UNCLASSIFIED

1

SEP-227

METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

FUNDAMENTALS OF DIFFUSIONAL
BONDING—I

First Annual Progress Report, June 30, 1955
to June 30, 1956

By
L. Castleman
L. Seigle

August 13, 1956

Atomic Energy Division
Sylvania Electric Products, Inc.
Bayside, New York

Technical Information Service Extension, Oak Ridge, Tenn.

UNCLASSIFIED

583 01

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA. Price 30 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

**DO NOT
PHOTOSTAT**

DISCLAIMER

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

DISCLAIMER

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

FUNDAMENTALS OF DIFFUSIONAL BONDING - I

L. Castleman and L. Seigle

First Annual Progress Report
June 30th, 1955 to June 30th, 1956

Contract AT-30-1 GEN 366
AEC Division of Research

Issued: August 13, 1956

Atomic Energy Division
SYLVANIA ELECTRIC PRODUCTS INC.
Bayside, New York

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT.....	5
I. INTRODUCTION.....	6
II. EXPERIMENTAL PROCEDURE.....	7
A. Specimen Preparation.....	7
B. Diffusion Bonding Runs.....	8
C. Measurement of Layer Thicknesses.....	9
D. Microhardness Measurements.....	9
III. EXPERIMENTAL RESULTS.....	10
A. Diffusional Bonding Phases In The Al-Ni Alloy System.....	10
B. Growth of Intermetallic Phases.....	12
C. Other Studies.....	13
IV. DISCUSSION OF RESULTS.....	14
A. Appearance of Phases During Diffusional Bonding.....	14
B. Kinetics of Layer Growth.....	15
C. Future Work.....	17
V. CONCLUSIONS.....	18
REFERENCES.....	19
APPENDIX.....	34

ABSTRACT

A detailed study has been initiated of the formation of intermediate layers in the diffusion zone of Al-Ni diffusion couples. This system was chosen because of its significance in fuel element technology. It has been confirmed that only two out of four possible layers form observably during diffusion - the Ni_2Al_3 and NiAl_3 phases. The growth of the intermediate layers occurs initially at a rate different from that predicted by the ideal diffusion equations; however, once a minimum thickness is reached, behavior becomes more normal.

I. INTRODUCTION

Investigations of bond formation in the cladding of fuel elements by pressure welding have shown that the size and nature of the diffusion zone are significantly affected by variations in applied pressure^(1,2,3,4). Increasing pressure alters the thicknesses of intermediate phase layers in the diffusion zone and changes the strength of the bond. Since this effect may be important from both a practical and a theoretical point of view, a study was undertaken in December 1954 to investigate the phenomenon in detail. The first phase of the investigation consisted of a literature survey of those phenomena considered to have a bearing on the problem; i.e., the kinetics of intermediate phase formation, and the effect of stress on diffusion rates. The findings are summarized briefly below.

According to the literature, intermediate alloy layers, once formed, should grow parabolically with time if bulk diffusion through the layers is the rate-controlling factor and if concentrations are maintained constant at phase interfaces; for such cases analytical or graphical solutions^(5,6) are available. The equilibrium phase diagram for a given alloy system was formerly thought to be useful in predicting the appearance of phases during diffusion; it was believed that phases occurring over a highly restricted range of compositions would tend not to grow in competition with adjacent phases having much wider ranges of solubility (if the diffusion coefficients were not too dissimilar). However, the experimental studies made^(7,8) indicated that the simple parabolic law was not obeyed in general, and that a highly restricted range of solubility was neither necessary nor sufficient to insure the non-appearance of an intermediate alloy phase during diffusion.

The number of investigations concerning the effects of stress upon diffusion are few, and practically all of them have been made within the past decade. Hydrostatic pressure decreases the self diffusion coefficients of sodium⁽⁹⁾, phosphorus⁽¹⁰⁾, and zinc⁽¹¹⁾. In zinc, the anisotropy of diffusion is also decreased. The effect of hydrostatic pressure on the diffusion coefficient of

copper in aluminum is ambiguous⁽¹²⁾. Uni-axial compressive stress below the elastic limit reduces the diffusion coefficient in zinc; in iron⁽¹³⁾, however, uni-axial compression has no effect unless plastic distortion occurs, and then the diffusion coefficient increases linearly with increasing strain rate. Information as to the effects of pressure upon intermediate alloy layer growth, other than the Sylvania work previously mentioned^(1,2,3,4) is practically non-existent.

