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**HIGH-STRENGTH, LOW-TEMPERATURE BONDING OF
BERYLLIUM AND OTHER METALS**

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HIGH-STRENGTH, LOW-TEMPERATURE BONDING OF BERYLLIUM AND OTHER METALS

ABSTRACT

I conducted an investigation to determine the feasibility of techniques for bonding beryllium as well as other metals at low temperatures and to establish the relationship of the bond parameters to the bond strength. This study was guided by the following conditions:

1. bonding temperature should be less than 600°F,
2. plastic deformation of the parent metal should be minimized,
and
3. the bond should be nearly as strong as the parent metal.

The final condition, that the bond be nearly as strong as the parent metal, was intended to apply to type S 200 C beryllium. Most of this study concerned beryllium, but made additional tests on molybdenum, stainless steel, tungsten, and commercially pure copper.

It was established early in the investigation that bonds could not be accomplished within the required temperature range and with small parent metal distortion without the use of an intermediate material. Consequently, all the results reported herein are for specimens with a plated dissimilar metal, generally silver, on the surfaces being joined. A special cleaning treatment was required after this second material was applied.

I studied bonding atmospheres varying from a vacuum of 2×10^{-6} Torr to helium, oxygen, and air. These widely differing bonding environments have no significant influence on bond strength.

Variations in the bonding procedure, with a consequent resulting difference in strengths obtained, lead to the conclusion that the elastic strain energy in the substrate acts to destroy some portion of the bond by fracturing a portion of the bond area.

For a fixed applied bonding compressive stress, bond strength increased when the modulus of elasticity of the substrate was increased. The thickness of the intermediate material was also significant in determining bond strength for the same processing conditions. When the plating thickness was varied from 35 $\mu\text{in.}$ to 200 $\mu\text{in.}$, the bond strength was approximately doubled.

The presence of the plated material and the subsequent preparation of the surface resulted in a very small notch in the surface of the specimen at the bond interface. When this imperfection was removed after bonding, the bond strength was again almost doubled.

Data from beryllium tests show that a partial bond was formed at a temperature of slightly less than 225°F. At 280°F, bond strengths in beryllium can be obtained approaching that of the bulk material with a plating thickness of approximately 200 $\mu\text{in.}$ Also, bond strength increases linearly with increased applied bonding compressive stress. This result fits the adhesion model of bonding.

It may be concluded from this study that bonds that exhibit beryllium fracture strength (40 ksi) and that have been especially prepared after plating can be made at 225°F on plated beryllium. The data also invalidate a conclusion reached by at least one other

investigation that the minimum theoretical temperature for such bonding is 390°F.

Experimental data obtained from this investigation indicate that an adhesion or cohesion model is the bonding mechanism. This conclusion is based on the linear relationship of the bond strength to bonding compressive stress and the independence of bonding time.

Bond strengths are very dependent upon the thickness of the plating; the strengths increase with increasing thickness up to 600 μ in.

INTRODUCTION

Background

The most common methods for joining metals may be classified as mechanical and metallurgical. The latter category may be further divided into liquid and solid-state joining. Fusion welding is a typical example of the former, diffusion bonding the latter, while brazing involves both.

Fusion welding and brazing are the most common techniques employed because they are the most economical. Not all applications lend themselves to these techniques, however. Fusion welding is not normally used to join dissimilar metals having widely differing properties. In addition, because of the high temperatures used, unfavorable metallurgical changes often occur in the materials welded and high residual stresses may lead to distortions or even failure of the structure. Many similar and dissimilar metal couples can not be brazed for lack of a braze material which will adhere to or "wet" the metals. Again, relatively high temperatures are required, which may lead to degradation of the material properties and physical distortion of the structure arising from thermally induced stresses. The necessary high temperatures also limit the selection of materials which may be used in the vicinity of the weld. Beryllium, for example, is used quite extensively in inertial guidance instruments. Many nonmetallic components used inside these instruments are not able to survive the temperatures used to braze or weld the assembly. Thus, mechanical joints that increase the weight of the system are used—a very undesirable feature for most inertial guidance applications.

Some of the disadvantages associated with liquid-phase joining can be overcome by solid-state bonding. This process is, by definition, the joining of materials at temperatures less than the melting temperature of the materials involved. Many techniques exist for solid-state joining and equally as many terms have been coined to characterize these techniques. Forge, deformation, pressure, friction, ultrasonic, adhesion or cohesion, recrystallization, diffusion, solid-state, and solid-phase welding are just a few of the terms used to characterize the welding techniques and mechanisms used.

Although the time, temperature, and bonding environments necessary to achieve good bonds vary considerably with the technique used, there is one common parameter: the interfaces to be joined must be brought into intimate contact. The load necessary to achieve this will depend upon the surface finish and flatness of the bond interfaces as well as the mechanical properties of the materials and will also vary with the bond technique. The interrelationship of the bond parameters and material properties are so complex that none of the bonding techniques have been thoroughly analyzed. A discussion of all the solid-state bonding processes is unnecessary in this report because many do not apply to the problem investigated herein.

Voluminous literature now exists on solid state bonding beginning with the first scientific observation of adhesion by Desaguliers in 1725.¹ However, there was relatively little activity in the field until the mid 1930's. Since that time many techniques have been developed for solid-state bonding. A comprehensive report on the subject has been published by Tylecote² and Milner and Rowe.³

The technique by which the bonds were formed in this investigation involved compressively loading the bond interface surfaces at some temperature for a period of time. The three general areas that will be discussed are 1) pressure and deformation bonding, 2) diffusion, and 3) adhesion (or cohesion). The first refers to a bonding technique, whereas the latter two may be classified as bonding techniques or mechanisms, or both together. These three areas are interrelated, and much of the discussion found in one area may apply equally as well to the others.

Pressure and Deformation Bonding

Solid-state bonding can theoretically be achieved between two atomically flat, perfectly clean surfaces by bringing the surfaces into intimate contact. The bond thus formed would result from the interatomic forces of the atoms on either side of the interface. In practice neither of the requirements, atomically flat and perfectly clean, can be achieved. Real surfaces are very rough atomically, and the surfaces are contaminated with physically and chemically adhered films.

Solid-state bonding is accomplished by loading the interfaces in such a manner as to achieve intimate contact at the interface. This can be accomplished by deforming the interfaces to break up the surface films and dispersing them outside the interface such as in ultrasonic, friction, and upset bonding or by applying sufficiently large loads to deform the interface and break through the surface films as in pressure or deformation bonding. Prior to 1946 elevated temperatures were used for pressure bonding and the surface films were

believed to be dispersed by diffusion.⁴ Sowter found that high-strength joints could be made at room temperature by very large deformations.⁵

Many factors influence the pressure joining of metals. Some of these are deformation and bond pressure, bond temperature, surface preparation, metal purity, solubility of the surface films, mechanical properties of the metals joined, relative motion at the bond interface, lattice structure, prior cold work, and the bond time. The following discussions will emphasize the results of work performed on silver, when available, and implications relative to this investigation will be noted. The reason for emphasis on silver will become evident in a later section "Selection of Intermediate Bonding Metal."

Deformation and Bond Pressure

There exists a threshold value of deformation for each metal above which bonding occurs. Tylecote et al. reported the threshold deformation for degreased and wire-brushed silver as 80% at room temperature for circular tools, although their data show some strength at deformations as low as 20%.⁶ Vaidyanath et al. showed that threshold deformation was related to the tool configuration and that the strength of roll-bonded aluminum and copper sheets as measured in increments along the width of the sheet was related to the roll-bonding pressure.⁷

Tylecote⁶ believed that the threshold deformation was an indication of the interfacial extension necessary to cause break-up of surface oxides, but he discarded this concept when Williamson and Tripp⁸ showed that the interfacial extension to rupture surface oxides

was much less than that which corresponded to the threshold deformations. Tylecote's revised concept is that large deformations (or pressures) are necessary to make the bond at areas of virgin metal where the oxide films have broken or to prevent breaking the embryonic welds so formed (p. 27).² He attributes the breaking of embryonic bonds to the release of elastic stresses.

The influence of selected surface contaminants on the deformation required for seizure is reported by Semenov.⁹ Aluminum coated with oleic acid was joinable with sufficiently large deformations. Thus, the threshold deformation may be related to relatively mobile surface films, such as adsorbed gasses, that prevent bonding after the oxide films have been broken.

Presently there is no answer to the above implication as to whether the localized pressure or the localized interfacial deformation is responsible for the bond formation. Ludemann¹⁰ has achieved strong bonds at elevated temperatures through oxide films where the metals were constrained so that no general deformation occurred; and Dowson¹¹ bonded silver at elevated temperatures in a constrained die, which practically eliminated any deformation. Results of Butts and Van Duzee¹² in the deformation (25%) bonding of silver were reported by Dowson to be in good agreement with his data. McEwan and Milner, in the roll bonding of metals, pinned the plates to be bonded such that no interfacial movement was possible.¹³ The threshold deformation was not changed and they assumed pressure to be the basic parameter in forming a weld.

In summary, there appears to be some question as to the role that deformation plays in pressure bonding. The controlling parameter may very well be interfacial pressure.

Temperature

The amount of deformation necessary for seizure decreases with increasing temperature. At high temperatures the bond may be developed by diffusion, as discussed later. The dissociation of metallic surface compounds and the evaporation or dissociation of physically and chemically adsorbed films at higher temperatures may also be expected to reduce the deformation required to achieve metal-metal contact across the bond interface. Pure silver, pressure bonded in oxygen-free argon by Semenov,⁹ required a deformation of seizure of 83% at -300°F, 53% at 300°F, and 5% at 840°F. An inflection in the curve at approximately 330°F may be related to the change in the mechanical properties of silver as described later.

Tylecote demonstrated that by subjecting silver to a heating cycle that dissociated the oxide film prior to room-temperature pressure bonding, a decrease in the required deformation was realized.¹⁴ Parks pressure bonded 1/16-in. silver sheet with a 1/8-in.-diam heated die.¹⁵ The deformation was controlled to a 5 to 10% thickness change, and the bond surfaces were prepared by diamond scraping. Bond temperatures at 250°F and above produced bulk-strength bonds. He argued that the bond formation for pressure joining was one of recrystallization, although he showed no metallographic evidence to support this theory. Ainbinder and Klokova convincingly refuted the necessity for recrystallization in pressure bonding by computing

the maximum temperature rise developed by adiabatic compression and noting that pressure bonds are frequently made with materials at temperatures, ambient plus heat generated, much less than the recrystallization temperature.¹⁶ They also show metallographic evidence of bonds made with no apparent recrystallization. The fact that tin and lead, which recrystallize at room temperature, require deformations equal to those of metals that recrystallize at higher temperatures was also cited as evidence that recrystallization is not necessary for pressure bonding.

Surface Preparation

Since pressure bonding usually involves gross deformation at the bond surfaces, flatness and surface finish are generally not important considerations.

Contamination on the bond surfaces in the form of metallic compounds are generally to be avoided,^{6,7,12,14,17,18} although some bonding may exist at the oxide layer.¹⁰ Most investigations have involved degreasing and wire brushing the contacting surfaces before bonding. Significant decreases in bond strengths have been noted if degreasing in trichloroethylene follows the wire brushing.⁷

Parks noted that silver-clad aluminum etched in nitric acid did not bond as well as diamond-scraped specimens.¹⁵ Although he attributed this to the lack of cold work on the acid-cleaned specimens, it seems more likely that contaminants were introduced on the surface in the form of silver-nitrogen compounds, water, or other contaminants. This study showed that diamond-scraped bonds at 225°F and 5 to 10% deformation were stronger than other investigators reported

when a wire-brush surface preparation was used. This may possibly be attributed to the smoothness of the bond interfaces thus produced.

Price and Thomas in a study of the tarnishing of silver desired to clean the silver surfaces so that a controlled experiment could be performed.¹⁹ They state: "chlorinated hydrocarbons might give a film of silver chloride, most commercial hydrocarbons contain sufficient sulphur to give a film of silver sulphide, other hydrocarbons fail to remove fingerprints, ... the solvent used was A. R. acetone..."(p. 34).

