INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600

DIRECT BONDING OF METALS TO CERAMICS: INTERFACE INVESTIGATIONS

by

Victor Curicuta

A DISSERTATION

Presented to the Faculty of
The Graduate College at the University of Nebraska
Fulfillment of Requirements For the
Degree of Doctor of Philosophy

Major: Interdepartmental Area of Engineering
(Chemical & Materials Engineering)

Under the Supervision of Professor Dennis R. Alexander

Lincoln, Nebraska

August, 1998

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

DIRECT BONDING OF METALS TO CERAMICS: INTERFACE INVESTIGATIONS

Victor Curicuta, Ph.D.

University of Nebraska, 1998

Advisor: Dennis R. Alexander

There is a growing interest in metal/ceramic bonding for a wide range of applications from electronic packaging to biomedical implants. In this research work, results are reported for direct bonding of copper to ceramic (e.g., Al_2O_3 and ZrO) in a furnace under inert atmosphere (e.g., N_2 and Ar_2). Other, metals such as Cu, Ni, SS-316 were directly bonded to ceramics (e.g., α-Al_2O_3, sapphire) using laser heating (e.g., 247 nm and 10.6 μm wavelengths) in the presence of N_2 atmosphere. Cu flakes have bean bonded to industrial alumina ceramic and sapphire in the presence of methyl, ethyl and isopropyl alcohols using a CO_2 laser. All these experiments were performed by heating the metal or metal-organic media member for a sufficient time in order to create a metal-metal oxide eutectic melt at the interface with the ceramic substrate.

Thermal wave imaging (TWI) was used to investigate the bonding at the metal/ceramic interface. It was found that the method of direct bonding of metals to ceramics using lasers performed better than the furnace. The properties of the copper bonded layer on alumina ceramic was investigated using scanning electron microscopy (SEM). Also, the elemental distribution at the metal/ceramic interface was analyzed, using energy dispersive x-ray spectroscopy (EDS). With the help of x-ray diffraction (XRD), the phase present at the copper/industrial alumina ceramic interface was determined to be $CuAl_2O_4$. This was different from the $CuAlO_2$ phase found at the copper/sapphire interface for the furnace

bonding case. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) was also used to investigate the aspects of metal/ceramic interfaces. It was found that the samples processed by furnace heating and by laser beam heating have a diffused transition interface. The electron diffraction patterns revealed the phase present at the interface (Cu/α-Al_2O_3) to be a cubic one, with the $CuAl_2O_4$ crystallographic structure. The TEM images show that the samples heated using excimer laser have an amorphous top copper layer. The HRTEM images of the samples heated with the excimer laser beam under N_2 atmosphere revealed that the inter-atomic spacing at the Cu/α Al_2O_3 interface region to be 0.365 nm in average. In order to investigate inter-diffusion between the copper layer and the sapphire and also to measure the percentage of diffused of copper in sapphire, Rutherford backscattering spectroscopy (RBS) was performed. Based on heat transfer theory and on diffusion theory, a model was derived to explain and predict the behavior of furnace and laser beam bonding of metals to ceramics. The predictions of the model were in agreement with the experimental percentage values of diffused copper in sapphire obtained in the RBS investigations. Experimental investigations and the theoretical model concluded that the direct bonding phenomenon is a thermal effect. The direct bonding phenomenon is similar to transient liquid phase bonding (TLP). The major advantage of direct bonding is that no filler element is required between the metallic member and the ceramic substrate. Finally, the method of direct bonding of metals to ceramics using laser beam is capable of directly drawing a metallic pattern on a ceramic substrate.

Acknowledgments

I like to dedicate this work to Ilinca (Coca) and Nolan.

I am deeply indebted to many individuals for their help in the completion of this work. Without their help this dissertation could not have been completed.

