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An Analysis of Kirkendall Effect in Cu-Ni Laminate Composites

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Abstract

Nucleation, growth, migration and coalescence of diffusion-induced pores in Cu-Ni laminate composites were observed. The pore structures were interpreted based on an analysis of Kirkendall porosity formation.

With the development of new engineered materials which may consist of several components, Kirkendall pore formation has been observed in materials with more than three components. For example, during heat treatment, porosity related to diffusion appeared in systems such as Nb_3Sn multifilamentary superconducting composites [1], nickel-base superalloys [2] and Ni-Cr-Al alloys [3]. To completely utilize the potential of new materials, a complete understanding of porosity formation is required.

The Kirkendall experiment with diffusion couples [4] demonstrated that the rate of diffusion of zinc is much greater that that of copper in alpha brass, and that the diffusion interface shifts to compensate at least partially for the difference in these rates. In general, if there is a difference in diffusivity between the two types of atoms in a binary solution couple, the element with the low melting point diffuses faster. Atoms from the low melting temperature component migrate toward the high melting temperature component.

As a result, the low melting temperature material loses mass, and voids, or pores, form.

Kirkendall pore formation has been observed in simple binary systems such as Cu-Ni couples [5–8], alpha brass sheets [5–9], Cu-alpha brass sheets [5, 8], nickel- or cobalt-coated beryllium powder [10], and Au-Ag couples [8]. It was concluded [5–9, 11] that pores result from the heterogeneous nucleation of supersaturated vacancies produced by the unequal diffusion flow of atoms. The nuclei could be dislocations [7], grain boundaries [7, 9], small voids [12] or inclusions [5, 6, 11, 12]. While porosity nucleation in the perfect lattice may be possible, Balluffi [5] pointed out that it seems almost certain that heterogeneous nucleation sites must be present since the supersaturation required for nucleation of pores in the perfect crystal is prohibitively high.

Barnes and Mazey [6] observed aligned pore formation in a Cu-Ni sandwich couple. However, other researchers [5, 8, 9] generally observed widely distributed porosity in Cu-Ni, alpha brass, and Cu-alpha brass systems. Seitz [12] stated that it is not clear why porosity varies so much from one specimen of a given material to another, or why porosity is more widely distributed in brass specimens than in Cu-Ni couples. The variation in porosity structure arising from the comparison of the various results was a result of the difference in test materials and conditions. To provide an insight into the differences between the various pore structures which have previously been reported, this study systematically interpreted the mechanisms of pore nucleation, growth and migration in Cu-Ni laminate composites during heat treatment in vacuum and under argon.

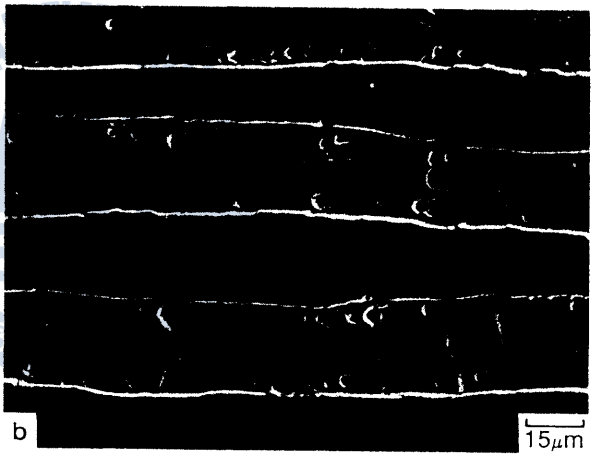
Cu–Ni laminate composite were fabricated [13] by hot and cold rolling compacts 32mm thick which consisted of 40 alternating layers of Nickel 270 (> 99.97% Ni) and Copper alloy C102 (> 99.98%) sheets with dimensions 0.4mm×100mm×150mm. The compact material was encased in a welded

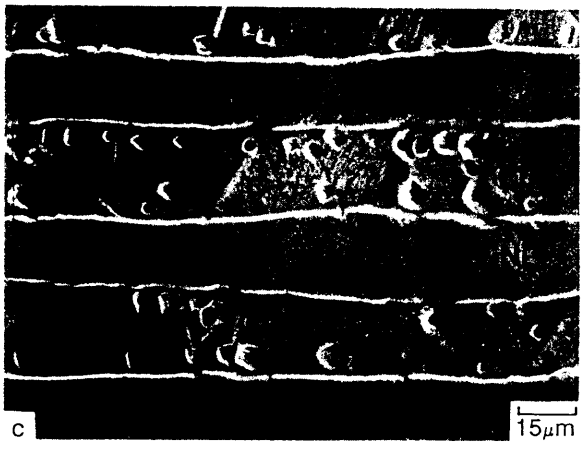
stainless steel can attached to an active vacuum system during annealing and was preheated before hot rolling at 870°C for 30 min.

The compact was hot and cold rolled to a final thickness of 1.65mm. The cold-rolled sheet consisted of layers 20μm thick and the interfaces between the layers were free of oxide particles.

Coupons were heat treated in vacuum and under argon at 1000°C for various lengths of time from 1 min to 24 h. Specimens for optical microscopy were prepared by mounting as-rolled and heat-treated samples and mechanically polishing them through 0.05 μm alumina. To enhance the appearance of the pores for the short annealing times, specimens were etched for 5–20s with a 50:50 nitric-glacial acetic acid solution.

