A Shaft Furnace Line for Producing Oxygen-Free Copper for Electron Devices Applications

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ABSTRACT In recent years the level of environmental awareness has been rising world-wide, with increased emphasis being placed on measures to stop global warming and energy-saving initiatives, but these have been largely ineffective. In this work we present a shaft furnace as a replacement for induction furnaces in the melting of oxygen-free copper, and it has been possible, using this shaft furnace line, to produce oxygen-free copper that exceeds both the JIS standard for use in electron devices applications and the ASTM Grade 1 standard. We also succeeded in achieving an energy saving of approximately 10 % in terms of primary crude oil equivalence units.

1. INTRODUCTION

From the viewpoint of preventing global warming in recent years, there have been increasing demands for energy-saving measures to reduce the emission of greenhouse gases such as CO_2, and the accumulation of small improvements by various companies has been effective. The same is true in molten copper casting, where large amounts of gas and electricity continue to be consumed in melting, so that the need for energy saving becomes more urgent every year. And it is obvious that gas is superior to electricity in terms of lower use of crude oil overall, including electric power generation for melting. Analyzing by product category, the use of gas-fired shaft furnaces is predominant for tough pitch copper, and energy efficiency is high. In the manufacture of oxygen-free copper, on the other hand, the properties required of the material mean that the admixture of oxygen and hydrogen must be avoided. It is thus necessary to melt the base metal using electrical induction heating, so that huge amounts of energy continue to be used. In an effort to promote energy savings in the production of oxygen-free copper there are manufacturers that produce rough-drawn oxygen-free copper wire by means of the shaft furnaces normally used in making tough pitch copper and phosphorus deoxidized copper, but this has not been extended to the oxygen-free copper ingots (slabs and billets) supplied for electron devices applications.

In this work, we have, in the course of replacing our line for the production of oxygen-free copper, installed a shaft furnace in place of the conventional induction furnace as a means of saving energy, where oxygen-free copper of the highest quality is required. We therefore report here our success in producing oxygen-free copper satisfying both JIS standards for electron devices applications [1)] and ASTM Grade 1 [2)].

In terms of the special properties required for superconductivity, the oxygen-free copper manufactured through this development has a residual resistivity ratio (RRR) in excess of 500. And because of the outstanding energy saving results in terms of crude oil equivalence units, this project has been recognized as a project supported by the New Energy and Industrial Technology Development Organization (NEDO).

2. GENERAL DESCRIPTION OF THE SHAFT FURNACE

In the 50 years since they were developed, shaft furnaces have achieved the status of a mature technology. They have been used for the manufacture of tough pitch copper having oxygen contents of from 300 to 500 ppm (i.e., g/ton) and phosphorus deoxidized copper, and Furukawa Electric at present has seven in operation at our Chiba, Mie, Osaka and other plants. A shaft furnace is one that melts copper using a burner fueled by gas (natural gas, butane or propane) that is characterized by large-scale operation to improve productivity, and by high energy efficiency.

As can be seen from Figures 1 and 2, gas burners are disposed radially around the lower part of a cylindrical furnace. The base metal is melted, and a path for the exhaust gas produced by combustion is provided in

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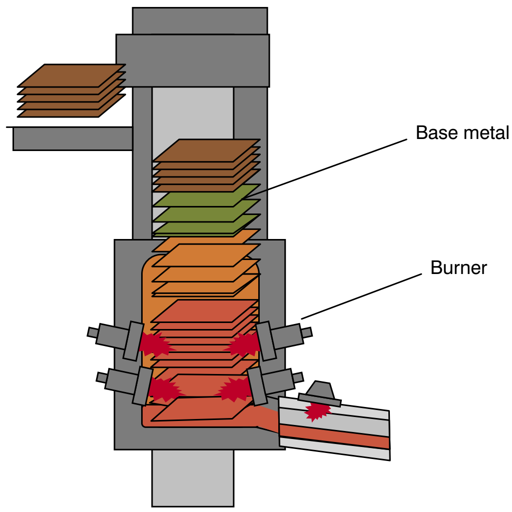


Figure 1 Structure of shaft furnace.

