Void Formation due to Oxidation in a Copper-Chromium Alloy

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Void formation during oxidation of copper-0.8% chromium alloy in air was observed both by optical and by scanning electron microscopes. The voids formed predominantly within the grains before extensive intergranular oxidation occurred. Void formation is explained on the basis of vacancy injection into the metal during oxidation. Possible explanations for voids being present within the grains are discussed.

High temperature oxidation of metals can introduce vacancies into the metals; this occurs for metals such as nickel, cobalt and copper. The vacancies thus created may condense into voids at metal/oxide interface. This has been observed since the early work of Carter and Richardson on oxidation of cobalt as discussed by Kubaschewski et al(1). The effect of excess vacancies in the metal has been elucidated by more recent studies. Firstly, the vacancies may be annihilated by migration to dislocations, leading to climb processes; for instance, Dobsen et al have observed the increase in dislocation loop radius in zinc during oxidation(2). Secondly, vacancies can form voids at the grain boundaries (cavitation)and at grain triple junctions(3,4). Thirdly, vacancies can condense into voids within the grains. The void formation has been extensively studied for nickel and nickel-chromium alloys. The voids were observed both at grain boundaries and at grain interiors(4). The formation of voids in copper during oxidation was observed and identified as a source of stress(3).

The present study is devoted to a study of void formation during oxidation in air for copper-0.8% chromium alloy. Copper forms oxide (Cu_2O and CuO) by outward migration of copper ions from metal/oxide interface to oxide/gas interface(5). The introduction of vacancy into the metal can lead to voids near the metal/oxide interface. Further, in the case of copper-chromium alloy, the selective oxidation of chromium can occur with formation of Cr_2O_3 in the subscale (internal oxidation). Formation of Cr_2O_3 near the metal/oxide interface can interfere with the void formation. The present study is aimed towards understanding the mode of voids formed in copper-chromium alloys.

EXPERIMENTAL

The alloy was prepared by melting and casting rods with nominal composition of copper with 0.8% Cr. The rods were subsequently hot forged and cut into square specimens of 20x20 mm area and nearly 10 mm thickness. The specimens were mechanically polished for metallorgraphic exmination. The were oxidised in air in an electrical muffl furnace maintained at specified temperatur +0.5°C. After oxidation, the specimens wer cooled to room temperature. The oxide layer o scale spalled during cooling (due to diffrentia contraction). The surface was again lightl polished with alumina and observed both unde optical as well as scanning electron microscope Specimens were etched with a 3M $FeCl_3$ solution The void size and density (no. of voids/cm²) wer measured.

The selection of temperature and time of oxidatio is of considerable importance since high temperatures and longer times lead t intergranular oxidation while lower temperature did not result in voids that could be observed.

RESULTS

Preliminary experiments were made by oxidising specimens at 800°C for one hour. Voids could not be observed in the microstructure. Further trials showed that voids could be observed at 875°c. Therefore, all experimental runs were made at 875°C for various times, from 1 to 9 hours. (This temperature is 0.85 T_m where T_m is the melting point in °K. Such a high temperature is required for considerable vacancy migration in the metal). After one hour of oxidation, small voids could be observed (in the unetched condition) under SEM at 3600X. (Fig.1). Under optical microscope, the nearly spherical voids showed bright reflections from the bottom of the voids; there was no oxide or other particles in the microstructure. Oxidation for longer duration resulted in voids of greater size and larger numbers, as seen in Fig.2. In certain places, two voids coalescing into a larger void or with neck formation between the voids, could be seen. For these durations, voids were observed mostly inside the grains. The size and void density measured are given table 1.



Fig. 1 Scanning electron micrograph of the specimen aft er oxidation for one hour at 875°C, unetched condition (3600x).

TABLE 1

VOID SIZE AND DENSITY FOR OXIDATION AT 875°C

Time (hours)	Size of the void smallest (μm)	Size of the void largest (μm)	Void density (no/cm^2)
1	0.3	0.72	(not possible to measure)
3	1.25	4	1.19×10^5
7	0.75	6.75	1.61×10^5

Oxidation for a duration of 9 hours at 875°C revealed intergranular oxidation. Etching showed extensive oxidation at the grain boundaries and oxide particles within the grains, perhaps of Cr_2O_3. (Fig. 3).



Fig. 3 Optical photomicrograph of a specimen after oxidation for 9 hours at 875°C in etched condition.



Fig. 2 Optical photo micrograph of a specimen after oxidation for 7 hours at 875°C, in etched condition (400X).

DISCUSSIONS

The results show that the voids due to oxidation form mostly in the grain interiors in copper-0.8 chromium alloy. The size of the voids increases with oxidation time, to about 7μm. From the size of the voids, taking the dimeter of a vacancy to be 0.6 of the atomic diameter (due to relaxation of atoms surrounding a vacancy), calculation shows that, for void density of $10^5/cm^2$ with average size 3μm, the vacancy concentration corresponds to 2.8×10^{-2}. This figure appears reasonable for vacancy concentration leading to void formation(6).

Appleby and Tylecote observed voids in pure copper predominantly at grain boundaries and at grain triple points(3). They consider such voids as a source of stress. In contrast, the present work showed that voids are formed mostly in grain interiors in the copper-chromium alloy.

In this alloy, preferential oxidation of chromium with formation of Cr_2O_3 in the scale and formation of Cr_2O_3 in the sub-scale (internal oxidation) can occur (1). As noted earlier, the intergranular oxidation became extensive during oxidation for 9 hours at 875° C. Therefore, the formation of voids mostly within the grains instead of grain boundaries indicate that the grain boundaries may already be segregated with chromium or oxygen atoms. Thus, in alloys such as copper-chromium, void formation within the grains is more likely than along grain boundaries.

CONCLUSIONS

1. Voids were observed after oxidation at 875°C in Cu-0.8% Cr. alloy.

2. The void size is in the range 7μm and the void density is around $10^5/cm^2$.

3. The formation of voids due to vacancy condensation occurs mostly within the grains in this alloy.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance rendered by electron microscopy section of CECRI, Karaikudi. Anil and Srinivasan appreciate the encouragement and extension of facilities by the management of P.S.G. College of Technology.

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