The microstructures of the specimens heat treated





under argon (1 atm) and in vacuum are shown in Figs. 1 and 2 respectively. Samples heat treated in both environments exhibited extensive porosity in the copper layers.

Copper diffuses faster than nickel which is in agreement with the fact that the melting point of copper is lower than that of nickel. Thus, a net flow of vacancies occurs from the nickel-rich side toward the copper-rich side. This movement reduces the equilibrium number of vacancies on the nickel-rich side of the diffusion couple, while increasing the vacancy concentration on the copper-rich side. Once a critical vacancy concentration develops in the copper layers, pores form.

In addition to nucleation, Figs. 1 and 2 show that the pores are aligned in two rows in the copper layers. Furthermore, with an increase in the heat treatment time

Fig. 1. Light micrographs of laminate composites heat treated at 1000 °C under an argon atmosphere for (a) 1 min, (b) 5 min, (c) 10 min, and (d) 15 min. Etchant: nitric-acetic acid.

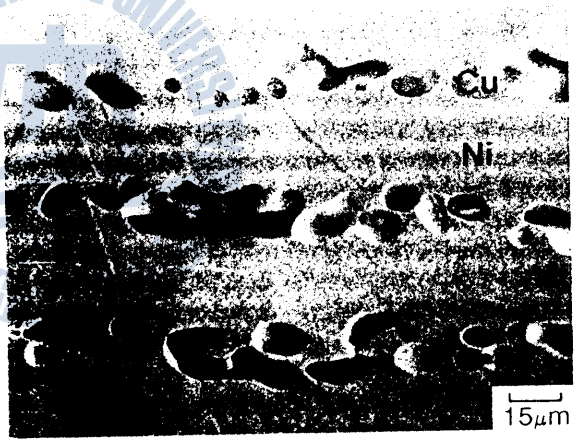


Fig. 2. Scanning electron micrograph showing pore coalescence in copper layers after heat treatment at 1000 °C in vacuum for 24 h. Etchant: nitric-acetic acid.

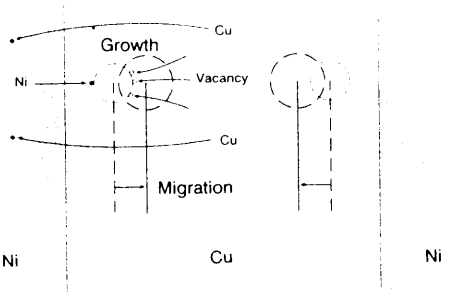


Fig. 3. Schematic diagram depicting pore growth and migration in the copper layer. Also shown are the relative movements of nickel and copper atoms and vacancies.

(1) the number of pores remains essentially constant, (2) the average pore diameter increases, (3) the spacing between the two rows of pores in a single copper layer decreases and (4) coalescence of pores occurs.

Figure 1(a) shows that the pores nucleate within the copper layer in distinct planes parallel to the interface. The location of the planes can be predicted based on an analysis of interdiffusion within a two–component system [14]. With interdiffusion, composition and flux gradients develop for both the copper and nickel atoms. The pores nucleate on a plane where there is a maximum loss of solute and which thus has the highest vacancy concentration. The position of this plane corresponds to the maximum curvature in the composition *vs.* distance curve for the element with the higher diffusivity and is where the second derivative of the flux with respect to distance is zero.

Once pores nucleate, the vacancies will not accumulate to nucleate new pores but will move to the existing pores to produce growth as shown in the schematic drawing in Fig. 3. Included in Fig. 3 are pores in the copper at two different times and the corresponding anticipated atom and vacancy diffusion paths. Pore growth can be explained [7] by the diffusion and adsorption of excess vacancies on the pore surfaces. The location of the maximum vacancy concentration will move away from the interface with increasing annealing time and will be between the two rows of pore nuclei. Vacancies will then diffuse to preferentially adsorb on the pore surfaces away from the Cu-Ni interfaces as shown in Fig. 3. In addition, nickel will diffuse to the side of the pore adjacent to the interface and copper will diffuse from the central portion of the copper layer to the nickel. As a result of vacancy adsorption and mass movement, the pore centers appear to migrate to decrease the spacing between the two pore rows which is consistent with the observation in Fig. 1. With long annealing times, the pores will eventually coalesce as shown in Fig. 2.

This letter has considered the nucleation growth, migration and coalescence of pores in Cu–Ni laminate composites. Barnes and Mazey [6] and Barnes [7] have also observed the formation of aligned pores but other researchers [5, 8, 9] observed widely distributed porosity. The reason that Balluffi and coworkers [5, 8, 9] observed widely distributed porosity is that they used thick diffusion couples with one layer of each material and long heat treatment times. As the couple was very thick, continued nucleation could occur during the long heat treatment and this allows for a wider dispersion of the porosity. In our study, pores were observed in less than 1 min. It is probable that Balluffi and coworkers would have observed similar results if they stopped the heat treatment after a very short time. In the present study, the fact that the pores formed in two rows in the copper layers after heat treatment for only 1 min strongly suggests that the supersaturation of vacancies at a particular location significantly influences pore formation.

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