227
8-1-78

12. 301

MLM-2526

MASTER

**The Migration of Iron, Nickel, Cobalt
and Chromium Associated with Silver
Brazing during Ceramic-To-Metal
Joining**

**Don E. Etter, Eugene E. Egleston and
Ralph R. Jaeger**

June 30, 1978

Monsanto

MOUND FACILITY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

The Migration of Iron, Nickel, Cobalt and Chromium Associated with Silver Brazing during Ceramic-To-Metal Joining

MASTER

Don E. Etter, Eugene E. Egleston and Ralph R. Jaeger

Issued: June 30, 1978

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MOUND FACILITY

Miamisburg, Ohio 45342

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

Abstract

During the study of bond strengths of ceramic-to-metal seals under various brazing conditions, it was observed that the strength was affected by the length of time that the braze material was in the liquid state. Brazing times as short as 10 min sometimes adversely affected the strength of the seal. Photomicrographs of a typical weak bond clearly show silver braze penetration deep in the metallizing layer after 10 min at 20°C above the melting point of the braze. A reaction layer was also observed in the photomicrographs. Considerable iron has migrated from the Kovar pin through the silver braze and formed an interface between the silver braze and the molybdenum metallizing material. Significant concentrations of cobalt and nickel were also found in the reaction zone, indicating a diffusion reaction of Kovar through the silver. Further investigations showed that while braze durations as short as 1 min at 20°C above the liquid temperature gave much stronger bonds than 10 min did, significant migration of material was evident. In view of the significant migration of both the pin alloy and the braze material, it was concluded that brazing time and temperature should be minimized to achieve maximum bond strength.

Metallizing and brazing studies

During the course of developing satisfactory ceramic-to-metal sealing techniques for various designs of detonator headers now fabricated at Mound Facility, a great deal of effort was directed toward studying and developing hermetic ceramic-to-metal seals with relatively high bond strengths. Various metallizing formulations and brazing alloys were investigated and evaluated -- primarily by a standard tensile strength test, ASTM-F-19.

While studying bond strengths under various brazing conditions, it was observed that the strength was affected by the length of time that the braze material was in the liquid state. Sometimes, the strength of the seal was adversely affected by brazing times as short as 10 min. Figure 1 is a typical example of a weak bond. It clearly shows silver braze

penetration deep into the metallizing layer after 10 min at 20°C above the melting point of the braze. A reaction layer, which was subsequently examined by the Electron Microprobe X-Ray Analyzer (EMA), is also apparent in this photomicrograph.

The EMA examination included line scans and x-ray mapping for the following elements: aluminum, molybdenum, silver, iron, cobalt, and nickel. The resulting photomicrographs for each are shown in Figures 2-7, respectively. All of the above scans and mappings were done on the exact same location for direct comparison purposes.

Figure 2 shows the outline of the metallizing and ceramic interface when elemental aluminum, present as Al_2O_3 , was examined. The line scan also supports the aluminum location and intensity. The molybdenum metallizing location is defined in Figure 3. From both the line scan and the mapping, it is apparent that a reaction zone exists between the

molybdenum and the silver; and it has a low molybdenum concentration. The line scan for silver, Figure 4, revealed the above reaction zone is essentially void of silver. However, silver has obviously migrated across the reaction zone into the area previously identified as molybdenum. Since the sample shown was poorly metallized, this migration of silver into the metallizing zone is not surprising; for the specimen shown as the sample was only chosen to illustrate the problems that arise with a very porous metallizing layer.

Figure 5 depicts the location of iron. Somewhat surprisingly, considerable iron has migrated from the Kovar pin through the silver braze and formed an interface between the silver braze and the molybdenum metallizing. Similarly, Figures 6 and 7 are examinations of the other two elements in Kovar, namely, cobalt and nickel. These two elements are also found in significant concentration in the reaction zone, which indicates a diffusion reaction of the Kovar through the silver. In view of the relatively short 10 min braze time, this observation seemed phenomenal.

Similar results were observed when alumina-to-stainless steel (21-6-9) was fabricated with Nicusil-3 (27-Cu, 72.25-Ag, 0.75 Ni) braze. The results showed that chromium, along with iron and nickel, would diffuse through the braze material. Further investigation showed that while braze durations as short as 1 min (at 20°C above the liquid temperature) gave much stronger bonds than 10 min, significant migration of the above materials was still evident.

The mechanism for the formation of the reaction zone is not obvious. Clearly there is some reaction or extraction of

these elements from the Kovar pin by the braze alloy followed by diffusion or migration of some sort to the molybdenum metallizing. If solid solubility were the driving force, the molybdenum would migrate toward the Kovar because it is considerably more soluble in silver than in iron, nickel, and cobalt. However, the data show no evidence of molybdenum migration; and a considerable amount of additional work must be performed to define the mechanistic aspects.

In closing, it was not the authors' intent to discuss mechanism, but to elucidate potential problems which could affect the physical and mechanical characteristics of ceramic-to-metal joining and sealing.

In view of the significant migration of both the pin alloy and the braze material, it was concluded that brazing time and temperature should be minimized to achieve maximum bond strength.

FIGURE 1 - Cross section of an alumina-to-Kovar pin seal using silver braze and molybdenum-manganese metallizing.

FIGURE 2 - EMA examination of alumina-to-Kovar pin seal for aluminum (2000X).

FIGURE 3 - EMA examination of alumina-to-Kovar pin seal for molybdenum (2000X).

FIGURE 4 - EMA examination of alumina-to-Kovar pin seal for silver (2000X).

FIGURE 5 - EMA examination of alumina-to-Kovar pin seal for iron (2000X).

FIGURE 6 - EMA examination of alumina-to-Kovar pin seal for cobalt (2000X).

FIGURE 7 - EMA examination of alumina-to-Kovar pin seal for nickel (2000X).

Distribution

EXTERNAL

TIC-4500, UC-25 (227)

R. K. Flitcraft, Monsanto Research Corporation

D. F. Griffing, Miami University

R. M. Munson, DOE/Dayton Area Office

G. W. Powell, Ohio State University

Technical Report Library, St. Louis

INTERNAL

R. T. Braun

E. E. Egleston

D. E. Etter

C. W. Huntington

R. R. Jaeger

L. V. Jones

J. R. McClain

H. L. Turner

Library (15)

Publications