Microstructure and thermal analysis of Cu-Cu_2O eutectic – Can we mimic archeological remains?

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Abstract

An attempt was performed to reproduce in laboratory the microstructure observed in ancient artefacts and metallurgical remains made of nearly pure copper cast under ambient atmosphere. Two samples of pure Cu were prepared for thermal analysis, then heated and held for various times in the liquid state under ambient air for oxidizing, and finally cooled down at given rate. It was observed that a thick Cu_2O oxide layer developed around the samples which gives the metal the same outer appearance than reported for metallurgical remains, namely a highly oxidized surface with large voids. Further, the microstructure of the metal consisted of (Cu) or Cu_2O dendrites and a (Cu)-Cu_2O eutectic showing strong similarity with the observations made on remains and artefacts.

Keywords: Cu-Cu_2O eutectic, eutectic grain, rod-like structure

1. Introduction

Numerous archeological artefacts and remains containing metallic copper have been discovered in various sites all around the world revealing a Cu-Cu_2O eutectic. Some of these artefacts have been dated back to several thousands of years [1]. They all show a specific microstructure with a fibrous Cu-Cu_2O eutectic (Figure 1) surrounding dendrites of a primary phase that can be either (Cu) – the copper-rich fcc phase - or Cu_2O. This eutectic has been rarely studied. Eastwood [2] showed that the eutectic grains consist in densely packed fibers in the center, which bend and coarsen at the periphery. The similarity of these observations with the microstructure seen in the ancient artefacts suggested that laboratory experiments could help understanding the original metal process. This report presents preliminary results obtained within this line of thinking.

2. Experimental details

Pure copper (better than 99.9 wt%) was used to prepare two cylindrical samples 16 mm in diameter and 13 mm in height. These samples were placed in an alumina crucible designed to fit on a thermocouple and then introduced in a thermal analysis apparatus for remelting and solidification under ambient atmosphere. They were heated up to 1190-1200°C at 4.5 °C.min^{-1}, hold at that temperature for two minutes (sample 1) or one hour (sample 2), and finally cooled down to room temperature at the same rate of 4.5 °C.min^{-1}. Then, they were cut in halves, mounted for classical metallographic preparation, mirror polished and observed with optical microscopy.

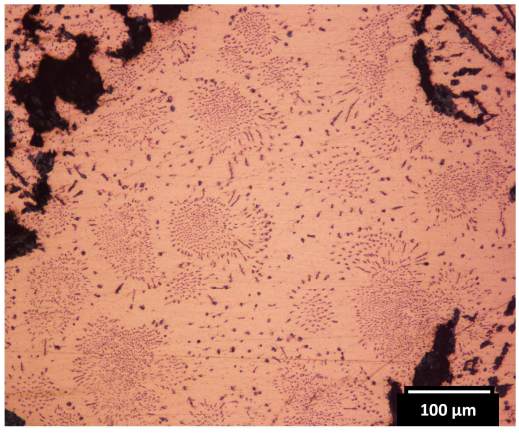

Figure 1: Micrograph of sample 360-4_6 from Bibracte.

3. Results

Figure 2-a shows the whole thermal records of the two samples where are also indicated the Cu-Cu_2O eutectic (1066°C) and the Cu melting (1085°C) temperatures according to Neumann *et al.* [3]. Examination of the heating records shows that the signals bent before a sharp decrease in temperature that must be associated to bulk melting. The first slope change occurred at 1066°C, *i.e.* the eutectic temperature. This suggests that some oxidation took place during the heating stage that led to incipient melting when the eutectic temperature was reached. It was verified with a third sample (not presented here) heated to 1066°C and immediately cooled to room temperature that its surface was effectively oxidized and this oxide may have led to an incipient melting at 1066°C.