In summary, the above cited works suggest that smoother surfaces will require less deformation to bond than rough surfaces and that acetone is preferred to most hydrocarbons for surface degreasing of silver.

Metal Purity

McEwan and Milner pressure bonded aluminum by rolling and determined that super-purity material required 25% deformation while commercial-purity material required 40% deformation to bond.¹³ Hofmann and Kirsch noted the same trend for pure silver compared to silver containing copper up to 0.02% in weight.²⁰ They extended their analysis by determining the recovery of cold work (10% elongation of wires at -297°F) from resistance changes in 30 min at various temperatures. From a comparison between the recovery measurements and experiments with cold-pressure bonding, they concluded that, with cold-pressure bonding of silver, atomic site change processes are participating similar to those connected with recovery. An inflection in the curve showing resistance change with temperature occurs at approximately 380°F which agrees quite

favorably with the inflection temperature (330°F) in the curve showing deformation for seizure as a function of temperature obtained by Semenov.⁹ It should not be concluded from these results, however, that the bonding mechanism is by atomic site changes across the bond interface. The mechanical properties of the bond material are temperature sensitive, and thus more intimate contact may result from increased ductility at higher temperatures.

The above results indicate that strong intermetallic bonds can be achieved at lower temperatures with higher-purity metals. Silver that is plated by vacuum evaporation is of higher purity than that plated by normal electroplating techniques and thus is to be preferred for this study.

In the above discussions some of the other factors that influence the pressure joining of metal such as the solubility of the surface films, mechanical properties of the metals joined, and relative motion at the bond interface were included. The latter factor is not considered significant in this study because the plate material is thin and the requirement that the substrate deformation be minimized should prevent any relative motion at the bond interface. The effects of prior cold work at the interface are uncertain (p. 441),³ and the lattice structure (FCC) of the silver is not a variable. The last parameter, bond time, will be discussed next.

Diffusion

The Mechanism of Diffusion Bonding

Diffusion bonding is a solid-state joining process that has been characterized as proceeding in three stages by King and Owczarski²¹ and Gerken and Owczarski.²² In the first stage, the surfaces to be joined are brought into contact and a load is applied sufficient to achieve some degree of intimate contact by deforming the asperities at the surface. Upon initial heating, these contact areas increase and new ones are generated as a result of the decrease in strength of the deformed asperities. The interface may then be characterized as 1) regions where metal-to-metal contact is prevented by virtue of a contaminating barrier, 2) voids where contact was not achieved, and 3) a grain boundary at areas of intimate contact. In the second stage, several diffusion-controlled processes that simultaneously strengthen the bond may occur. The regions containing impurities become areas of intimate contact as a result of diffusion of impurities into the metal and diffusion along the interface to voids. Some impurities may not diffuse and will remain, thus preventing complete intimate contact. As a result of grain boundary and bulk diffusion of the metal atoms to the surface of the voids, the voids shrink and many are eliminated. The interfacial grain boundaries may also migrate out of the plane of the junction to a lower-equilibrium configuration. In the third stage, bulk diffusion of atoms to the surface of the remaining voids eliminates many of them.

At the first stage of joining, the partial bond achieved is sensitive to surface contamination and the mechanical properties of the

materials at the weld temperature. This stage is not time dependent.

The second and third stages are controlled by diffusion and are therefore dependent upon both time and temperature. The average distance, δ , traveled by the average atom in a diffusion process can be expressed as $\delta = K\sqrt{Dt}$,

where: K = a constant

D = diffusivity

t = time.

The diffusivity, or diffusion coefficient, D , at a temperature, T , can be expressed as $D = D_0 \exp -Q/RT$,

where: D_0 = atomic vibrational frequency factor

Q = activation energy for some specified diffusion process

R = gas constant

T = absolute temperature.

The activation energy, Q , and the frequency factor, D_0 , are dependent upon the location of the diffusion atoms, that is, surface, grain boundary, or bulk. These equations are very simplistic and it should not be assumed, for example, that the bond strength of a diffusion-bonded specimen is related to $t^{\frac{1}{2}}$. The important implication is that the strength of a bond that is enhanced by diffusion should be time and temperature dependent.

Temperature

Diffusion can occur at any finite temperature; however, there are some general rules that indicate a temperature range for various diffusion processes. Shewmon notes that, as a general rule, bulk or

volume diffusion of atoms predominates at approximately $0.75 T_m$, where T_m is the absolute melting temperature of the material.²³ At temperatures less than $0.75 T_m$, grain-boundary diffusion predominates, as is shown in the case of silver by Turnbull.²⁴ Recrystallization, which involves movement of atoms and is therefore a diffusion process, requires temperatures in excess of approximately $0.4 T_m$.²⁵ Data obtained by Parks¹⁵ confirms this approximation. However, his technique, as previously argued, involved deforming the specimens by 5 to 10% by high pressures, and thus there is a degree of uncertainty about his contention that the bond was a result of recrystallization. His data on copper and silver indicated a bond-temperature limit of 0.32 and $0.34 T_m$, respectively. Creep, at temperatures greater than $0.5 T_m$, is another diffusion activated process.²⁶ The mechanism for the sintering of loose silver-powder aggregate at 0.46 to $0.47 T_m$ by Salkind et al.²⁷ was concluded to be one of plastic flow (creep) by dislocation motion. They also noted that the activation energy decreased with increasing stress. Gerken and Owczarski (p. 7)²² report the diffusion-bonding results of several investigators and note that unalloyed refractory metals bond at $0.5 T_m$ ²⁸ but that most metals require temperatures of 0.6 to $0.85 T_m$.

Many of the same factors discussed in the previous section, such as metal purity, pressure, and surface contamination, influence the bond formation. An additional correlation regarding surface contamination as related to diffusion was found by Nicholas and Milner.²⁹ They observed that upon post-heat treatment, partial bonds in roll-bonded aluminum became complete if 1) the contaminant was primarily water vapor and the post heat temperature was 122 to 302°F and

2) the contaminant was trichloroethylene and the post-heat treatment was 1112°F. The diffusion of these entrapped contaminants would be dependent upon temperature as indicated and on time, the parameter to be discussed next.

Time

Time and temperature have an inverse effect on bond strength. That is, to achieve some specified bond strength, a decrease in temperature implies an increase in bond time, or, conversely, an increase in temperature may be accompanied by a decrease in bond time. Temperature is clearly a more important consideration because, if the temperature is decreased below a certain minimum value, no amount of time will produce the desired bond strength.

In roll bonding, Nicholas and Milner have shown that by decreasing the rolling speed, bond strengths can be increased or the threshold deformation decreased.²⁹ They also showed that a similar specimen statically loaded increased strength with increasing loading times up to approximately 30 min.

King and Owczarski diffusion-bonded commercially pure titanium and determined the bond strength as a function of temperature and time.³⁰ At the lowest temperature (1400°F), full bond strength was achieved in 2 hr. They also showed that bond contact area increases with bond temperature and time. In a later study, they determined that the contact area increases at the same rate for two different surface roughnesses and that the contact area for the smoother surface was greater.²¹

Barta concluded that time was not a critical factor in bonding Alclad aluminum alloys.³¹ He also stated that the bond strengths obtained after 1 hr exceeded those obtained for 3 hr bonding time for the same temperature. However, the scatter of data was large, and this conclusion may not be valid.

In another technique for bonding metals by using solid-state techniques, an intermediate material that diffuses into the metals being joined is used. In an investigation of the roll bonding of dissimilar metals, McEwan and Milner noted that in joining at high temperatures or by post-heat treatment, the properties of the joint were determined by the extent and effect of interdiffusion.¹³ Bonds in immiscible and slightly miscible metals were unaffected by post-heat treatment. Some miscible metals exhibited diffusional porosity (Kirkendall effect) while others formed intermetallics. In the latter case the thickness of the brittle intermetallic determined the strength of the bond. If the thickness exceeded a critical limit, which varied with the metals joined, the bond was weakened. These effects have also been noted in diffusion bonding by other investigators.³¹⁻³⁵

Pressure

The effect of pressure and deformation on the diffusion rate was reviewed by Tylecote (pp. 46-55).² Pressure also promotes diffusion by increasing the surface area of contact. Cunningham and Spretnak state that boundary pinning by voids and impurities can be avoided by heating the specimens to the bonding temperature prior to applying the bond pressure.³⁶ They postulate that boundary

migration thus proceeds immediately after the interface is formed before it can be effectively restrained by voids.

Surface Contamination

Surface contamination affects the self diffusion of surface atoms. Rhead noted that the activation energy for surface self-diffusion of silver is lower in vacuum than in air.³⁷ Above 1300°F the diffusivity was increased by the adsorption of oxygen in a pressurized oxygen atmosphere. Additional work showed significant increases in the surface self-diffusion of silver with adsorbed sulphur.³⁸

In diffusion bonding, the increased surface self diffusion by controlled environments or surface contamination may enhance void elimination and thereby lead to a stronger bond. On the other hand, the presence of contamination may also create a weakened region in the bond.

In summary, the important consideration relative to diffusion bonding is that the final strength is primarily time and temperature dependent. From a review of the literature it is noted that for a bond strengthened by diffusion, time in the order of 1 hr is generally reported. A relatively small increase in bond temperature significantly reduces the importance of bond time. Other factors such as surface flatness, finish, and cleanliness also influence the importance of time, other parameters remaining fixed.

Adhesion (Cohesion)

Definition and Laws

Adhesion refers to the molecular attraction exerted between two dissimilar metal surfaces after the surfaces have been brought into contact. Cohesion is defined in a like manner except that it applies to similar metal pairs.

Two general laws of adhesion, which closely resemble the classical laws of friction, have been advanced by Bowden³⁹:

1. adhesion is directly proportional to the applied load, and
2. adhesion is independent of the apparent area of the surfaces in contact.

A coefficient of adhesion is frequently reported in the literature and is defined, in a manner analogous to that for the coefficient of friction, as the ratio of the force necessary to break an adhesion bond to the applied load. These rules are general and many conditions can be found where they are not obeyed.

An Extended Definition

In the previous section three stages of progression were presented for the formation of a diffusion bond. The second and third stages were time and temperature dependent. The first stage involved bringing together the surfaces to be bonded and developing some intimate contact at the interface as a result of elastic and plastic deformation of the surface asperities. It was stated that this stage of bonding was independent of time, although clearly the physical act of deforming is time dependent. The intent was to imply

that, relative to the time necessary to strengthen the bond by the second and third stages, the first stage is not time dependent. The molecular attraction achieved during this first stage should be classified as adhesion (or cohesion), and this stage will be referred to as adhesion bonding.

The above extended definition of adhesion applies, for example, to data by McFarlane and Tabor on the adhesion of a clean steel sphere on indium as a function of the loading time.⁴⁰ Their results clearly show that a metallic bond is achieved at essentially zero time and is strengthened with time. The rate of increase in strength decreased until some steady-state rate was maintained. This correlates well with the first three stages of creep.⁴¹

The initial contact of materials may not result in a measurable force necessary to separate the surfaces. This is generally conceded to result from contamination on the surfaces which prevents intimate contact. Bowden and Tabor (p. 100)⁴² determined the temperature at which measurable adhesion was first recorded for various metals to be $0.4 T_m$ or greater (silver: 414°F or approximately $0.4 T_m$). This strongly suggests that creep and recrystallization are the mechanisms by which these bonds were formed. An equation correlating the time and temperature for "adhesion" bonds was derived by Ling, based upon the known time-temperature relationships for recovery and recrystallization.⁴³

Some Factors Influencing Adhesion

Many investigators have attempted to correlate adhesion to material properties. A comprehensive study was done by Sikorski.⁴⁴

Various metals were joined by compression and twisting, that is, relative motion at the interface, and the coefficient of adhesion was compared to crystal structure, hardness, surface energy, elastic modulus, work hardening properties, recrystallization temperature, purity, and atomic volume. He concluded in part that higher-purity metals, capable of greater plastic flow, develop greater strengths.

