples in aquaregia. Transverse sections at 20 mm from top of the ingots were cut and examined for casting defects like slag entrapment, shrinkage/piping *etc.* For EPMA (electron probe microanalysis) studies, samples were cut from the crucible melted ingots, mounted in bakelite and mechanically polished to $0.5\ \mu\text{m}$ diamond powder finish. The polished samples were subsequently etched with potassium dichromate solution for examination under optical

Fig. 4. Typical EPMA back scattered electron image (a) and X-ray map from the same area showing chromium distribution (b) in a Cu-Cr ingot (Melt-8).

microscope.

3. Results

All the ingots were found to be sound and free from casting defects, and possessed good surface finish (**Fig. 2**). However, some shrinkage (filled with solidified slag) was observed in the sections cut off from top of the ingots. A significant number of chromium pieces were also found to be trapped in these sections. **Figure 3** shows the shrinkage (from which the slag has been removed) and undissolved chromium pieces observed in ingot sections. When large (4–5 mm) chromium pieces were charged and the melt was held for only 5 min (Melt-1, Table 1), only 0.15% chromium was retained in the ingot (Table 2) under these process conditions. Consequently, finer chromium pieces and longer holding times were employed in subsequent experiments. However, some undissolved chromium was observed in all the sections cut off near the top of the ingots.

Even when fine ($< 1\ \text{mm}$) chromium pieces were charged and higher power was supplied, a holding time of 10 min (Melt-2, Table 1) resulted in segregation of chromium, with chromium content increasing from bottom to top

of the ingot (Table 2). Increasing the power from 30 to 45 kW (Melt-3 and 4, Table 1) did not result in significant increase in the chromium content of the ingot (Table 2). The use of longer holding time (Melt-5 and 6, Table 1) results in greater chromium dissolution during melting (Table 2). Decreasing the size of the chromium charge from 2–3 mm to <1 mm (Melt-3 and 5, Table 1) also results in greater dissolution of chromium (Table 2). Increasing the amount of chromium charged from 1.5 to 2.5% (Melt-6 and 7, Table 1) resulted in only a marginal increase in chromium content of the ingot (Table 2). Further decreasing the charge to 1% chromium (Melt-8, Table 1) also resulted in ingots with comparable chromium contents (Table 2). Typically 0.15 to 0.2% chromium was also detected in slag samples taken after melting.

The cast ingots exhibited a dendritic structure with significant chromium segregation to the interdendritic regions (Fig. 4). A fine dispersion of chromium particles was also observed within the copper matrix.

4. Discussion

A significant fraction of the chromium charged is not dissolved in the melt even after holding the melt at high temperature. Typical slag and metal temperatures expected¹⁾ are 1500 and 1400°C, respectively and are below the melting point of chromium. The density of chromium is between that of liquid copper and liquid slag. Due to these reasons, the undissolved chromium is present as discrete chromium pieces at the slag-metal interface. The presence of slag cover prevents the oxidation of chromium particles from atmosphere. Noting that copper and chromium are completely miscible in the liquid state, it may be inferred that the following kinetics limit the dissolution of chromium in copper. Dissolution is rendered more difficult because the chromium pieces remain near the top of the ingot thereby greatly reducing the surface area available for dissolution. As may be noted, even 1% chromium charged could not be completely dissolved despite holding for 30 min (Melt-8, Table 2). Further increasing the amount of chromium in the charge does not affect chromium content in the ingot which is controlled by dissolution kinetics. This also explains the observed increase in chromium content when finer chromium pieces are used. Use of very fine (*e.g.* powder) charge is not practical as the charge is likely to suspend in the slag.

Initially, a concentration gradient may exist in the bath as the chromium charged stays just below the slag cover. Though the slag is expected to undergo electromagnetic stirring during crucible melting, the same is not true for liquid metal underneath the slag cover.⁶⁾ Some stirring of the liquid metal may occur due to mechanical agitation transferred from the liquid slag. The chromium concentration gradually equalizes during holding at high temperature. The segregation of chromium observed when the melt was held for only ten minutes (Melt-2)

may have been caused by insufficient holding time for dissolution and diffusion of chromium. Apparently, the gradient was retained during transfer of melt to the mould and subsequent solidification. The molten metal richer in chromium may have a relatively lower density and may float to the top prior to solidification. As is evident from the analyses reported for subsequent melts, dissolution of more than 0.7 wt% Cr in copper is unlikely. It is probable that the samples taken from the top 100 mm of Melt-2 ingot contained entrapped chromium pieces which could not float to the top during solidification. The chromium contents reported from these locations is anomalously large (Table 2).

Since use of larger amount of chromium in the charge does not result in a significant increase in chromium pick up in the melt, a charge of around 1% chromium appears to be adequate for the process as most of the chromium is dissolved in metal or absorbed in the slag (probably as chromium oxide). The good surface finish of the ingots observed in the present work is a characteristic of the process¹⁾ and may be an added advantage.

5. Conclusions

Electroslag crucible melting is a viable process for production of copper-chromium alloys where the alloys can be directly melted using a charge of copper and chromium, thereby obviating the use of expensive and proprietary master alloys. The ability of the process to remelt fine copper scrap may further reduce the processing costs. The cast ingots of Cu-Cr alloy have uniform composition, good surface finish and are free from internal defects. The chromium content of the ingots may be maximized by the charging practice and holding time and to a limited extent by the power used in the process. The chromium content of the ingot is limited by kinetics of chromium dissolution to a maximum of 0.7%. The factors affecting chromium dissolution in copper are also discussed.

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