

Nickel-Cobalt Diffusion Barrier Coating

By J.S. Russo

A study was initiated to determine the surface contamination of gold as a result of nickel diffusion through the gold grain boundaries. The oxidation of nickel in air, forming an oxide film on the surface of the gold, has been found to interfere with subsequent hermetic sealing of a ceramic package, resulting in non-wetting of the sealing surface. Auger Electron Spectroscopy (AES) profile analysis has shown that the diffusion of nickel through gold is suppressed when nickel and cobalt are co-deposited. It has also been found that an increase in cobalt concentration from 10 to 40 percent by weight did not further reduce the nickel diffusion.

High-temperature component application during fabrication of beryllium oxide (BeO) ceramic packages at 300 to 500 °C, has resulted in the diffusion of metal from an underlying deposit through grain boundaries to the outer coating. Consequently, some degradation has been experienced, because of surface oxidation during hermetic sealing of a package. To retard or minimize diffusion, a barrier layer is typically inserted between the package and the final gold deposit. Electrodeposited nickel, among other metals, has been shown to be a suitable barrier coating.¹ Electrodeposited nickel-cobalt, however, has been reported to act as a better thermal barrier than nickel.² It has also been reported that increased concentrations of cobalt in the alloy, as much as 40 to 60 percent by weight, minimized further the transport of nickel through the gold deposit.³

Nickel diffusion through grain boundaries in gold has been shown, in high-temperature applications (300 to 500 °C) to cause problems during lid sealing, using Au-Sn preform, of ceramic covers for hermetic requirements. The amount of nickel that diffuses to the surface and which then becomes oxidized, will subsequently cause poor wetting, as shown in Fig. 1. The ability of the gold surface to remain free of nickel oxide is essential to hermetic sealing.

It has been determined from earlier studies, that solderability is optimized when the nickel surface level is below 10 atomic percent. Above this concentration, additional surface preparation of the cover seal area is required to insure complete wettability and void-free sealing of the covers.

Experimental Procedure

Nickel and nickel-cobalt alloy was deposited from a sulfamate solution. Cobalt concentration for the various alloys was obtained by adjusting the cobalt content of the electrolyte, so that cobalt concentration of the alloy would vary from 10 to 40 percent. The cobalt content was maintained and quantitatively measured, using atomic absorption technique (A.A.). Alloy concentrations below 10 percent and above 40 percent cobalt were not considered during this investigation.

To control the nickel-cobalt content, it is necessary to control not only the composition of the plating solution, but the other parameters, such as current density, temperature, agitation, total metal and anode composition as well. Plating nickel-cobalt, as opposed to other alloys, is a more complicated process, because co-deposition is characterized by the anomaly that the less noble metal (cobalt in this case) tends to deposit preferentially.⁴ Special anodes are also necessary, or an anode for each metal in the deposited alloy, providing they are controlled by separate rectifiers. For this study, sulfur-depolarized nickel anodes were used and the cobalt content replenished from a cobalt sulfamate concentrate automatically, utilizing a commercial chemical feeder. Electrodeposited nickel-cobalt alloys were tested as a thermal barrier for nickel diffusion through gold. Surface characterization was conducted using AES.

The ceramic packages used for this study were initially measured after plating of nickel/gold and subsequently processed through a belt furnace for 30 min in air with a peak temperature of 450 °C. In an effort to simulate the thermal cycling conditions a package undergoes, the package was cycled five times through the furnace. AES surface analysis was conducted after each exposure and the atomic percent of nickel at the seal ring surface recorded after each exposure. Test packages with varying concentrations of cobalt were prepared, along with controlled stainless steel monitor strips, which were subsequently used to measure the cobalt content in the alloy plating.

From previous investigations,² it was determined that the barrier thickness should be maintained between 100 and 150 $\mu\text{in.}$, with approximately 200 $\mu\text{in.}$ of final gold. Plating thickness measurements were verified, using metallographic methods, according to ASTM B 487 (02.05).



Fig. 1—Diffusion of nickel to gold surface and subsequent oxidation.

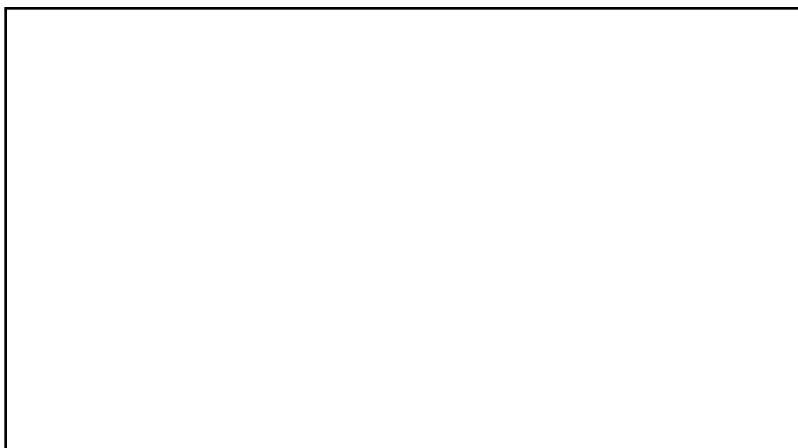


Fig. 2—Comparison of diffusion of nickel with nickel-cobalt alloy.

Verification of Cobalt Content of Deposits

Targeted Cobalt % by wt.	Actual Cobalt % by wt.	
	A.A.	EDAX
10	12	16
20	19	19
30	32	33
40	40	42

Results and Discussion

It was observed, during the initial study, that the cobalt content of the deposit increased with solution temperature and cobalt concentration, but decreased with increase in current density. In this investigation, the operating parameters were constant, with variations only in the cobalt concentration and nickel/cobalt ratios. The cobalt in the deposit was verified via the stainless steel strips and the cobalt content analyzed, using both atomic absorption and energy dispersive analytical X-ray (EDAX), as shown in the table.

The nickel-plated packages typically exhibited significant amounts of nickel on the gold surface. The amount of nickel measured was approximately 22 percent, following two thermal exposures, and leveled off to approximately 25 percent after five exposures, as shown in Fig. 2. Co-deposition of 10 to 40 percent cobalt was found to be significant in the reduction of diffused nickel. The experimental results suggest, however, that additions of as much as 40 percent cobalt do not provide additional reduction of nickel diffusion. The reduction appears to level off at approximately 10 atomic percent, as shown in Fig. 2. This 60-percent suppression of nickel diffusion ultimately resulted in reduction of void formation, with improvement of sealability of the cover to the package.

Conclusions

1. Based upon the above test results, this study has shown that nickel-cobalt is a more efficient thermal barrier to nickel diffusion than nickel alone.
2. Addition of 10 to 40 percent by weight cobalt resulted in reduction of nickel diffusion by 60 percent; however, within this range of cobalt content, the degree of nickel suppression is nearly constant, yielding no further reduction below 10 atomic percent of migrated nickel.
3. The investigation has also shown that codeposition of cobalt with nickel results in reduction of nickel diffusion to an acceptable level for ceramic packaging.

References

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