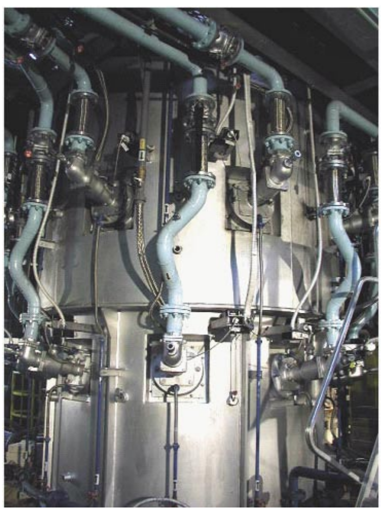


Figure 2 Appearance of shaft furnace.

the upper part of the furnace so that it pre-heats the base metal that is stacked there. For this reason the temperature of the exhaust gas when exhausted is approximately 473~673 K, making for a furnace of very high energy efficiency.

3. JIS STANDARDS FOR OXYGEN-FREE COPPER FOR ELECTRON DEVICES APPLICATIONS AND ASTM GRADE 1

In comparison with standards governing ordinary oxygen-free copper (C1020 specified in JIS), those governing oxygen-free copper for electron devices applications (C1011 specified in JIS) specify superior impurity levels, oxygen and hydrogen gas levels, electrical conductivity, and hydrogen embrittlement characteristics, for use originally in vacuum tubes and at present in magnetrons and electron tubes. ASTM Grade 1 specifies even higher performance in terms of impurities and hydrogen embrittlement characteristics than does C1011.

4. DEVELOPMENT STATUS

4.1 Behavior of Melt Constituents due to Shaft Furnace

In the production of oxygen-free copper its characteristics require that the amounts of oxygen and hydrogen in the melt be reduced as much as possible. It can, however, be expected that if a shaft furnace is used, melting will proceed until the concentration of gases in the combustion atmosphere reaches equilibrium with those in the melt. The equilibrium relationship between the partial pressure of steam in the furnace atmosphere and oxygen and hydrogen in the melt may be expressed as:

$$H_2O \rightleftarrows 2\underline{H} + \underline{O}$$
$$K = [\underline{H}]^2 \cdot [\underline{O}] / P_{H_2O}$$

where:
K is the equilibrium constant,
$\underline{O}$ is the oxygen concentration in the melt,
$\underline{H}$ is the hydrogen concentration in the melt, and
P_{H_2O} is the partial pressure of steam.

It is this, together with the balance between CO, CO_2, H_2O and H_2 is the combustion atmosphere, that determines the concentrations of oxygen and hydrogen in the melt discharged from the shaft furnace. Also the adjustment of CO, CO_2, H_2O and H_2 in the combustion atmosphere can be controlled by adjusting the excess combustion air ratio using CO as an index. Figure 3 shows the results of measurements of oxygen and hydrogen at the discharge port of the shaft furnace [3)~5)]. It can be seen that the oxygen-hydrogen equilibrium conditions in molten copper at 1453 K and 1493 K are in good agreement. Thus when a shaft furnace is used for the melting of oxygen-free copper, it is essential that oxygen and hydrogen be adequately removed, and it is for this reason that in the past it has been induction furnaces that were used for melting oxygen-free copper.