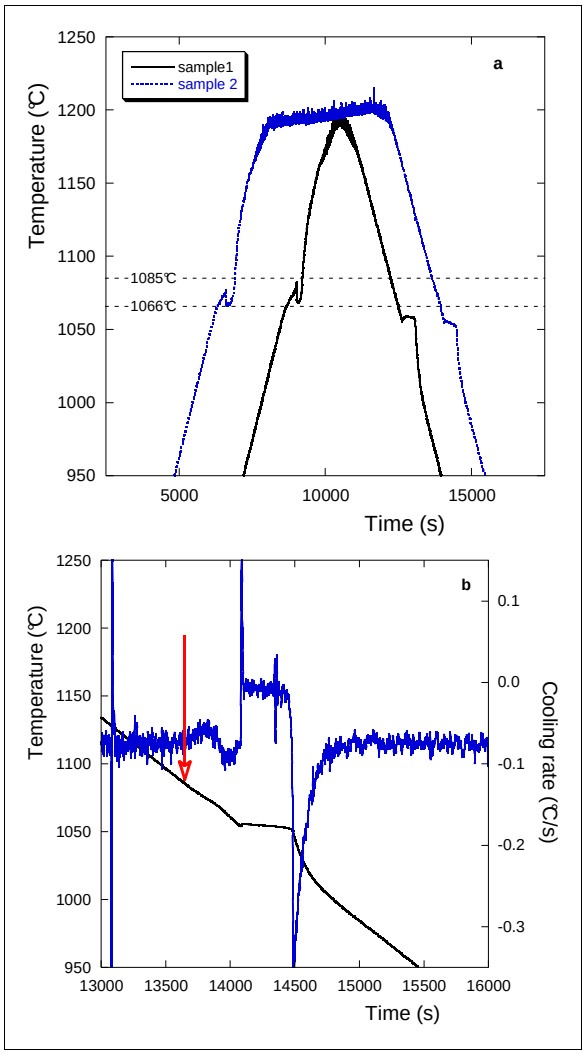

Figure 2: a) Heating-holding-cooling schedule of samples 1 and 2; b) enlargement of the thermal record on cooling of sample 2 and time derivative of the record showing the primary arrest starting far above the eutectic arrest as indicated with the downwards (red) arrow.

As the samples were further heated above 1066°C, oxidation proceeded until bulk melting occurred with the temperature falling back to nearly the eutectic temperature. This is certainly related to the fact the material was then saturated in oxygen. After a short while, the samples were fully liquid and their temperature started increasing again. During holding of sample 2 at the upper temperature, it is seen that the temperature increases from 1190°C to 1200°C when it should have been constant. This is supposedly related to heat release by further oxidation of copper.

Upon cooling, both curves exhibit a strong thermal arrest which must correspond to the eutectic reaction. It is marked by recalescence and a time plateau of about 5 min at a eutectic undercooling of 8 and 11°C for samples 1 and 2 respectively. The time-derivative of the temperature record did not show any thermal effect for sample 1 but did for sample 2 as seen in figure 2-b where the start of the primary arrest is indicated with the downwards arrow.

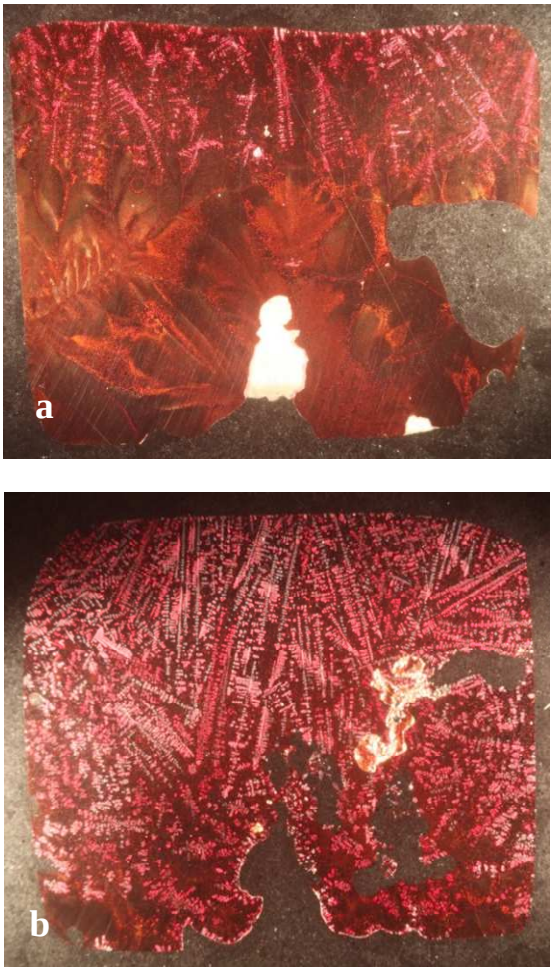

Figure 3: Bright field light microscopy macrographs of the vertical section of samples 1 (a) and 2 (b). The samples were 16 mm in diameter.

Figure 3 shows bright field light macrographs of the samples. The hole in the middle of the bottom was the location of the thermocouple while the many other cavities formed during the melting/solidification process. This latter feature seems to correlate with the presence of a huge amount of voids in ancient copper ingots [4]. Both

samples reveal a hyper-eutectic structure with cuprous oxide dendrites emanating from the top surface and filling half the samples. Furthermore, equiaxed Cu_2O dendrites are seen in the bottom half of sample 2 while none appears in sample 1. Instead, one can see in sample 1 a structure of grains emanating from the thermocouple hole in the central area.