Most adhesion studies have emphasized the importance of surface contaminations.^{39,40,45-55} Efforts to clean surfaces in vacuum include 1) partial evaporation of the metal and cooling to room temperature for adhesion tests^{39,46,47}; 2) heating to outgas surface contaminants^{39,45,46}; 3) electron and/or ion bombardment^{45,47,48}; 4) wire brushing⁴⁹; 5) fracture in high or ultrahigh vacuum⁵⁰⁻⁵³; and 6) heating in a reactive atmosphere.^{54,55}

Bowden and Rowe, using the first technique above, noted that the adhesion of silver exposed to 10^{-6} Torr for 1 hr dropped measurably as compared to the adhesion recorded as soon as the denuded specimens reached room temperature.⁴⁶ The 10^{-6} Torr pressure was obtained with a liquid-nitrogen, trapped-silicone, oil-diffusion pump. The same results were also obtained on a 10^{-8} Torr system consisting of a liquid-nitrogen, trapped-mercury, diffusion-pumped system.

Johnson and Keller cleaned silver surfaces by argon-ion bombardment, followed by electron bombardment to degas entrapped argon. A coefficient of adhesion of 1 was obtained in $\sim 10^{-4}$ Torr of argon and 0 in 40-Torr wet air after 4 hr of exposure. It was concluded that the dispersal of contaminants is the prime barrier to adhesion. Two classes of contaminants were defined: 1) those

removed by vacuum, and 2) stable films such as those formed under long exposure to atmospheric conditions, which could only be removed by argon-ion cleaning.

Of fundamental importance, especially as regards vacuum-evaporation plating of silver on tungsten, is the fact that clean, insoluble, metal surfaces will develop significant adhesion strengths.^{48,54} Adhesion couples were also formed with negligibly soluble metals at room temperature,⁴⁹ and adhesion was measured for an insoluble couple, Cu-W, after sliding.⁵⁶ Although Hansen⁵⁷ and Elliott⁵⁸ are the standard references used to determine solubilities of bulk materials, recent work by Taylor⁵⁹ has shown that copper, vacuum evaporated onto tungsten, is soluble in tungsten at least to a depth of five atomic layers from the free surface. Thus, conclusions about bulk solubility as deduced from phase diagrams are probably not valid for surfaces.

In summary, adhesion bonding is defined as a process whereby molecular attraction at the interfaces of two materials is developed in the solid state, and the force necessary to separate the surfaces is that which is achieved independent of contact time. The degree of surface contamination and the bulk metal purity dictate the adhesion bond strength. Metals that are mutually insoluble can also develop adhesion.

Selection of Intermediate Bonding Metal

A review of the literature on solid-state welding of beryllium by Hauser et al. revealed that it is possible to achieve solid-state bonds; however, the welding temperatures required were far in excess of

600°F.⁶⁰ Batzer and Bunshah measured bond strengths of approximately 16% the bulk strength of beryllium after bonding at 572°F by using an ultrahigh vacuum and an ion-sputter surface-cleaning technique before bonding.⁶¹ Although this procedure for achieving high-strength, low-temperature bonding appears promising, the techniques employed were not considered feasible from a production point of view.

Beryllium has also been successfully joined by introducing another metal at the interface and elevating the temperature until a liquid phase is achieved.^{45,62-65} This process has been referred to as diffusion or eutectic bonding but generally is considered to be a braze joining process. The minimum bond temperature reported was 1330°F with an aluminum foil.⁴⁵ Maloof and Cohen⁶⁴ brazed beryllium with silver foils, silver electroplates, and a ductile beryllium-20 at% silver-alloy foil.⁶⁶ During the brazing cycle, intergranular penetration of silver into beryllium was suspected. This was not considered harmful, because of the ductile nature of this alloy. They also established that liquid silver would wet the beryllium surface.

Cline and O'Neill reported that solid-state bonding with pure silver in a purified inert atmosphere, below the Ag-Be eutectic temperature (1616°F), results in excellent high-temperature-strength brazements of beryllium to a dissimilar metal.⁶⁵ Although there was little reason to suspect that this diffusion bond could be developed at less than 600°F, the use of silver on beryllium appeared promising.

Crane et al. diffusion bonded aluminum to stainless steel with electroplated silver on each surface at temperatures of 375 to 700°F.³² A nickel strike and a copper flash were used prior to

electroplating the stainless steel, and a zincate treatment and copper flash were used on the aluminum alloy prior to silver electroplating. Bonds were made in an air environment, and the compressive load was adjusted to achieve a deformation of approximately 0.005 in. in the 0.125-in.-thick aluminum. A diffusion reaction occurred in the silver-copper-aluminum zone, and bonds made at 700°F were unsatisfactory because of joint brittleness. Peel tests on bonds made at 375 and 400°F exhibited lower peel strength than bonds made at 500°F. Metallurgical examinations of the silver-silver joint for all time-temperature combinations (note: 14 hr at the minimum temperature, 375°F) revealed a fine-grained, recrystallized-silver structure that was void free. The ability to develop a solid-state bond at the silver-silver interface in an air environment was attributed to the lack of detrimental oxides or other nonmetallic films. The free energy of formation of Ag_2O is zero at approximately 380°F.⁶⁷ Since Ag_2O will decompose at higher temperatures, it was concluded that an oxide barrier at the silver-silver interface would not impede the formation of a silver-silver bond at temperatures of 400°F or greater and for reasonable bond times.

In summary, it was concluded that beryllium could not be joined to itself under the limitations imposed by this investigation without an intermediate material. There was no evidence to indicate that a beryllium-metal diffusion bond could be developed at less than 600°F. Thus, it was decided to plate the bond surface of the beryllium with another metal and rely upon the plating process to achieve a strong beryllium-plate adhesion. The plated surfaces would then be joined while subjected to a compressive load at a low temperature.

Silver was considered a logical selection because it wets beryllium, and silver-silver bonds had been achieved at 500°F.

Relation of Film Thickness to Bond Strength

It is generally accepted by most brazing technologists that a thin, void-free braze joint is stronger than a thick one. This relationship was mentioned often in the early trade literature; however, Crow is credited with the first systematic study.⁶⁸ This relationship was further reinforced by Leach and Edelson, who showed that in brazing stainless steel with a quaternary silver alloy (50% Ag, 18% Cd, 16.5% Zn, 15.5% Cu) a maximum butt-joint strength was obtained with a 0.0015-in.-thick braze joint.⁶⁹ Either an increase or a decrease in the thickness of the joint resulted in a significant decrease in the bond strength. Later investigators concluded that the bond strength continuously increases with decreasing joint thickness as long as the braze joint was void free.

It was also observed that the strength of the braze joint approached that of the base material, which was often several times that of the bulk braze-material strength. Bredzs, for example, reports that a braze joint 0.00029 in. thick made with pure silver (ultimate tensile strength 21,000 psi) on 1020 steel (ultimate tensile strength 69,000 psi) fractured at 67,200 psi.⁷⁰ Since iron and silver were reported by Bredzs to be insoluble at the braze temperature used, the increase in strength with decreasing joint thickness was not attributed to an alloying effect. Thus it was concluded that the increase in tensile strength of brazed joints with decreasing thickness of the joint is due primarily to the influence of plastic constraint. It

is now well established that a ductile material, if constrained from deforming, is capable of supporting extremely high stresses as compared to its unconstrained strength. It may thus be concluded that the increase in breaking strength of braze joints with decreasing thickness of the braze material results from the development of triaxial stresses within the joint due to differences in the yield strength and work-hardening rates of the braze material and the base material.

Meissner and Baldauf concluded that if the triaxial stresses in the joint were in fact responsible for the increase in thin-film strengths, the joint strength should be a function of the geometry of the specimen.⁷¹ Bond strengths measured from polystyrene on steel, paraffin wax on steel, and eutectic lead-tin solder on brass revealed that the bond strength was related to the thickness-to-diameter ratio of the joint. Although this relationship is now generally accepted, the shape of the curve expressing this relationship has not been established. The curves found in the literature vary from linear, to exponential, to hyperbolic, to nondescript.

At least two investigators have studied reportedly sound braze joints with a thickness of less than 100 μin .^{72,73} In both investigations the bond strength exhibited the expected increase with decrease in the thickness-to-diameter ratio until the braze thickness was 100 μin . or less. For these ultrathin joints a leveling off or a decrease in strength was noted.

From the foregoing discussion it may be concluded that solid-state bonds made from silver-plated metals could exhibit strengths in excess of the ultimate strength of silver. However, the formation of a solid-state bond differs considerably from the formation of a

liquid-state braze joint in that a compressive load is necessary to establish contact of the interface surfaces. The stresses at the interface are not purely compressive but will again be influenced by the constraints imposed by the base material. Since there is general agreement that, except in the case of ultrathin joints, the bond strength increases as the joint thickness decreases, a logical extension appears to be that the bond formation, that is, contacting area at the interface, decreases as the joint thickness decreases for a given compressive load. The strength of bonds thus formed will depend not only upon the triaxial state of stress dependent upon the thickness-to-diameter ratio at the joint, but also upon the bond area. The relationship of the bond strength to the joint thickness for solid-state bonds is indeed more complicated than for braze joints. In view of the fact that the curve expressing this relationship for the simpler case of brazed joints has not been established, no prediction of the curve shape could be made for the solid-state bonds investigated herein.

EXPERIMENTAL EQUIPMENT

Experimental Procedure Summary

I joined silver-plated, cylindrical specimen pairs end-to-end by applying an axially compressive load at an elevated temperature. Preliminary studies revealed that the adherence of electroplated silver to beryllium was considerably less than the bulk strength of beryllium but a vacuum-evaporation plating technique developed by Westlund⁷⁴ provided the necessary adhesion of silver to beryllium. Attempts to duplicate this technique resulted in the vacuum evaporation plating system used in this investigation.

The thickness of the silver plate was measured nondestructively by x-ray fluorescence, and I developed a polishing and cleaning technique for preparing the silver surfaces before bonding. I used a hydraulically actuated loading fixture to bond the specimens as well as to test the bond for its ultimate tensile strength. I achieved vacuum bonding by installing the bonding fixture in a second vacuum system.

Specimens

The specimens shown in Fig. 1 were solid cylinders with an enlarged tapered end to permit tensile testing. The bond end of the specimen—surface C—was polished flat to within 20 μ in. and parallel to the loading end—surface B—to within 30 μ in. Surface finish on the bond surface was 2 rms or better, except on the copper specimens where it was 3 to 4 rms.

Fig. 1. Specimen details.

Specimen bonds indicated by the abbreviation N (necked) were standard specimens that were bonded and then reduced in diameter to 0.350 in. by machining a 1.625-in.-radius notch centered along the bond interface (Fig. 2) and in the future referred to as necked bonded specimen.

Plating System

The vacuum system, shown schematically in Fig. 3, consisted of a baffled diffusion pump in which a silicone-base oil was used. Liquid-nitrogen cold traps separated the diffusion pump from the bell jar and the foreline mechanical pump. This system would achieved a base pressure of 2×10^{-7} Torr.

A schematic of the components inside the bell jar is shown in Fig. 4. A maximum of eight specimen halves could be inserted through holes in a carbon heating block that suspended them vertically from their tapered ends. The carbon block, heated by high-frequency induction, heated the specimens by conduction to the desired temperature. Temperatures were measured by a thermocouple attached to the carbon block.

The specimens were plated by vaporizing silver (0.9995 pure) using an electron beam. The beam was bent 180 deg and focused onto the material to be vaporized. The specimen bond surface was 4.5 in. from the silver source. To control the plating thickness between runs a crystal-type thickness monitor was used.

Fig. 2. Necked bonded specimen.

Fig. 3. Vacuum plating system.

Fig. 4. Vacuum evaporation plating—bell jar components.

Thickness Measurement

The plating thickness obtained on each specimen was measured by x-ray fluorescence. High-purity silver foils of known thickness were used as a calibration reference.