4.2 Oxygen and Hydrogen Concentrations Required in Shaft Furnace Melts of Oxygen-Free Copper

In producing oxygen-free copper to the ASTM Grade 1 standard, Furukawa Electric has a target of 2 ppm or less

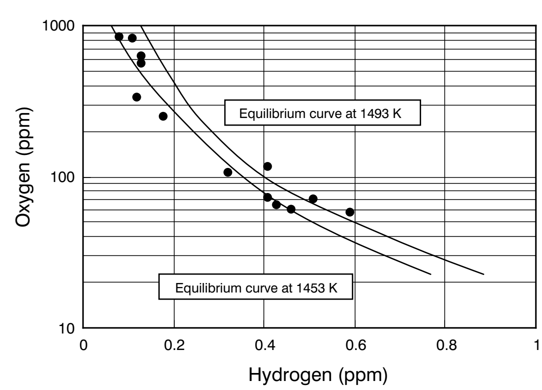


Figure 3 Measured concentrations of oxygen and hydrogen in copper melt at discharge port of shaft furnace.

of oxygen and 0.2 ppm or less of hydrogen. This requires oxygen- and hydrogen-removal treatment to be applied to the shaft furnace melt. Thus with a view to the ease of implementation of various methods of melt treatment, we have constructed a facility with target concentrations for the shaft furnace melt set at 100 ppm for oxygen and 1 ppm for hydrogen.

Stable production of oxygen-free copper also requires the stable discharge of the melt from the shaft furnace, but as has been mentioned above, the furnace melt is strongly affected by the combustion atmosphere from the burners so that if any changes should occur in the combustion atmosphere, fluctuations in the oxygen and hydrogen concentrations of the shaft furnace discharge melt will also occur. This is not a desirable situation in the manufacture of oxygen-free copper for electron devices applications or ASTM Grade 1 applications, and gives the greatest importance to controlling burner combustion to obtain a stable melt.

However in the interior of a shaft furnace, unlike that of a conventional furnace, the base metal for the melt appears in front of the burner in a condition that changes from moment to moment making it difficult to maintain a constant pressure loss in front of the burner. As a result minute changes are made to the excess air ratio of the burner. This makes it necessary to constantly monitor and control this combustion air ratio, but with the problems with the response and control range of existing systems, it is difficult to obtain a stable air ratio conducive to maintaining the melt level required for the production of oxygen-free copper for electron devices applications.

To solve these problems we have constructed a novel system that provides real-time monitoring of all 15 burners of the shaft furnace and individual control of the excess air ratios of each, and have been successful in obtaining the target melt level in a stable manner.

We have also carried out melt treatment in subsequent process steps using previously developed technologies for the removal of oxygen and hydrogen, succeeding in the production of oxygen-free copper for electron devices applications having an oxygen content of 2 ppm or less and a hydrogen content of 0.2 ppm or less.

4.3 Technologies Introduced with the Shaft Furnace

With this introduction of the shaft furnace, attention has been given to developing a system that allows for fully automated operation. We therefore established automated charge control for the base metal and automated combustion control for the burners. Specifically in the case of burner control, a system that keeps constant track of combustion conditions in each of the burners automatically controls excess air ratios in real time, and a system that automatically controls the amount of combustion in response to the amount of melt discharged from the shaft furnace. By these means fully automated operation is being carried out.

5. EVALUATION OF PROPERTIES OF OXYGEN-FREE COPPER

5.1 Analysis of Impurity Concentrations

Table 1 shows the results of analyses of the constituents of the oxygen-free copper for electron devices applications that was successfully produced in this work. Results were satisfactory with respect to all of the impurities, significantly exceeding the levels set forth in ASTM Grade 1. With the start-up of the new line there were concerns relating to the admixture of iron in particular, but by changing the structural materials used for the furnace and by coating them, it was possible to reduce admixture to a negligibly low level. Sulfur was also at an extremely low value, and it is thought that this was due to the full benefit of the pre-heating effect of the shaft furnace, a particular phenomenon having a desirable effect on the production of oxygen-free copper for electron devices applications. This means a further improvement with respect to iron and sulfur in comparison with the conventional line. It was also possible to achieve similar levels for other impurities.