I would first like to thank my advisor, Dr. Dennis R. Alexander, for his support and advice. Also, I wold like to thank, Dr. Robert J. DeAngelis and Dr. Brian W. Robertson for their help, advice and discussions. For the RBS investigation which was performed at the California Institute of Technology, I appreciate the help of Dr. E.A. Kolawa and S. Gasser. I would like to thank to Dr. Dana E. Poulain for computer debugging help and information. I am indebted for the help and discussions regarding Matlab software to Joseph K. Krause. I appreciate the help of Dr. Yi Liu with the TEM and HRTEM. I want to thank to David Doerr and Mark Rohlfs for their helpful discussions and with computer work. I appreciate the help of Nek Debry with the sputtering work. Credit should be given to Brian E. Jones for x-ray diffraction assistance.

Preface

The purpose of this dissertation is first to improve furnace bonding of metals to ceramics and to introduce a new method using a laser for heating. The second objective is to investigate and characterize the direct bonding interface phenomenon by comparing the furnace direct bonding with that obtained by direct laser bonding. In order to characterize the interface, the studies include: thermal wave imaging (TWI), x-ray diffraction (XRD), scanning electron microscopy (SEM), electron disperse x-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectroscopy (RBS) methods. A computer model based on heat transfer and diffusion phenomena was developed to help interpret the metal/ceramic interface diffusion and bonding phenomenon. Supporting information has been included as appendices.

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

Understanding the relationship among processing, phase structure, and properties of the metal/ceramic interfaces is becoming increasingly important as performance requirements demand the use of metal/ceramic composites in applications such as electronic devices, high temperature aircraft structures, and biomedical implants. In metal/ceramic composites, the overall composite properties depend critically on the properties of the metal/ceramic interface. Also, in recent years lasers are used in manufacturing plants for ablation, cutting and welding, and become more competitive with traditional manufacturing method systems. There also appears to be an advantage in using a laser in the metal/ceramic bonding process.

1.1 Problem Foundation

The original justification for this work came from a need to improve and to understand the metal/ceramic bonding process. In this work the improvement of directly bonding of metals to ceramics was studied by using a simple inert atmosphere during the bonding process. This study also includes a rapid and accurate bonding method using laser beam heating with an inert atmosphere. Finally, to understand the metal/ceramic interface reaction phenomenon samples from both the furnace and laser processes were investigated using non-destructive techniques such as thermal wave echo imaging (TWI), scanning electron microscopy and transmission electron microscopy (SEM, TEM), x-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS) methods.

1.1.1 *Direct Bonding of Metals to Ceramics*

The method of direct bonding of metals to ceramics was first implemented in the 1970's by Babcock et al.[1] and has undergone minor changes as the technology has grown. The basic process comprises placing a metal member such as copper in contact with a non-metallic substrate such as alumina and then heating in a furnace to a temperature slightly below the melting point of the metal (e.g., between approximately 1,065 °C and 1,080 °C for copper). Heating is performed in a reactive gaseous atmosphere, such as an oxidizing atmosphere, for a sufficient time to create a metal/metal oxide eutectic melt, in the copper/oxygen case (see Fig. 1.1), which upon cooling bonds the metal to the substrate. Gas flow rates used are approximately two cubic feet per hour of an argon-oxygen mixture with an oxygen content of approximately 0.04 molar per cent[2] or between 0.01 and 0.5% a.w.[2] The big problem was the oxidation and precipitation of copper oxide in the bonded member. To eliminate this problem, it was proposed to heat the copper and ceramic in a vacuum at a pressure no greater than one millibar and a partial oxygen pressure between 0.001 and 0.1 mbars, with the oxygen pressure under 0.005 mbars at the time of cooling.[3] This, however, requires expensive equipment, control over the oxygen partial pressure, and, moreover, it could limit mass production.