Silver-Plate Polishing

A steel ring, 2 in. in diameter and $\frac{1}{2}$ in. thick, containing a hole approximately 0.001 in. larger than the bond end diameter of the specimen, was used as a guide for holding the specimen while hand polishing after plating. The polishing media was 0.3- μ aluminum oxide suspended in an oil-base lapping fluid. A glass plate was placed under the polishing cloth to provide a flat surface. Specimens were hand cleaned with reagent-grade acetone followed by low-energy ultrasonic cleaning in an acetone bath.

Bonding System

A schematic of the bonding fixture is shown in Fig. 5 and details of the vacuum side of the fixture in Fig. 6. The specimens were held in place with a specimen nut and split collet. One half was attached to a shaft that was strain gaged to provide a direct reading of the applied load. The other half was connected to a close-fitting piston guide that permitted axial motion only. The necessary vacuum seal was welded to this guide. Forces for compressive and tensile loads were provided by a double-acting hydraulic ram. Temperatures were measured by thermocouple wires spot welded to the specimens using chromel-alumel and chromel-constantan. The output of these

Fig. 5. Schematic drawing of bonding fixture.

Fig. 6. Photograph of bonding fixture.

couples was used as a control sensor that adjusted the induction-power output to maintain a predetermined temperature.

Both specimen shafts conducted heat away from the specimens. Hydraulic cooling oil was pumped through the center of the load cell, to avoid overheating the strain gages, and around the piston guide, to prevent excessive thermal expansion of the piston guide.

The split specimen nuts and collets (Fig. 6) were lubricated with tungsten diselenide on all surfaces where relative motion during assembly and disassembly occurred.

The strain-gaged specimen shaft that served as a dynamometer was attached to an end plate, which in turn was connected to the piston-guide walls by four rods. The nuts holding the end plate to the rods were adjusted to make the planes of the bond interfaces parallel.

The bonding fixture was aligned and the dynamometer was calibrated by using a solid bar machined to the configuration of a perfectly bonded specimen pair, the ends of which were lapped parallel to within 10 μ in. Four strain gages were equally spaced at 90-deg increments around this bar and the gages wired as a Wheatstone bridge, such that the output signal indicated bending strains. A second Wheatstone-bridge configuration indicated the axial strain. This bar was calibrated in both tension and compression. The use of this method of adjustment and calibration permitted a maximum resolved bending strain of less than 25 μ in./in. when the calibration bar was loaded in compression from zero to 40 ksi.

The dynamometer was calibrated in tension and compression, and its output was recorded on a chart recorder.

Tensile Tests

The hydraulic loading system was limited for safety reasons to 5000-lb tension, which corresponds to a tensile stress of 25 and 50 ksi on the standard 0.50-in.-diam specimens and the 0.35-in.-diam necked specimens, respectively. Specimen bond strengths exceeding these values were tested on a commercial tensile tester. Because of the relatively poor alignment with the tensile fixture on the tester, bonds frequently failed at stresses less than the bonding-fixture pre-test. Further evidence of the effect of misalignment was obtained on solid-necked beryllium tensile bars, which fractured at lower stresses on the commercial tester than on the bonding fixture. Thus, unless otherwise noted, all tensile-test data reported herein have been obtained from the bonding fixture.

Vacuum System—Bonding

The schematic shown for the vacuum plating system is typical of the vacuum bonding system, except that a LN_2 cryoadsorption pump was used on the diffusion-pump foreline rather than a mechanical pump.

An overall view of the bonding system is shown in Fig. 7.

Materials

Substrate

Gold and Silver were considered to be the best plate materials for bonding at low temperatures, because of the relative absence of

Fig. 7. Overall view of bonding system.

metallic compounds on their surfaces. Since a technique that resulted in good adhesion was not found for plating gold on beryllium, the study centered around silver plates. In an effort to understand the bonding parameters more thoroughly, variations were made in the substrate materials. The substrate materials were selected primarily for their differences in moduli of elasticity.

All specimens were machined from 0.750-in.-diam stock. The chemical analysis of the beryllium substrate is shown in Table 1.

Table 1. Typical chemical analysis of beryllium (S 200 C).

Elements	Weight percent	
	Heat 1	Heat 2
Be	98.2	98.33
BeO	2.0	1.90
C	0.15	0.14
Fe	0.17	0.18
Al	0.08	0.09
Si	0.05	0.04
Mg	<0.02	<0.02
N	<0.04	<0.04
Mn	<0.01	<0.02
Total (Cr, Cu, Ni, Ti)	<0.20	<0.20
Others, each	<0.04	<0.04
Materials specification: MEL-507D		

The other materials were obtained from available stock and may be classified as follows:

1. Copper: Hard temper, electrolytic tough pitch. Material specification: QQ-C-502C, ETP.
2. Molybdenum: Arc cast, centerless ground, hot-cold rolled, leveled, fully stress relieved. Material specification: AMS 7805.
3. Stainless steel: Cold finish and centerless ground, class 304, annealed, round. Material specification: QQ-S-763.
4. Tungsten: 99.9% pure, centerless ground. Material specification: MIL-T-14507A.

Some mechanical properties of the substrates used are shown in Table 2. The ultimate tensile strength of beryllium was obtained from an average of tests conducted on necked solid beryllium specimens tested in the bond fixture. Table 3 shows these values as well as results submitted by the material supplier.

Table 2. Some typical mechanical properties of the silver plate and substrate materials.

Material	Tensile modulus of elasticity, 10^6 psi/in./in.	Tensile yield stress, ksi	Ultimate tensile stress, ksi
Ag	10	8 (annealed)	22 (annealed)
Cu	17	44	48
SS (304)	28	30 (min)	75 (min)
Be	40	32-37 ^a	40.8 ^b
Mo	47	75	90
W	58	220	220

^aMaterial supplier's data, range of four tests.

^bSee Table 3.

**Table 3. Ultimate tensile strength of beryllium (S 200 C)—
longitudinal.**

Test ^a	Ultimate tensile strength, ksi ^b
1	41.9
2	41.4
3	40.2
4	42.3
mean $\pm$ 1 st dev	41.5 $\pm$ 0.9
5	39.5
6	39.2
7	38.1
8	39.1
9	44.1
10	42.6
11	42.8
mean $\pm$ 1 st dev	40.8 $\pm$ 2.3

^aTests 1-4: data submitted by material supplier.
5-11: data obtained on necked specimens tested in the bond fixture.

^bMaterial specification (MEL-507D) specifies a minimum of 37 ksi.

Plate

All plate materials used were premelted in the vacuum evaporation system. The premelted material was removed and any foreign residues on the surface were scraped off. The gold and copper materials were of unknown origin and purity. The silver was obtained from 0.50-in.-diam bar stock of 99.95% purity. For comparative purposes some typical mechanical properties for silver are also included in Table 2.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Specimens were machined and the bond surfaces were lapped, using conventional techniques. The diameter of each specimen at the bond end and the flatness of the bond surface were measured and recorded. Immediately before the specimens were inserted in the vacuum plating system, they were twice ultrasonically cleaned in uncontaminated trichloroethylene or reagent-grade acetone. The specimens were closely examined for any foreign particles on the bond surface after insertion into the carbon heating block.

Vacuum Evaporation Plating

The plating system containing the specimens was evacuated to 2×10^{-6} Torr in approximately 17 min. An induction coil around the carbon heating block was energized when the pressure was 2×10^{-6} Torr or less. During the heating cycle outgassing of the carbon block caused a pressure rise, but the heating rate (less than $80^\circ\text{F}/\text{min}$) was adjusted so that the pressure never exceeded 2×10^{-5} Torr. When the desired temperature was reached, the pressure was less than 2×10^{-6} Torr.

The plating sequence was started after the specimens had been maintained at the desired temperature for periods of time ranging from 1 to 35 min. A shutter was inserted between the specimens and the premelted-silver source. An electron beam was focused on the silver and beam power adjusted to achieve a steady vaporization rate.

The pressure rose to 4×10^{-6} Torr during this operation. The induction heating source was then turned off and the shutter removed by a remote manipulator. The electron beam power was adjusted to provide a nominal vacuum evaporation plating rate on the specimens of $0.8 \mu\text{in./sec}$ ($200 \text{ \AA/sec}$). Plating rates of 0.5 to $1.5 \mu\text{in./sec}$ were not found to be critical to the bonding process. When the approximate desired plating thickness (indicated by the deposition thickness monitor) was obtained, the shutter was inserted between the specimens and source.

When the specimens cooled to 750°F or less, the diffusion pump was valved off and the bell jar backfilled with argon. The backfill was used to provide a thermally conductive environment for the specimens, thereby increasing the cooling rate and permitting earlier removal from the system. Studies showed that bonds made on unpolished silver specimens were not influenced by either argon or nitrogen backfills at elevated or room temperatures. The vacuum and thermal conditions for a typical beryllium plating sequence are shown in Fig. 8.

Plating Thickness Measurement

After the specimens were removed from the vacuum plating system, representative specimens were measured by x-ray fluorescence for thickness. The variation in plating thickness for eight specimens plated simultaneously was less than $\pm 30 \mu\text{in.}$ for a nominal $200 \mu\text{in.}$ of silver. This was verified by metallographic examinations.

Fig. 8. Vacuum evaporation plating sequence for a typical beryllium specimen.

Plate Polishing and Cleaning

During the early phase of this program, the specimens were bonded. However an intermediate step was developed, namely, the polishing of the silver interface, which resulted in a very significant decrease in the bond temperatures required.

The as-plated silver was a very light cream color and non-reflective. The plated surface was then polished, with a light load applied to the specimen. Polishing continued until the full bond interface surface was silver in color and highly reflective. After polishing, the specimens were rinsed with reagent-grade acetone, and a saturated cotton swab was rubbed over the surface until all polishing compound residues were removed. The bond surface was then measured for flatness, and the specimens were finally cleaned twice with low-power ultrasonic energy in an uncontaminated reagent-grade acetone bath.

Specimen Installation in the Bonding Fixture

After the final cleaning operation, the specimens were brought to the bonding fixture in the acetone bath. They were usually removed from the acetone within 15 min and installed in the bonding fixture. After installation, the specimens were compressed or preloaded to 4.2 ksi, and the thermocouples were then spot welded to the specimens approximately 1/16 in. from the bond interface. The total elapsed time they were exposed to air was less than 15 min after removal from the acetone.

Bonding Procedure—Standard

For bonds to be made in air, the induction heating coil was energized and the specimens were heated to the desired bond temperature at a rate of 20 to 50°F/min. When the bond temperature was reached, the compressive stress was increased to the desired bonding level at a rate of 250 psi/sec. The recorded bonding time began when the desired compressive stress was obtained and was terminated when the induction heating power was turned off. The compressive stress decreased approximately 3 ksi during cool-down, as a result of thermal contraction. Except for this small decrease, the compressive stress was maintained until the specimens reached room temperature. The cooling rate varied widely depending upon the specimen material, the environment, and the bond temperature. All specimens reached room temperature between 15 and 90 min after the heating power was turned off. After a period of time ranging from several minutes to several days after the specimens reached room temperature, the compressive stress was removed at a rate of 250 to 500 psi/sec.

A typical temperature and bonding compressive-stress sequence for the cleaning, installation, and bonding cycles are shown in Fig. 9.

Bonding Procedure—Special Environments

The above procedure for bonds made in air was followed for bonds made in helium, oxygen, and vacuum environments with the following additional steps. For helium and oxygen, specimens were installed in the bond fixture and thermocouples were attached in air

Fig. 9. Cleaning, installation, and bonding cycle.

without preloading the specimens. A helium environment was obtained by placing a plastic bag around the bond fixture, flushing the bag several times, and then maintaining a positive pressure of helium in the bag; an oxygen environment was established by maintaining a flow of oxygen around the bond interface. With the environment established, the specimens were preloaded, heated, and bonded. The vacuum was established in essentially the same manner as discussed for the vacuum evaporation plating technique. The specimens were separated in the vacuum for periods of time ranging from several minutes to several days to permit outgassing from the bond surfaces and were then preloaded to 4.2 ksi in a vacuum of 3×10^{-6} Torr or less. The standard bond cycle then resumed. After the specimens were cooled to room temperature, the system was backfilled with air and the compressive load was removed as previously discussed.