5.2 Analysis of Oxygen and Hydrogen

As Table 1 shows it was possible to achieve the target values of 2 ppm or less for oxygen and 0.2 ppm or less for hydrogen. The results for oxygen were substantially the same as with the conventional line, but for hydrogen, the improvements in the melt treatment effect of the new

Table 1 Concentration of impurities in oxygen-free copper.

Ingot	RRR	Cu %	Impurity (limit, ppm)																	E.C. I.A.C.S%
			Oxygen	Hydrogen	P	S	Ag	Pb	Sn	Fe	Ni	Bi	As	Sb	Se	Zn	Te	Hg	Cd	
C1020		≥99.96	NS																	≥100
C1011, oxygen-free copper for electron devices applications	NS	≥99.99	10	NS	3	18	NS	10	NS			10	NS		10	1	10	1	1	≥101
ASTM Grade1		≥99.99	5	NS	3	15	25	5	2	10	10	1	5	4	3	1	2	NS	1	≥101
Conventional	300	≥99.99	<2	<0.3	<1	4	10	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	≥101
Shaft furnace product	≥350	≥99.99	<2	<0.2	<1	<1	8	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	≥101

NS = not specified

line gave even better results, with a lower concentration than in the conventional line. Analysis for oxygen was carried out by the JIS quantitative method using inert gas atmosphere melting and infrared absorption [6].

5.3 Ingot Density

Ingot density was improved to 8.932 g/cm^3, from the 8.930 g/cm^3 obtained using the conventional line. Provided there is no change in the solidified state, ordinary density indicates the possibility that defects such as bubbles are present, but the improvement of the ratio in this case is also backed up by the fact that, as shown in Sec. 5.2, the gas content has been reduced. This inevitably produced the result that gas exhaust characteristics are also improved.

5.4 Results of Hydrogen Embrittlement Tests

Hydrogen embrittlement is the most important characteristics in oxygen-free copper for electron devices applications. Figure 4 shows the results of heating in a hydrogen gas stream. The tests were conducted on ingots this time. JIS provides for 30 min at 1123 K, but in anticipation of more rigorous conditions, we used 30 min at 1273 K. In checking for the presence of voids in the microstructure of the ingots we found that in all cases no voids occurred and no hydrogen embrittlement occurred. In repetitive bending tests as well, 15 times or more was obtained --satisfactory results that were equivalent to those obtained in the past.

5.5 Annealing Characteristics

Figure 5 shows the annealing properties of oxygen-free copper manufactured under a high reduction rate (95 %) and a low reduction rate (9.6 %) using the shaft furnace line and the conventional line. In all cases no abnormalities were found in comparison with previous oxygen-free copper. As shown in Figure 6, no changes were observed in the growth of crystal grain in either temperature range.

5.6 Residual Resistivity Ratio

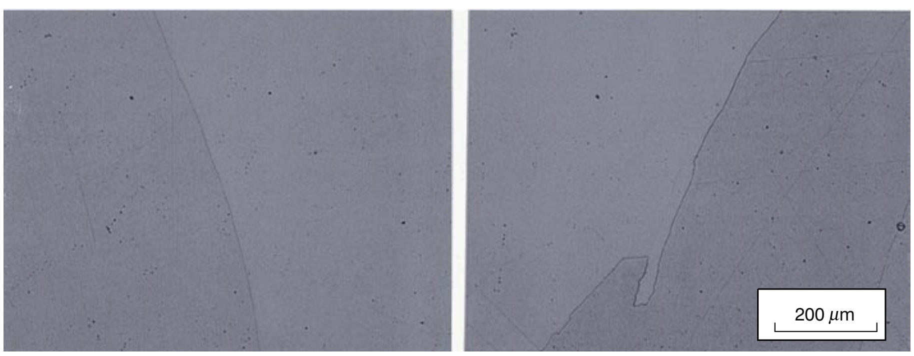
For specialized applications, such as in super-conductivity, the ratio between the electrical resistance at the temperature of helium liquefaction (4 K) and normal temperature, known as the residual resistivity ratio (RRR), is an index to how good electrical conductivity is at low temperatures and is thus an extremely important characteristic. Indexes in excess of the 350 required for superconductivity applications were obtained, with a maximum of 503. When impurities are present in the copper, the conductivity decreases with their concentration, so this result shows that the impurity concentration is very low.