Figure 4 compares the microstructure of the upper surface of both samples. This clearly shows that sample 2 (Figure 4-b) contained much more oxygen than sample 1 (figure 4-a) when cooling was initiated and Cu_2O dendrites started growing inwards. Accordingly, there is much more Cu_2O-Cu eutectic in sample 1 than in sample 2. Also, the formation of equiaxed Cu_2O dendrites at the bottom of sample 2 (figure 2-b) indicates that the remaining liquid became supersaturated in oxygen with respect to the Cu_2O liquidus at some stage of the cooling process.

Figure 4 shows also that Cu_2O dendrites are enveloped with a thick halo of fcc (Cu) solid solution, *i.e.* that the coupled eutectic is not initiated at the Cu_2O/liquid interface but at the (Cu)/liquid interface. This is in line with the fact that (Cu) seems needing a significant undercooling for nucleation as already reported by Eastwood [2]. It may be stressed that this microstructure is highly similar to the one seen in archaeological artefacts.

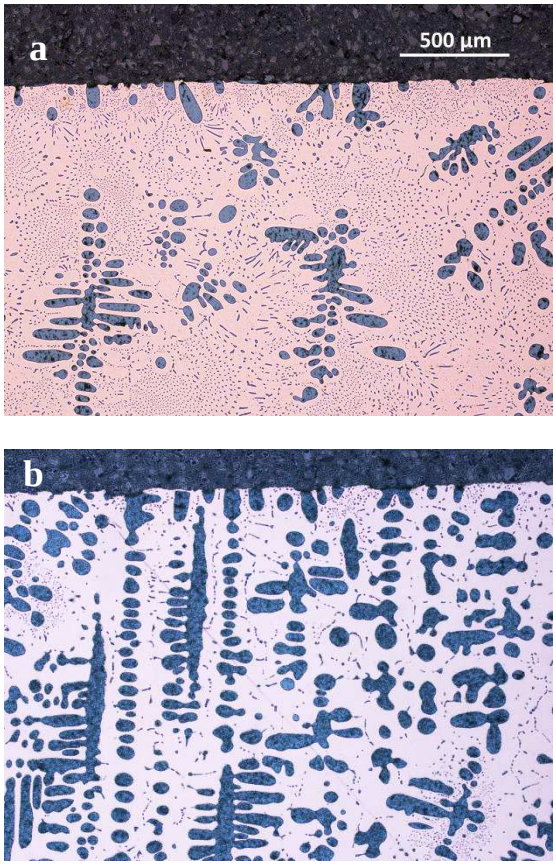

Figure 4: Low enlargement optical micrographs showing the top-surface microstructure of samples 1 (a) and 2 (b). The same scale applies to both micrographs.

When the eutectic develops, the composition of the liquid evolves because of rejection of oxygen from (Cu). During recalescence, the oxygen content in the liquid in equilibrium with Cu_2O increases while that of the liquid in equilibrium with (Cu) decreases. Due to the shape of the Cu-O phase diagram, this latter quantity is much higher than the former one. Further, because recalescence is very rapid, it may be suggested that this oxygen is prone to transform to gas. Though the oxide shell around the metal is porous, it certainly limits its exhaust so that there can be a pressure build-up in between the metal and the oxide shell. According to the assessed Cu-O phase diagram [3], a recalescence of 2°C as seen in figure 2 corresponds to a difference in composition along the (Cu) liquidus of 0.2 at.%. For a sample of 2600 mm^3, this corresponds to $3.3 \cdot 10^{-4}$ moles of oxygen gas. At 1330 K, this would correspond to a pressure of 2 MPa, which is certainly sufficient to lead to some creep of the Cu_2O crust and deformation of the sample [4]. Hence the cavities seen systematically on the samples as illustrated in figure 3, which give the material an aspect very much alike that noticed on Cu ingots [5].

The other important feature shown by the macrograph of sample 1 in figure 3 is the grain structure emanating from the bottom of the sample. These are eutectic grains which nucleated at the bottom surface and invaded the bulk sample from bottom to top. Figure 5 shows the eutectic structure at the bottom of sample 1 where it can be seen that it is much finer than at the top of the sample (compare with the micrograph in figure 4, top row). This is in line with a development of the eutectic from the bottom to the top of sample 1 with a decreasing growth rate leading to increased coarseness of the microstructure.