Bond-Strength Tests

Bond strength was measured by loading the specimens in tension to fracture. The loading rate for specimens tested in the bond fixture was 100 psi/sec but was limited to 5000 pounds, which corresponded to 25 ksi on the standard bonded specimens and 50 ksi on the necked specimens.

Plating Parameters

Four major parameters were found to influence the adhesion of the plate to the substrate: 1) cleanliness of the vacuum plating system,

2) temperature of the substrate, 3) plate material, and 4) substrate material. The vaporization technique also influenced bond cohesion.

The vacuum evaporation plating system initially used was designed to duplicate the plating procedure of Westlund⁷⁴ but differed from the final system in two important respects: a baffle was not used between the diffusion pump and the liquid-nitrogen cold trap, and a less efficient cold trap was used on the first system. Bonds made from the first few specimens plated in the initial system exhibited high strengths with no evidence of silver peeling from the beryllium. However, after about 30 days of operation, bonds began failing at the silver-beryllium interface. A systematic effort to find the cause of this change led to the observation that diffusion-pump oil had migrated past the cold trap and into the bell jar. After the system was cleaned with a light solvent containing light petroleum naphtha, acetone, and alcohol, good adhesion was again obtained between the silver and beryllium.

After the vacuum plating system was operated for approximately 20 more days, oil could be seen migrating up the sides of the cold trap toward the bell jar. Shortly after that, silver again began peeling from the beryllium. A spectrochemical analysis of wipes made from the plating fixtures revealed a high percentage of silicon (60% Ag, 15% Si, 25%: Al, Cu, and Fe). Because the diffusion-pump oil had a silicone base, I concluded that diffusion-pump oil in the vacuum plating bell jar was detrimental to a good plate adherence.

Diffusion pumps are known to backstream oil during start-up, shutdown, and steady-state operations.⁷⁵⁻⁷⁷ Since this cannot be avoided, a baffle and a more efficient liquid-nitrogen cold trap were

installed between the diffusion pump and the bell jar. This final system (Fig. 3) operated satisfactorily for 6 mo and then again for 4 mo, before bonds began failing at the silver-beryllium interface. In both instances oil had clearly migrated above the cold trap; when the system was cleaned as previously discussed, subsequent bonds did not fail at the silver-beryllium interface. Residual gas analyses obtained when the system produced both acceptable and unacceptable plate adherence failed to reveal any notable differences.

It would be undesirable in production work to have periodic plating failures. Thus, either a periodic system clean-up would have to be scheduled, or a different vacuum-system design, such as an ion-pumped, high-vacuum system, would have to be considered.

The adherence of a plated material to its substrate is frequently reported in the literature as acceptable if it passes the tape test proposed by Strong.⁷⁸ Pressure-sensitive transparent tape is firmly pressed over the plated material and then removed. If the plated material remains on the substrate, adhesion is considered acceptable. However, in this investigation, specimens that passed the tape test and were bonded but subsequently failed in pure tension at the silver-beryllium interface revealed that the tape test is good to a tensile stress of only 5 to 10 ksi. Thus this adhesion test was inadequate for this study.

Westlund had demonstrated that the adhesion of silver to beryllium would exceed the bulk strength of beryllium if the beryllium was plated while at a temperature of approximately 1200°F.⁷⁴ Table 4 lists the plate and substrate materials, the substrate plating temperature, and the maximum adhesion measured. Except for the making of the

Table 4. Plating parameters.

Plate	Substrate	Substrate temp., °F	Maximum adhesion, ksi
Ag	Be	1110-1380	44 ^a
	Cu	570	42 ^a
	Mo	1430	58 ^b
	SS(304)	1380	55 ^b
	W	1600	42 ^c
Au		1430	10-20 ^b
	Be	930	— ^d
	SS(304)	1380	33 ^e
Cu	Be	1200	10-15 ^c

^aSubstrate fractured, that is, no plate peel.

^bNearly 100% plate peel.

^cFracture surface showed substrate fracture and plate peel.

^dPlate removed with transparent tape—intermetallic probably formed.

^eFracture occurred at the Au-Au interface.

silver-beryllium couple, no effort was made to optimize the plating procedure. Thus, a cleaner vacuum system or higher substrate temperatures (lower for the gold-beryllium couple) would probably improve the plate-substrate adhesion.

Three different methods were used to vaporize the silver:

1) electron bombardment of a molybdenum crucible, 2) resistance heating of a tantalum boat, and 3) use of the 180-deg electron-beam gun previously described. The third technique was used for all specimens that were polished on the bond interface before bonding.

Specimens plated with each of the three vaporization techniques were bonded in the as-plated condition, and no differences in bond

strengths were noted. However, the first time the electron-beam gun was used, four specimen halves were plated and a difference in bond strengths was obtained. One specimen pair was installed in the vacuum plating carbon heating block such that the tungsten-filament electron-beam source was in line of sight to the plating surface of the specimen. This specimen pair, when bonded and tested, failed at 9.5 ksi; the other pair, which was shielded from the filament, exhibited a normal unnecked bond strength of 22.3 ksi. Two additional specimen pairs, unshielded and shielded, exhibited bond strengths of 8.8 and 24.9 ksi, respectively. I thus concluded that the hot tungsten filament contaminated the silver bond interface surface; this contamination probably came from the filament or from some reaction of stray electrons with the plating system. Although the exact cause for the suspected contamination is unknown, the problem was overcome by placing a line-of-sight shield between the filament and the specimens.

Rebonded Specimens

Many specimens failing at the plate-plate interface were rebonded without any additional surface preparation. Bond strengths thus obtained agreed well with other specimens bonded under the same conditions if the bond parameters for the rebond cycle were adjusted to achieve the same or higher bond strengths than any of the previous bond cycles on that specimen. Except for a special study on gold-plated stainless steel, there are only two rebond-bond strengths reported.

Bond Geometry

As-bonded specimens, that is, unnecked, whether polished or as-plated, revealed 95 to 100% beryllium fracture surfaces and bond strengths of 20 to 36 ksi when the bond parameters were maximized. These strengths were considered low because bulk beryllium fractures at 40 ksi. Photomicrographs of sections perpendicular to the bond interface revealed that the specimen shank and bond interfaces were highly twinned as a result of the machining process used. Consequently, additional specimens were carefully machined to eliminate this source of twinning. However, high-strength bonds made from untwinned specimens exhibited the same range of strengths as the twinned specimens.

With the elimination of twinning as a possible explanation for the lower-than-expected bond strengths, a study was conducted to determine the influence of bond geometry on bond strength. It was previously mentioned that the bonding fixture was aligned such that the bending strain on specimens under compression was minimized, that is, the bond interface surfaces were parallel. However, there was a radial misalignment at the bond interface of approximately 0.010 in. Thus, a bonded specimen pair had a built-in notch. This notch was even more severe, as shown in Fig. 10, for specimens polished at the silver interface, because the silver tended to round off at the edges as a result of the hand-polishing technique used.

Notches were removed by machining the shank as shown in Fig. 2. These necked specimens exhibited the same percentage beryllium fracture (95 to 100%) for high strength bonds; however, the bond strengths were 35 to 44 ksi, that is, bulk beryllium strength.

Fig. 10. Bonded specimen pairs — notch.

Most of the results reported herein were obtained on the 0.500-in. diam specimens tested as-bonded for bond strengths less than 20 ksi.

Fracture Mode

Specimens tested for their ultimate bond strength fractured at any of the following: the plate-plate interface, plate-substrate interface (that is, peeled), within the substrate, or combinations thereof. Since bonds under investigation were made by joining the surfaces of the plate material, it follows that any correlation between the measured fracture strength and the bonding parameters should only be obtained from specimens failing at the bonded surface, that is, the plate-plate fracture mode. Fractures at the plate-substrate interface are a measure of the adhesion accomplished by the plating process and do not reflect the true bond strength achieved by the particular bonding parameters used. Likewise, a fracture mode revealing some base-metal fracture is not a true measure of the "bond" strength.

For all results reported herein, the failure mode is at the plate-plate interface unless otherwise noted. The only exception is for silver-plated beryllium, where recorded bond strengths of 8 ksi or greater resulted in some beryllium fracture. Contrary to the above comment that recorded bond strengths revealing some base-material fracture are not a measure of the true bond strength, unnecked beryllium specimens that fractured at stresses up to 20 ksi correlate well with other materials bonded under the same conditions that fractured at the plate-plate interface.

RESULTS

A standard bond, defined below, will be assumed in this section unless otherwise noted:

1. silver-plated substrate,
2. a nominal 200 μ in. of silver on each specimen half,
3. silver polished before bonding,
4. air preload (4.2 ksi) before bonding,
5. bonded in air, and
6. bonding compressive load released at room temperature.

Effect of Bond Time

Beryllium specimens bonded for nominal times of 0.5, 5.0, and 60.0 min reveal that the bond strength is insensitive to the bond time. Results shown in Fig. 11 were obtained for the following bond conditions:

<u>Temperature (°F)</u>	<u>Compressive Stress (ksi)</u>
225	30.0
280	30.0
400	10.0

These results are also indicated in Fig. 12 with additional data from molybdenum and stainless-steel (310 μ in. of silver) specimens bonded at 225°F and 30 ksi compressive stress. Again the bond strength is shown to be independent of the bonding time.

In the results to follow, I do not indicate the bond times; however, the majority of the bonds were obtained at either 5 or 60 min.

Fig. 11. Effect of bonding time for beryllium.

Fig. 12. Effect of bonding time for various metal substrates.

Effect of Bonding Compressive Stress

Beryllium was bonded at 225, 280, and 400°F at various compressive stresses. Results, Fig. 13, indicate a temperature-dependent linear relationship between the bond strength and the compressive bonding stress.

Numbers adjacent to the data points indicate the total number of bond strengths comprising the average value plotted. The absence of a number implies one test.

Results obtained at 225°F deviate from a straight line at approximately 27 ksi. This can be explained by the onset of plastic deformation in the beryllium. The data at higher temperatures do not clearly show this deviation because the bond strengths were very high and the limiting bond strength for unnecked specimens was nearly achieved. These data will be correlated later to the amount of plastic upset as a function of the bonding parameters.

Two lines are shown for data at 280°F. The data, obtained on specimens processed in two different ways, will be discussed in detail in the section "Effect of Bonding Environment and Silver-Surface Conditions."

Effect of Plating Thickness

Beryllium and stainless-steel specimens plated with varying thicknesses of silver (30 to 580 μ in. of silver per specimen half) were bonded at 225°F with a bonding compressive stress of 30 ksi. The bond strengths were found to linearly increase with increasing silver thickness. These data, Fig. 14, have been normalized in the

Fig. 13. Effect of bonding compressive stress for silver-plated beryllium.

Fig. 14. Effect of total silver thickness-to-diameter ratio (t/D).

conventional manner by plotting the bond strengths as a function of the ratio of total silver thickness to specimen diameter (t/D). Data for necked beryllium specimens bonded at 225°F and 30 ksi, plotted on the same figure, clearly show the increase in bond strength that results from removing the built-in notch. Additional data from necked beryllium specimens bonded at different temperatures and compressive stresses are also shown.

Effect of Bonding Temperature

Various substrate materials bonded at 30 ksi for temperatures ranging from 225 to 280°F reveal a linear relationship between the room-temperature bond strength and the bonding temperature, Fig. 15. The change in bond strength per unit change in temperature is reasonably independent of the substrate material for the temperature range reported. Additional data for beryllium bonded in a vacuum, Fig. 16, confirm this linear relationship.

Beryllium specimens bonded in the as-plated condition at 24 ksi bonding compressive stress in a vacuum indicate a rapid increase in bond strength with change in bonding temperature near $0.5 T_m$ of silver (650°F), Fig. 17.