6. EFFECTIVENESS OF ENERGY-SAVING MEASURES

Figure 7 shows the effectiveness of energy-saving measures. In the conventional line melting is accomplished primarily by inductive heating using electricity. In the new shaft furnace line, on the other hand, the heat is provided by gas burners. Since this makes it difficult to compare primary units directly, we have used a measure of crude oil equivalence. Basing the comparison on normal output, with conventional prime crude oil equivalence unit of 0.102 kl/ton, the figure was 0.090 kl/ton for the shaft furnace line, a reduction in energy of approximately 10 %. At this plant we have been working towards a target reduction of 1 % per annum, and if the savings obtained by the shaft furnace line are compared in terms of primary units for the plant as a whole, there has been a saving of 1.3 % in energy used in terms of primary crude oil equivalence units.

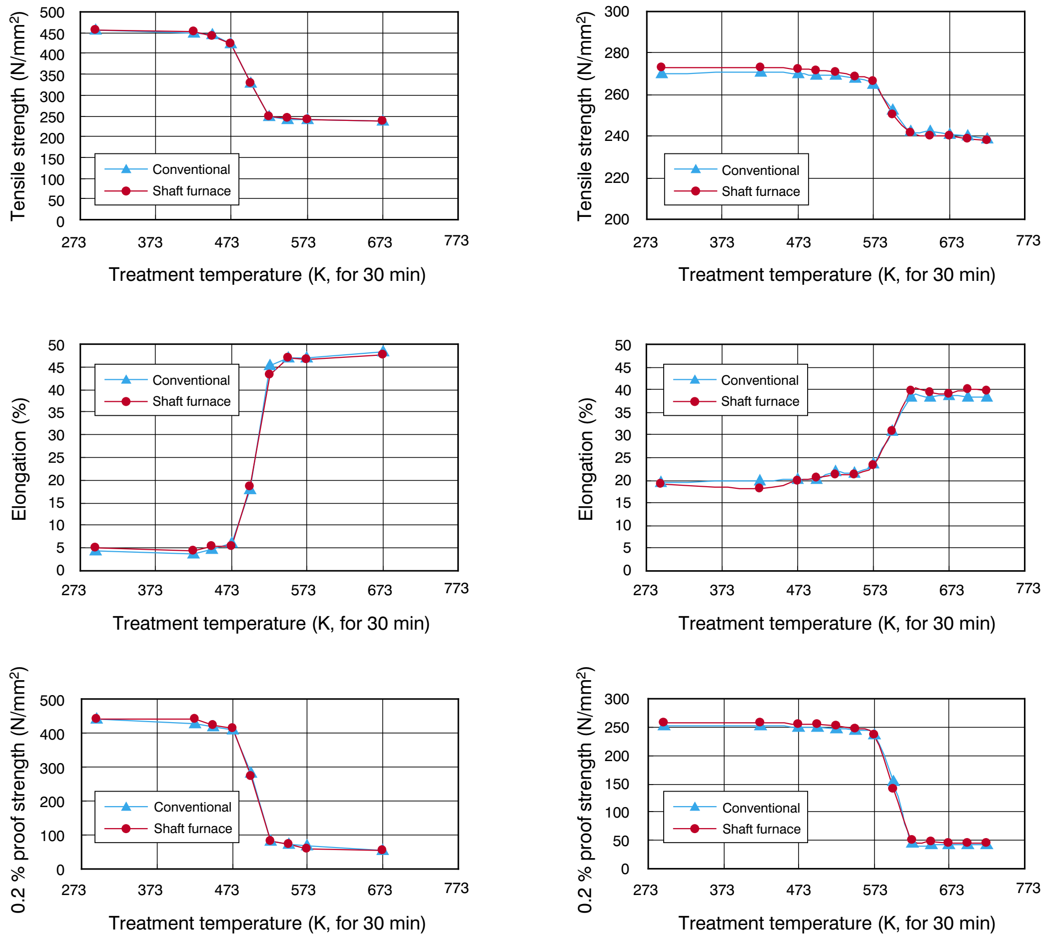
7. CONCLUSION

As part of our efforts toward energy saving we have introduced a shaft furnace into the line for producing oxygen-free copper. We have succeeded in our development objective of producing oxygen-free copper satisfying the JIS standard for electron devices applications and ASTM Grade 1. The oxygen-free copper produced here