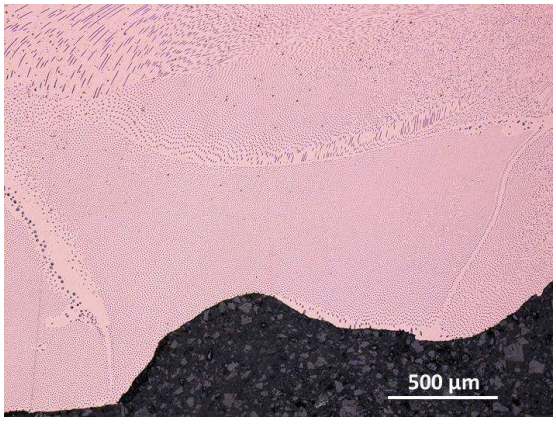

Figure 5: Micrograph of the bottom part of sample 1.

Such a grain structure cannot be evidenced in the macrograph of sample 2, figure 3. However, figure 6 shows that the eutectic structure is again much finer at the bottom than in the middle of this sample, suggesting the eutectic developed also from bottom to top.

A last feature of the Cu-Cu_2O eutectic that has already been stressed by Eastwood [2] is that the rods seen in the middle of the eutectic grains often bend and appear elongated on the outer grain boundaries. This is illustrated in figure 7. This suggest that Cu_2O rods changed their

crystallographic orientation during eutectic grain growth so as to remain perpendicular to the eutectic front at grain boundaries [6,7].

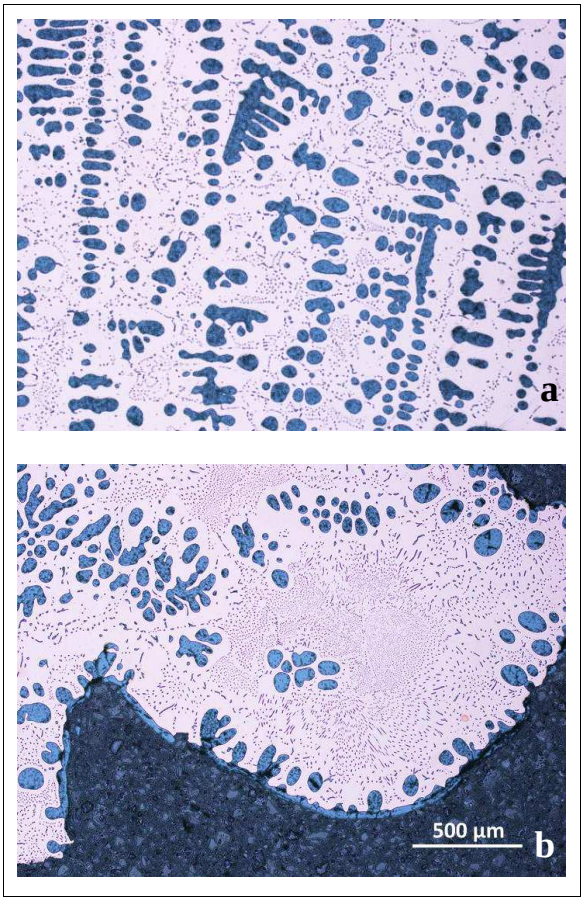

Figure 6: Micrographs showing the eutectic in the middle (a) and the bottom (b) parts of sample 2. The same scale applies to both micrographs.

4. Conclusion

Solidification of oxidized copper samples showed the development of Cu_2O dendrites followed by (Cu)-Cu_2O eutectic. Thermal analysis demonstrated this latter appears with significant undercooling and some recalescence. It is proposed that this recalescence leads to gas exhaust from the sample in a quantity that is sufficient for explaining the observation that samples show large voids.

These results correspond well to archaeological observations revealed on copper-based remains as detailed for example by Thoury et al. [1] and Haupmann et al. [5]. It is interesting to notice that the Cu-Cu_2O eutectic can be considered as a process marker of copper melting in aerated environment in relation with a precise thermal indicator. This approach opens a way to new considerations about smelting and melting copper since the beginning of the metallurgy.

References

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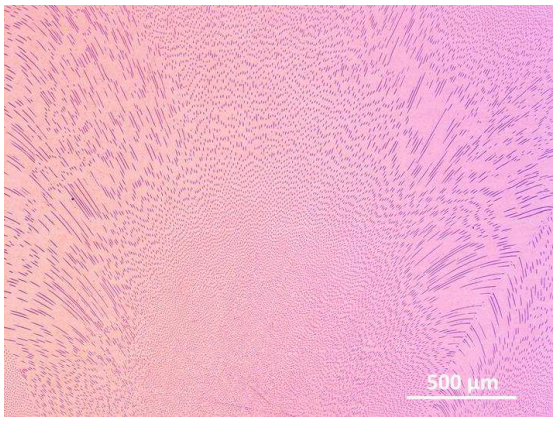

Figure 7: optical micrograph illustrating the rotation of Cu_2O rods during eutectic grain growth (sample 1).