Effect of the Release of Bonding Compressive Stress and Effect of Modulus of Elasticity of the Substrate

Also shown in Fig. 17 is the influence of the stored compressive energy. Bond strengths comprising the lower curve were obtained from specimens for which the compressive bonding stress was

Fig. 15. Effect of bonding temperature for various silver-plated metals.

Fig. 16. Effect of bonding temperature in air and vacuum environments.

Fig. 17. Effect of bonding temperature for as-plated specimens of beryllium.

reduced to 4.2 ksi after the bond cycle was complete, that is, when the specimens began to cool down to room temperature. Higher bond strengths were obtained on those specimens for which the bonding compressive stress was maintained until the specimens reached room temperature.

Bond strengths obtained on stainless steel, beryllium, molybdenum, and tungsten bonded at 225 and 280°F and at 30-psi compressive stress are shown in Fig. 18 plotted as functions of the modulus of elasticity of the substrate material. A copper specimen bonded at 225°F would not sustain the 30-ksi stress, and the maximum applied stress of 18.5 ksi resulted in a large amount of upset. This permitted more intimate contact of the silver bond interfaces; and the bond strength, as expected, was much higher (23.6 ksi) than those obtained on the other substrate materials, which exhibited very little or no upset as a result of the bond cycle.

Data from Moffatt and Wulff⁷⁹ on lead brazed joints in steel and molybdenum are also shown in Fig. 18. All results indicate a linear relationship between bond strength and modulus of elasticity of the substrate, and the slopes of the lines are approximately equal.

Effect of Bonding Environment and Silver-Surface Conditions

This study was begun under the assumption that the bonds in a vacuum environment would be superior to those made in air. This assumption proved to be invalid, as shown by Fig. 16. Beryllium specimens bonded at various temperatures at a 30-ksi bonding compressive stress in air and in vacuum (2×10^{-6} to 4×10^{-7} Torr) reveal no difference in bond strengths. In fact, bonding in other extreme

Fig. 18. Effect of substrate modulus of elasticity.

environments such as helium and oxygen does not significantly change the bond strength, as shown in Fig. 19, Tests 1 and 2.

All results in Fig. 19 were obtained at 225°F and 30-ksi bonding stress, except for Test 8, in which bonding was at 289°F and 30 ksi. The sectioned bars represent the bond strength to be expected for a standard bond cycle. Variations in expected strengths for Tests 1 through 7 result from corrections made for the silver-plating thickness actually used.

The test numbered 3 in the figure involved the deliberate contamination of the silver surface after polishing by exposure to H_2S gas. The surface became dark grey in color as a result of the formation of Ag_2S . The bond strength was less than expected for a standard polished specimen, but, based on a sample of one, no firm conclusion can be reached. In the tests numbered 4 and 5, the silver was polished with the standard aluminum oxide, but the carrier was changed from the lapping oil that was normally used to distilled water. These results clearly show the reduction in strength resulting from water contamination. The specimen in Test 5 was rebonded after repolishing with the standard vehicle. The bond strength was then approximately as expected.

Specimens bonded in the as-plated condition required bonding temperatures in excess of 500°F in order to achieve some measurable bond strength when plated with 200 μ in. of silver. Cleaning the silver bond interfaces with acetone, alcohol, or trichloroethylene showed no difference, but cleaning with ammonia resulted in a significant increase in bond strength. Since a chemical reaction was suggested by the ammonia solution treatment, specimens were acid-etched with

Fig. 19. Effect of silver surface conditions. All bonds except no. 8 were made at 225°F and 30 ksi compressive bonding stress; no. 8 was at 280°F and 30 ksi.

nitric and with potassium cyanide acid solutions to remove a thin layer of silver from the bond interface. This technique proved unreliable because small, randomly distributed, circular portions of the surfaces were not removed. Nevertheless, the bond temperature required to achieve good bonds was significantly decreased. One specimen etched with a 40% solution of nitric acid and bonded at 300°F and 24 ksi in a vacuum achieved a 13.7 ksi bond strength. This agrees favorably with the results indicated in Fig. 13 for polished silver bonds at 280°F.

At this stage of the investigation, I concluded that the silver surface was being contaminated in the vacuum evaporation plating system after the plating process was terminated. Backfilling the vacuum plating system with argon or nitrogen immediately after termination of the plating process did not change the bond strengths achieved on as-plated and bonded specimens.

The standard polishing procedure previously discussed exposed the polished silver surfaces to acetone for approximately 20 min. One specimen was permitted to soak in acetone for 1 hr, and the resultant bond strength was not considered significantly different than that of the standard specimen as shown in the test numbered 6 in Fig. 19. Over 100 bonds were made after this test, without a great deal of concern about the exact acetone exposure time. Near the end of this study, an attempt was made to obtain further data for beryllium specimens bonded at 280°F as a function of the compressive bonding stress. The specimens were not ultrasonically cleaned in acetone, and the bond strengths were considerably greater than had previously been obtained. These results are shown in Fig. 13 as

the upper 280°F bond curve. This prompted a further study of the acetone contamination as shown by Tests 7 and 8 in Fig. 19. It must thus be concluded that a static exposure for prolonged periods of time to acetone is detrimental to bond strength. Test 8 indicates that a dynamic or ultrasonic exposure is even more harmful.

Effect of Bake-Out Time and Temperature

The standardized bond procedure consisted of preloading the specimens to 4.2 ksi, heating them to the bond temperature, and then putting them under compressive loading. Specimens that were baked out were separated, heated to the bake-out temperature for various specified times, and then compressively loaded.

The results of these tests, shown in Fig. 20, indicate no substantial change in bond strengths. Test 1 is the only bond that shows an increase in the expected bond strength. This specimen was bonded during the time that the specimens were not ultrasonically cleaned with acetone. Thus the increase may be attributed to greatly decreased exposure to acetone. Tests 4, 5, and 6 were baked-out and bonded in a vacuum of 2×10^{-6} to 7×10^{-7} Torr. The last test was on an unpolished silver specimen.

Bond Strength of Gold-Plated Stainless Steel as a Function of the Bond Temperature

A technique for gold-plating beryllium was not developed. The results presented thus far indicate that the substrate is not critical to the bonding process if the compressive bonding stress does not

Temperatures and bake-out times are shown above the columns.

Bonding parameters			
Test No.	Temperature (°F)	Compressive stress (ksi)	Environment
1	225	30	Air
2	225	30	Air
3	225	30	Air
4	238	30	Vacuum
5	255	30	Vacuum
6 ^a	625	24	Vacuum

^a The silver was not polished.

Fig. 20. Effect of bake-out before bonding of silver-plated beryllium.

cause an appreciable amount of upset. Since gold was considered to be a material that might bond to itself at low temperatures, stainless-steel specimens were gold plated by vacuum evaporation and electroplating. The details of the vacuum evaporation plating process have been discussed; the electroplating process is outlined as follows:

1. electroclean 40 sec at cathodic 6 V in an electrocleaner;
2. rinse in tap water;
3. low-pH-nickel strike for 30 sec at room temperature;
4. rinse in tap water;
5. copper strike 30 sec; temperature as required for type of bath;
6. rinse in tap water;
7. dip in HCl acid (10 to 25 vol%) for 60 sec;
8. rinse in distilled water;
9. gold plate (acid bath at 3 A/sq ft; plating rate of 0.0001 in. every 15 min at 160°F):
10. rinse with distilled water and alcohol.

A stainless-steel specimen pair, each half electroplated with 1500 μ in. of gold, was bonded in the as-plated condition at 30-ksi compressive bonding stress and 350°F. No measurable amount of bonding was obtained. The specimen was rebonded at 700°F (0.5 T_m Au = 743°F), and a bond strength of 12.5 ksi was obtained. The specimen was next removed from the bond fixture and the gold interfaces were polished. When this specimen was rebonded at 400°F, some measurable bond strength was obtained. When it was rebonded at 700°F, a 23.8-ksi bond strength was achieved. Another specimen

plated by vacuum evaporation with approximately 200 μ in. of gold, polished, and bonded with the same compressive bonding stress as above at 280°F indicated a bond strength of 0.7 ksi. Rebonding at 350°F produced a bond strength of 2 ksi. Finally, the specimen was rebonded at 700°F, a tensile stress of 24.9 ksi as measured by the bonding fixture failed to break the bond. The specimen was next tested on a commercial tensile machine and broke at 33.1 ksi. All bonds were made for a 60-min bond time and all fractures were at the Au-Au interface. The above results are shown in Fig. 21. Lines connecting the data are estimates of the relationship of true functional strength to bonding temperature.

Plastic Strain Induced by the Bonding Process

One of the major objectives of this study was to develop a low-temperature bonding process that would result in little if any permanent deformation of the parts being bonded. The diameters of all specimens were measured adjacent to the bond interface before and after bonding, and the plastic strain was computed as twice the change in diameter divided by the original diameter. Since the original diameter was 0.50 in., this simply becomes $4 \Delta d$. A micrometer with a least count of 0.0001 in. was used to measure the diameter. A single operator made all measurements and was able to measure repeatably to within ± 0.00005 in. This represents a maximum measurement repeatability of $\pm 0.04\%$ strain.

For all the bonds reported herein on stainless steel, molybdenum, and tungsten, no permanent upset was obtained. A copper specimen bonded at 225°F and 18.5 ksi was upset by 3.4% strain.

Fig. 21. Effect of bonding temperature — gold-plated stainless steel.

Additional copper specimens bonded at 10 ksi at temperatures up to 400°F did not exhibit any upset.

Data obtained on the upset of beryllium bonded at 24 and 30 ksi for various temperatures are shown in Fig. 22. Some additional information is shown in Fig. 23, where the plastic strain of beryllium at 225, 300 and 400°F bonding temperatures is shown as a function of the bonding compressive stress used.

Reference was made in the Results section "Effect of Compressive Bonding Stress" to the influence that plastic deformation has on the bond strength of beryllium when bonded at 225°F. Referring to Fig. 13 will show that the bond strength for 225°F bonds deviates at approximately 27 ksi bonding compressive stress. The results in Fig. 23 also indicates the onset of an appreciable amount of upset around 27-ksi compression.

Data from Necked Specimens

Results presented thus far have been aimed toward an understanding of the bonding mechanism and the relationship of bonding parameters to bond strength. The present study was concluded by bonding specimens under relatively optimum conditions, necking the specimens to remove the built-in notch (or stress riser), and determining the ultimate strength of the bond. The results, Table 5, have not been indicated previously except for some beryllium data showing the influence of the silver thickness on the bond strength.

Table 5. Bond strengths for some necked specimens.

Material	Ag thickness, ^a $\times 10^{-4}$ in.	Temperature, °F	Compression, ksi	Bond strength, ksi	Fracture location ^b	Plastic strain, ^c %
Mo	2.1	400	25.5	52.7	P	1.7 ^d
	1.9	550	30	58.1	P	
	2.2	700	30	31.4	P ^e	
W	3.2	400	30	22.9	P	
	3.0	550	30	11.9	P	
	3.1	700	30	42.2	P	
Cu	2.6	280	10	40.3	S	
	2.4	400	10	41.5 ^f	S	
	2.6	400	10	42.3 ^g	S	
SS	4.7	400	30	49.5	P	
	4.2	700	30	54.8	P	
Be	1.8	225	35	18.2	Ag	0.5
	5.2	225	30	44.0	S	0.2
	0.4	280	30	15.5	Ag	0.4
	2.2	280	30	30.5	S + 5% Ag	0.3
	2.5	280	30	41.5	S	0.2
	1.8	350	25	40.4	S	0.1
	0.3	400	20	16.4	Ag	
	0.5	400	30	25.1	P + 30% Ag	0.4
	2.0	400	20	34.1	S + Ag ^h	
	5.4	500	10	37.5	S + 5% Ag	

^a Plate thickness per specimen half before polishing.

^b P = Plate peeled; S = Substrate; Ag = Ag-Ag.

^c Plastic strain was zero unless otherwise noted.