was satisfactory in terms of the levels of oxygen, hydrogen and impurities, and a residual resistivity ratio of 350 or more was achieved, confirming its usability in specialized applications involving superconductivity. And in terms of other mechanical



a) At 1123 K   b) at 1273 K

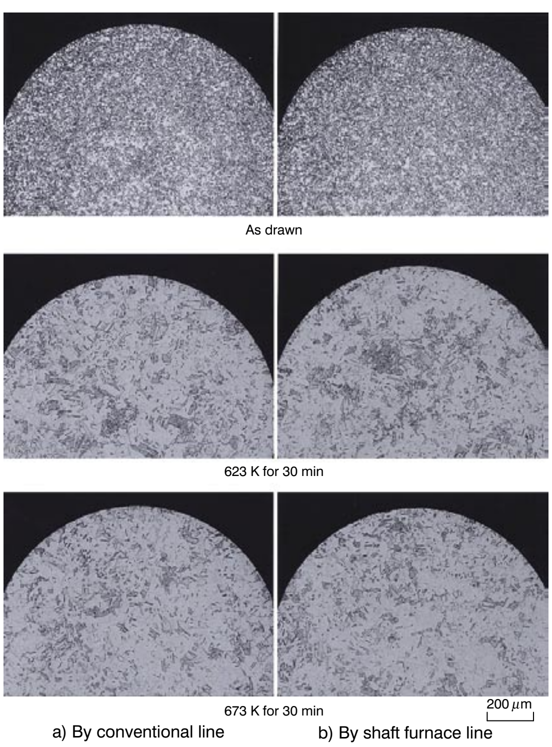
Figure 4 Results of hydrogen embrittlement tests.



a) High reduction rate (95 %)

b) Low reduction rate (9.6 %)

Figure 5 Annealing properties of oxygen-free copper manufactured under high and low reduction rates.



a) By conventional line

b) By shaft furnace line

Figure 6 Cross-sections before and after annealing.

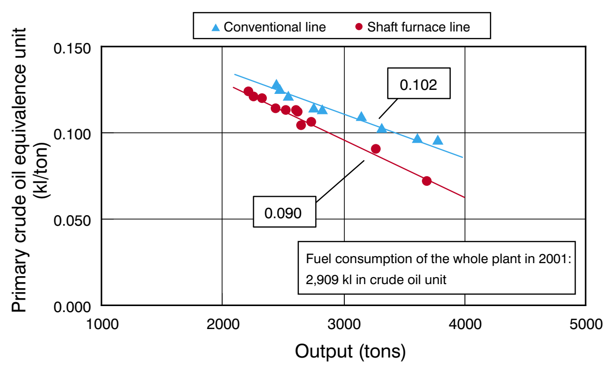


Figure 7 Comparison of energy efficiency of conventional and shaft furnace lines in terms of primary crude oil equivalence units.

characteristics, it was possible to obtain satisfactory oxygen-free copper, with properties in no way different from those of earlier oxygen-free copper. In terms of energy savings as well we succeeded in a reduction of 10 % on a shaft furnace plant basis in terms of primary crude oil equivalence units.

In closing we would like to extend our thanks to all those who cooperated with us in this development work.

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