Nobuyuki et al.[4] proposed a method that employed the heating of SiN, SiC (4% YrO, 4% Al_2O_3) and AlN (2% YrO, 2% Al_2O_3) in an air atmosphere furnace to produce an oxide layer. On top of this oxide layer an electrolytic tough pitch copper (300-500 ppm oxygen) can be directly bonded by heating in a furnace at 1,075 °C under a nitrogen gas atmosphere.

Information regarding Akihiro et al. work[5] was received long after the first successfully experiments of direct bonding of copper to alumina ceramic under inert atmosphere, were performed. Their patent idea was that the oxygen contained in the copper member (in a range of 150 to 600 ppm) alone can promote direct bonding of copper to alumina ceramic layer.

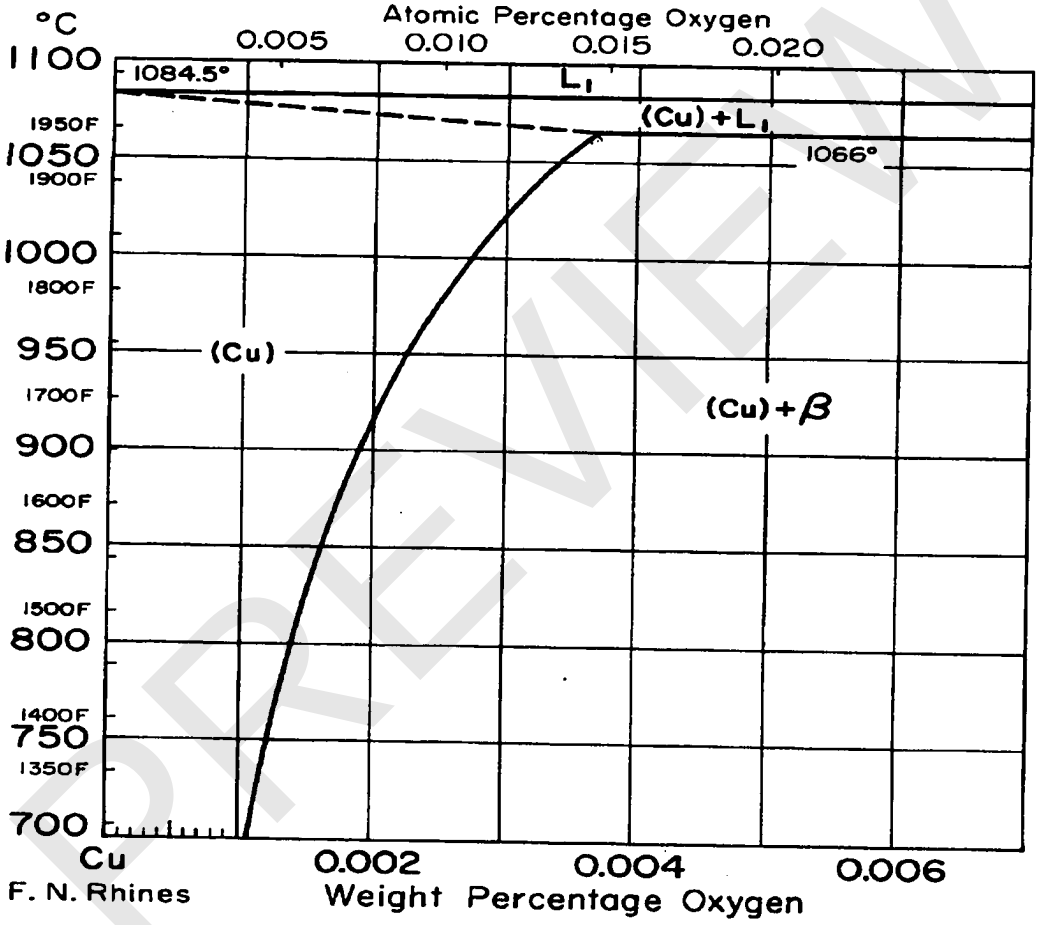

Figure 1.1: Phase diagram of the Cu - O system.