^d This specimen was previously plated and bonded. To remove the silver, the specimen was heated until the Ag evaporated; thus, the mechanical properties of the specimen were changed. The 25.5-ksi compressive stress caused a plastic upset ($\epsilon_p = 1.7\%$).

^e This specimen was back-heated prior to plating to 740°C; the other two specimens were heated to 775°C.

^f Bond time: 60 min.

^g Bond time: 0.5 min.

^h Ag fracture surface was only evident along unbonded regions of beryllium surface scratches.

Fig. 22. Plastic strain in beryllium induced by the bonding cycle as related to the bonding temperature.

Fig. 23. Plastic strain induced in beryllium by the bonding cycle as related to the bonding compressive stress.

Metallography and Related Examinations

The technique for plating silver on beryllium such that the adhesion exceeds the bulk strength of beryllium has been discussed. Examination of the plate-substrate interface by both optical and electron microscopy reveals a sharp transition at the silver-beryllium interface. Electron microprobe analysis indicates that if diffusion of silver into beryllium occurred it was less than $2\ \mu$.

Structure of the as-plated silver was determined by x-ray diffraction to be randomly oriented polycrystalline. The surface of a vacuum-evaporated, silver-plated beryllium specimen preheated to 1400°F , plated, and back-filled with argon while at 248°F was examined by scanning electron microscopy (SEM) (Fig. 24). The grain size was found to be approximately $2\ \mu$ in diameter. A stainless steel specimen heated to between 1200 and 1400°F and again back-filled with argon at 625°F was similarly examined. The grain size was again about $2\ \mu$. After the surface was polished, using the technique used prior to bonding, and subsequently etched with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2(5:3)$, the grain structure was observable with an optical microscope(Figs. 25 and 26).

The as-polished surface, cleaned in the normal manner, appeared to be smoother than the as-plated surface as shown in Figs. 27 and 24, respectively. Cold work of the silver surface is clearly evident by the smearing that occurs at the intersection of the polishing lines, as shown in Fig. 27.

The silver-grain structure in a plane perpendicular to the bond surface was not easily determined. This orientation was desirable because the bond interface could be examined and, hopefully, lead to

Fig. 24. Photomicrograph of as-plated silver surface — scanning electron microscope.

Fig. 25. Polished and etched plated silver, photographed at magnification of X600.

Fig. 26. Polished and etched plated silver, photographed at magnification of $\times 1400$.

Fig. 27. Photomicrograph of plated silver, as-polished before bonding — scanning electron microscope.

a better understanding of the bonding mechanism. The structure of the silver perpendicular to the bond interface is columnar as shown in Figs. 28 to 30. This is more evident for the specimen shown in Figs. 29 and 30, which had a silver thickness of 500 $\mu\text{in.}$ per specimen half.

The silver-silver interface as viewed in a plane perpendicular to the bond interface was severely etched for bonds made at low temperatures (Figs. 28 to 30). A silver-plated and polished beryllium specimen bonded at 225°F (Fig. 29) was reheated in a vacuum for 1 hr without a compressive load to 750°F, which is well above the recrystallization temperature of cold-worked silver. This specimen, metallographically reprocessed and etched twice as long as previously (Fig. 29), is shown in Fig. 30. The silver-silver interface is less evident after the annealing cycle.

As-polished silver bond interface surfaces contain many very fine polishing marks, as was shown in Fig. 27. These polishing marks remained evident on the fracture surfaces of those specimens that failed through the silver; that is, the silver-silver fracture surfaces were the original silver bond interface surfaces. Microscopic examination of these silver-silver fracture surfaces never revealed any transfer of silver from one surface to the other.

A high-strength (16.8 ksi, unnecked) silver-silver fracture surface obtained on stainless steel plated with 580 $\mu\text{in.}$ of silver and bonded at 225°F, 30 ksi, for 5 min as shown in Fig. 31a with the same location on the other surface in Fig. 31b. The flatter region of the photo resulted from a small surface imperfection, and no Ag-Ag contact was obtained. A careful analysis of the fracture surface,

Fig. 28. Photomicrograph of low-temperature bonded section -- standard bond cycle.

Fig. 29. Photomicrograph of low-temperature bonded section after standard bond cycle (thick silver plate).

Fig. 30. Photomicrograph of low-temperature bonded section, vacuum annealed at 750°F, 1 hr.

Fig. 31. Fracture surfaces of a low-temperature bond.

photographed with oblique lighting, leads to the observation that the fractures were of a cone-cone nature on a microscopic scale. No explanation for this fracture mode is advanced. The polishing marks are evident and may be seen passing over the tips of the cones. Again, there is no visual evidence of silver having transferred from one surface to the other. This lack of transfer of material, even at the cone tips, suggests that a cohesion bonding mechanism is valid. Had localized recrystallization occurred mass metal transfer would have been expected.

Since the columnar grain structure was not easily revealed, specimens were sectioned on a plane which was 6 to 10 deg from the plane of the bond interface surface. The silver-grain structure was very nearly that seen on the bond surface.

An unpolished silver specimen that was bonded at 750°F, 24-ksi compression for 1 hr and that failed to fracture at 25.7 ksi is shown in Fig. 32. Figure 32a shows the bulk of the silver, while Fig. 32b shows the bond interface. The region at the interface is readily identified. A light microscope picture, Fig. 33, shows some voids at the interface and, apparently, recrystallization.

A low-temperature bond revealed preferential etching at the polished interface. Figure 34, a photomicrograph of a 255°F bond, shows the wide bond zone. Changing the focus of the microscope revealed the preferential etching, and a sketch below the figure reveals the approximate surface profile. The heavy line shows the surface contour of the viewed surface and reveals why the plate thicknesses appear different.

a. Bulk silver.

b. Bond interface.

Fig. 32. Photomicrographs of high-temperature bonded section — scanning electron microscope.

Fig. 33. Photomicrograph of high-temperature bonded section viewed 10 deg from plane of bond interface.

Fig. 34. Photomicrograph of low-temperature bonded section viewed $6\frac{1}{2}\text{ deg}$ from plane of bond interface.

DISCUSSION OF RESULTS

Bonding Mechanism

The term cohesion, or adhesion for dissimilar metal couples, is generally used to explain the formation of a solid-state bond that cannot be attributed to another possible bonding mechanism such as diffusion or recrystallization. A cohesive bond is generally assumed to be derived from atomic forces. This is achieved by bringing the two surfaces to be bonded into such intimate contact that the force field of the atoms on either side of the interface interact. If either surface or both of them are contaminated, the distance separating the atoms may be too large to permit the interaction, and a bond will not be achieved unless the contaminating barrier can be broken through. The force required to separate the interfaces will be related to the total area of intimate contacts developed.

There does not exist any technique for measuring the total area of intimate contact, although resistance measurements have been used to approximate the area. This technique could not be used in this study because the area is large and the resistance to be measured is much less than can be measured with existing equipment. Techniques for detecting adhesion (or cohesion) on a microscopic basis are also undeveloped. Thus, if it can be shown that the bonding mechanism is not diffusion or recrystallization—the other recognized possible bonding mechanisms—it can be concluded that the bonding studied herein is cohesion.

The results clearly indicate that the bond strength is not a function of bonding time. Both diffusion and recrystallization are

time-dependent. The bond temperatures, 225 to 280°F, for which most of the data are obtained are considerably less than the temperature generally associated with diffusion-activated phenomena ($0.5 T_m$ or 650°F for silver) and less than the recrystallization temperature of silver (392°F). The recrystallization temperature of a metal is not a well-defined parameter, however, since it depends upon the degree of cold work and the purity of the metal. No analysis of the purity of the plated silver was obtained, but it may be assumed to be greater than the source material (99.95%) because of the selective manner in which vaporization occurs.

A comprehensive study on spectroscopically pure silver (99.999%) relating the ultimate stress and elongation to the degree of cold work and to annealing cycles of 15 min at various temperatures was done by Balicki and Leeds.⁸⁰ Although Christie⁸¹ questions the data for reductions of 80% or more, the results at lower deformations are apparently valid. Figure 35 shows the results of Balacki and Leeds for the ultimate stress related to the annealing temperature and the degree of cold work. The authors state that the temperature for the beginning of recrystallization for some specified degree of cold work can be determined by noting the annealing temperature at which the ultimate stress first begins to decrease; the temperature for the end of recrystallization is noted when the ultimate stress reaches some steady value. The temperature for the onset of recrystallization at 80% deformation is approximately 285°F; at a 20% deformation the temperature is 438°F; and at 5% deformation the temperature is 482°F. Thus, even for the most severe deformation the

Fig. 35. The ultimate stress of pure cold-worked silver as related to 15-min annealing cycles.

temperature for the onset of recrystallization is greater than the bond temperatures generally used in this study.

Photomicrographs of sections through the bond interface show a more rapid attack of the silver-etching reagent at the bond interface than elsewhere in the silver material. One specimen that was reheated to above the recrystallization temperature and re-etched revealed a more uniform etch and some grain growth across the interface. Since the polishing procedure used on the interface prior to bonding introduces a cold-worker layer, and because strain-hardened materials are generally more susceptible to attack by acids, this provides further evidence that recrystallization does not occur at the bond interface during the low-temperature bonding cycle.

The as-plated bonds require temperatures near $0.5 T_m$ for silver before a bond is formed. I therefore suspect that this bonding mechanism is diffusion. I also believe that a surface contamination barrier exists and, with the high thermal energy supplied, the barrier is overcome by diffusion of silver atoms through this barrier or diffusion of the contaminant into the silver. When this contaminating layer is removed by mechanical polishing, bonds can be achieved at much lower temperatures. This bonding mechanism, as discussed above, is cohesion. It might be argued, however, that the polishing introduces a high state of strain at the bond interface that is, upon bonding, somewhat released by diffusion or recrystallization at the interface on such a microscopic scale that it cannot be detected by available techniques. This argument can be opposed by examining the results of two different bond techniques used at the low temperatures. First, a thin layer of silver was removed from the bond interface

surface by acid etching. Thus the contaminating layer was removed and the bond interface was not strain hardened. The 300°F bond agreed closely with the results obtained on polished specimens. Secondly, several polished specimens, preheated to their bonding temperature in air and in vacuum for various periods of time while separated, showed no degradation in bond strength. If recrystallization is the bonding mechanism, the preheat cycle should have caused some recrystallization and a lower bond should have ultimately resulted. Thus it is concluded that the surface preparation after plating serves only to remove a contaminating film for the silver surface.

There exists one final aspect of this bonding process that may contribute to the bonding mechanism. The bond interfaces were brought into intimate contact by a compressive load. It was experimentally determined that the bond strength is linearly dependent upon the compressive stress applied, except for stresses that produced a plastic strain in the substrate. I believe that the increase in bond strength with increasing compressive loads results from an increase in the area of intimate contact at the bond surface. When the interfaces are brought together, contact is first made at one or several points. When the compressive load is increased, these point contacts deform elastically, whereupon other points of contact are made. Further loading results in elastic and plastic deformation of these points of contact, which therefore increases the total area of contact. Either the silver at each area of contact is deformed elastically or, if the contact has deformed plastically, the deformation is elastic with increasing degrees of cold work toward the center of the contact area. For these areas of plastic deformation, it might be argued that the

work introduced could be capable of lowering the recrystallization temperature, since the recrystallization temperature is lowest at the center of the contact area. Of course, for those specimens polished prior to bonding, all contact areas would be cold-worked because of plastic flow introduced by the polishing. Thus the strength in the acid-etched specimen should decrease, because some of the contact area would have been elastically deformed. The topography of the interface surfaces is unknown, and the state of stress for the individual contact points is difficult to estimate. It is, therefore, not possible to estimate the area percent that would be elastically deformed at the interface. If a localized recrystallization bonding mechanism is assumed, no estimate can be made for the expected decrease in bond strength resulting from acid-etched as compared to polished specimens.

The above discussion does not lead to an impasse, however. If the results are examined macroscopically, the conclusion that the bonding mechanism is cohesion is easily defended. However, a microscopic examination leaves open the possibility of recrystallization. The recrystallization temperature of silver is dependent upon the purity and upon the degree of cold work of the silver. It is inconceivable that, for the temperatures used, a bond time of 0.5 min would have resulted in complete recrystallization. The degree of cold work varied over the surface and therefore so would the recrystallization temperature. Even on a microscopic basis the bond strength should be sensitive to the bond time. Since this was not the case, the cohesion bonding mechanism may be assumed valid.

Effect of Plating Thickness and Purity

The strength of butt joints increases linearly with increased t/D (plate thickness to specimen diameter) ratios (Fig. 14). This relationship was established on 0.005-in.-diam beryllium and stainless-steel specimens bonded at 225°F and 30-ksi bonding compressive stress for plate thicknesses ranging from 30 to 600 $\mu\text{in.}$ of silver per specimen half. The fracture mode for all the stainless-steel specimens was Ag-Ag and, therefore, represents a true bond strength. The beryllium specimens exhibited varying degrees of Ag-Ag and beryllium fracture surfaces. For example, the maximum plate-thickness fracture surface showed approximately 80% Be fracture for the 17.3-ksi bond strength, and the minimum plate-thickness fracture was 100% Ag-Ag. It is therefore concluded that bond strengths up to 17 ksi for unnecked beryllium specimens are a true measure of the bond strength, because they correlate well to Ag-Ag bond fracture strengths obtained on the stainless-steel specimens.

Necked specimens typically show a significant increase in the bond strength that may be attributed to the removal of stress concentrations at the notched bond interface, an important consideration for HCP-brittle beryllium. For a t/D ratio of 0.0009, the bond strength increased by over a factor of 2 for necked specimens, compared to the as-bonded specimen, when bonded at 225°F and 30 ksi. Another necked specimen bonded under the same conditions but with a silver thickness of 500 $\mu\text{in.}$ per specimen ($t/D = 0.0028$) fractured approximately 1/16 in. from the bond interface at 44 ksi. This represents the limiting strength of beryllium but is again an increase of over 2 when compared to the unnecked-specimen strength. These

necked-specimen data points are not connected by a line in Fig. 14, because a specimen with a t/D ratio of less than 0.0023 may have also fractured completely in the beryllium. Additional data obtained on necked specimens bonded at 280°F, 30 ksi and 400°F, 20 ksi are connected because the fracture strengths are somewhat less than the bulk strength of beryllium. From these data I conclude that the change in bond strength with change in t/D ratios is not sensitive to the bonding parameters.

In a general sense two questions arise regarding the above conclusion: 1) why does the bond strength increase with increasing t/D ratios, and 2) can the data be extrapolated to large t/D ratios? The first question has been previously discussed in the "Introduction," in "Relation of Film Thickness to Bond Strength." Many investigators have shown that braze and adhesive bonds increase in strength with decreasing t/D ratios as long as the bond formation is sound. The triaxial state of stress responsible for the increase in bond strengths applies equally as well to this study; however, a sound bond can not be assumed. In fact, the bond formation that depends on intimate contact at the silver interfaces is impeded by lower t/D ratios, that is, thinner silver plates. For thin plates the stress at the interface will be triaxial compression for an applied bonding compressive load because the yield stress of the plate is less than that of the substrate. For thicker plates the radial compressive stresses are less, thus permitting more plastic deformation and therefore increasing the contact area. I conclude, therefore, that the increase in bond strength with increase in t/D results from improved bond formation, that is, increased area of contact.

There must be a limiting value of t/D beyond which either full bond formation has been achieved, or the decrease in bond strength resulting from the increasing t/D ratio becomes more significant than the increasing bond formation. This relationship is shown in Fig. 36. The region A-B represents the t/D ratios tested. The bond strength increases to point C, beyond which the bond strength decreases to the limiting value shown at D. This limiting strength represents the ultimate uniaxial tensile strength of the plated material. An upper limit might also exist depending on the bonding parameters and the substrate material. In this event, the curve would be truncated by a horizontal line. For the silver-beryllium combination, plating techniques were developed that produced a plate adhesion that exceeded the bulk strength of beryllium; this general curve would therefore be truncated at the ultimate strength of beryllium, 40 ksi. For the silver-stainless steel combination, the plating technique resulted in a plate adhesion strength of approximately 55 ksi, thus truncating the curve at this stress level.

Numerous investigators have shown that increased purity of the bonding material would be beneficial in developing a bond. The only attempt made in the present study to establish this was made on gold-plated stainless steel. The bond strength of vacuum-evaporated gold exceeded that of electroplated gold. It should also be noted that the electroplated gold was approximately seven times thicker than the vacuum evaporated gold and, other factors being equal, should have resulted in a much higher bond strength. Thus it can be concluded that the purity of the plate material is indeed important.

Fig. 36. Predicted bond strength of specimens vs thickness-to-diameter ratio.

Effect of Stress and Strain

The bond strength for unnecked specimens is linearly related to the bonding compressive stress over the range tested. For the lowest bond temperature used (225°F), the bond strength was found to increase at a greater rate when the compressive stress was sufficient to cause a plastic strain in the beryllium substrate. The increase in area of contact resulting from increased compressive loads would account for the increase in bond strength.

When the curves in Fig. 13 are extrapolated to zero compressive stress, the results indicate some significant bond strength, σ_0 . This probably results from the fact that the bond formation was accomplished at some temperature T_B while the bond destruction or bond-strength determination was conducted at room temperature, T_0 . If we assume that the bond area remains constant at T_B and T_0 , then the bond strength at T_0 should be greater than at T_B because there is a difference in the strength of silver at these temperatures. Thus σ_0 represents the increase in strength resulting from the difference in bond and test temperatures.

The bond and test procedures differed in a second way, however. The bonding compressive stress was applied at the bond temperature T_B and released at room temperature, T_0 . The results, Fig. 17, reveal that if the compressive load is released at T_B rather than at T_0 , a significant decrease in bond strength is obtained. This may be explained by assuming that the stored strain energy, $\int F d\epsilon$, fractures some of the bond when released. Assuming that the strain energy released is not a function of the specimen temperature when the load is released, and since the strength of silver is less at T_B

than at T_O , we see with the aid of Fig. 37 that more of the bond is destroyed by releasing the load at T_B than at T_O . Thus a decrease in bond strength measured at T_O is expected by releasing the load at T_B rather than at T_O .

Tests were not conducted for low-temperature bonds to determine the effect of stored elastic-strain energy on the bond strength. The state of stress at the Ag-Ag interface is not pure compression during the bonding cycle or pure tension during the tensile test. Thus it is not possible to compute the stored elastic-strain energy.

Further insight can be gained by considering the results obtained for low-temperature bonds on materials with varying moduli or elasticity, Fig. 18. The stored elastic-strain energy in the substrate material decreases with increasing modulus for a fixed compressive stress. Thus, if we focus our attention only on the substrate stored elastic energy, we would expect a greater bond strength for materials with higher moduli of elasticity. The analysis is not so simple, however. The triaxial state of stress in the silver is a result of differences in yield strengths and moduli of elasticity of the plate and substrate. Assume that the area of contact and the degree of bonding for some temperature, plate thickness, and compressive bonding stress are independent of these mechanical parameters. Then, the tensile radial stresses in the silver during the tensile test would be greater for the more rigid, that is, greater modulus of elasticity, substrate material. It follows that the measured bond strength would be greater, the higher the modulus of elasticity. Thus, the observed increase in bond strength with increasing substrate modulus of elasticity can be explained by the decrease in stored

Fig. 37. Effect of released bonding compressive load — idealized contact.

elastic strain energy and/or the increase in the radial stresses within the silver.

Also shown in Fig. 18 are results by Moffatt and Wulff of lead (with 0.1% nickel) braze joints in steel and arc-cast molybdenum.⁷⁹ The t/D ratios were between 0.0005 and 0.001, and the molybdenum bond contained a "few small nonwetted regions." The slope of the line agrees well with the data obtained during this study ($t/D = 0.0008$). The braze joints were not loaded in compression and therefore did not contain any stored elastic-strain energy except for that introduced by thermal contraction. I conclude that thin joint strengths linearly increase with increasing modulus of elasticity of the substrate. The change in bond strength per change in modulus is a constant not dependent upon the filler material (lead or silver) or upon the bond parameters (brazed or solid-state bonds at different bond temperatures) for a given t/D ratio. I attribute the increase in bond strength with substrate modulus primarily to the increase in radial stresses in the plate or braze material and secondarily to the reduction of the stored elastic energy.

Bond Environment and Surface Preparation

The bonding environments and surface cleanliness are generally considered to be very important considerations for successful bonding. The results of this study show that the bonding environment is not important (air, oxygen, helium, or vacuum). The surface preparation is indeed critical, however. Polishing the surfaces with aluminum oxide and water resulted in much lower bond strengths than polishing with aluminum oxide and lapping oil. Exposure of the

polished silver surface to H_2S did not drastically lower the bond strength. It may indeed be that the polishing of silver with oil, which probably contains some sulphur, was beneficial. It was pointed out that the surface self-diffusion of silver was enhanced with adsorbed sulphur. Polished surfaces were cleaned with acetone. Extended soak or ultrasonic cleaning with acetone reduced the bond strengths. Methods different from those used in this study for polishing and cleaning may reduce the required bond temperature still further.

SUMMARY AND CONCLUSIONS

A technique considered feasible for production has been developed for joining beryllium in air at temperatures of 225 to 280°F that results in bond strengths exceeding the strength of beryllium (type S 200 C). The interfaces to be joined are polished flat, evaporation-plated with silver in vacuum, polished with aluminum oxide and lapping oil to remove contaminants from the silver bond surface, cleaned with acetone, and bonded in air at the required temperature and compressive load. This bonding procedure, resulting in room-temperature bonds that exhibit beryllium fracture strengths, develops an upset in the parts of 0.2% strain or less.

The plating system consisted of a silicone-oil diffusion pump. To assure good adhesion of silver to beryllium, it was found necessary to plate the beryllium while heated to at least 1100°F and to maintain the vacuum system free of silicone-oil vapors. Neither requirement would prevent this method's being used on a production line, but the vacuum system must be either monitored for silicone oil or designed to eliminate this source of contamination.

The bond strength for beryllium specimens was sensitive to the radial alignment and interface flatness. The radial alignment is not a problem peculiar to this bonding process and is not considered to be any more restrictive than any other presently-used bonding techniques. Thus, the loss in bond strength resulting from the notch effect due to this misalignment is a common problem and does not reduce the potential of this process. The notch effect resulting from the interface flatness, however, is a problem uniquely associated with solid-state

bonding. Specimens were polished to a flatness of 20 $\mu\text{in.}$ across the 0.500-in.-diam end. After the silver was hand polished on a thick-nap cloth, the specimens were flat to within 30 $\mu\text{in.}$ except at the extreme outside diameter, which was rounded off severely as shown by Fig. 21. This built-in notch caused stress concentrations, and the measured bond strength was less than was achieved by machining away the notch—that is, necked specimens.

The rounded-off silver edge can be minimized by using a polishing cloth, such as silk or nylon, that has no nap. This procedural change is recommended for production application.

Results indicate that the bond strength

1. is independent of the bonding time;
2. linearly increases with the bonding compressive stress (for elastic substrate stresses);
3. linearly increases with plating thickness (35 to 600 $\mu\text{in.}$);
4. linearly increases with bonding temperature (225 to 280°F);
5. linearly increases with substrate modulus of elasticity;
6. is greater at room temperature if the bonding compressive stress is maintained until the specimen has cooled to room temperature;
7. is not sensitive to the bond environment (oxygen, air, helium, vacuum— 10^{-6} Torr);
8. is not influenced by baking-out at the bond temperature before compressively loading;
9. decreases if the polishing fluid is water rather than lapping oil;

10. decreases with extended exposure to acetone; and
11. is not influenced by air exposures after polishing and cleaning for up to $1\frac{1}{2}$ hr.

The bonding mechanism is one of cohesion for the polished silver specimens and is probably a diffusion mechanism for the as-plated specimens.

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