As a result of the literature survey, the aluminum-nickel alloy system was chosen as the first to be investigated. The following plan of attack was adopted:

- (1) The layers forming during diffusion bonding under atmospheric pressure and at higher pressures were to be identified.
- (2) The time law (or laws) governing the rate of growth of the intermetallic layers was to be determined for diffusion at atmospheric and higher pressures;
- (3) If, as appeared likely, pressure exerted its effect on layer growth by altering the diffusional mechanisms, measurements were to be made of the diffusion coefficients in the individual phases of the Al-Ni alloy system, and the influence of pressure on diffusion rates was to be determined.

During the past year, emphasis has been placed primarily upon the completion of the first two parts of the program. Progress made to date is reviewed in some detail in the succeeding sections.

II. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

All specimens were made from high purity aluminum (99.99%) and high purity nickel (99.79% Ni + 0.13% Co). Half-inch diameter discs of thicknesses ranging from 0.015 to 0.050 inches were punched from

strip and given a grain-coarsening anneal; the aluminum discs were annealed for one hour at 600°C in air, and the nickel discs were given a one-hour anneal at 1100°C in hydrogen. Subsequently, the aluminum discs were cleaned in 10 w/o sodium hydroxide solution at room temperature for one minute and rinsed; prior to assembly into diffusion couples, all discs were thoroughly degreased in clean acetone, electro-polished, and re-rinsed.

B. Diffusion Bonding Runs

1. Atmospheric pressure experiments

Most of the diffusion bonding experiments under atmospheric pressure were made on couples prepared by spot welding. An aluminum disc was placed between two nickel discs, and the assembly was spot-welded in two 1/8" diameter areas; a 20 KVA machine was used, and the power and time of application were kept to the minimum required to obtain adhesion without the formation of intermetallic layers of metallographically perceptible thickness (Figs. 1a and 1b). The spot-welded couple was then sectioned through the bonded areas; one half of the disc was kept as a control, and the other half was used for the diffusion runs. All diffusion runs were made in electrical resistance tube furnaces, in which the temperature variation was $\pm 2^\circ\text{C}$ or less. Samples run less than one hour were heated in air and quenched so that errors arising from heating and cooling times would be minimized. All other samples were encapsulated in evacuated Vycor tubes containing titanium chips as getter material; the titanium chips were preferentially heated in the evacuated capsules prior to the diffusion runs to getter the remaining oxygen and nitrogen. After the diffusion runs, the capsules were quenched in cold water.

2. Pressure experiments

Diffusion bonding runs under pressure were made in a hot pressing apparatus which was essentially a smaller version of the apparatus used by Storchheim, Zambrow, and Hausner⁽¹⁾; a schematic drawing of the

apparatus is shown in Fig. 2. At the start of a diffusion run, the specimen was placed on the bottom punch, and the apparatus assembled with the upper ram out of contact with the specimen. The system was evacuated to pressures of 0.5 microns or less, and the specimen was heated to the desired temperature. As soon as the temperature was stabilized, pressure was applied to the specimen and maintained by means of a 2-1/2 ton arbor press exerting force on the top of the ram through an SR-4 Type C load cell. At the end of the run, the load was removed, the power to the furnace was cut off, and the specimen was allowed to cool in the die. Pressure runs were generally made for times equal to or greater than 16 hours; consequently, the error introduced by the cooling time (the temperature dropped 100°C in 10 minutes) was less than one percent.

A few runs were made in the hot pressing apparatus at atmospheric pressure; the layer thicknesses were measured and compared with corresponding measurements made on spot-welded samples. The differences in results due to the bonding techniques were of the same order as variations in a group of spot-welded samples diffused under presumably identical conditions.

C. Measurement Of Layer Thicknesses

Layer thicknesses were measured with a filar eyepiece on a Bausch and Lomb metallograph; the magnifications used depended upon the width of the layers. Twelve to twenty measurements were made at each interface; an average thickness and its standard deviation were calculated for each interface.

D. Microhardness Measurements

Microhardness measurements were made on a Kenntron microhardness tester; a Knoop indenter was used, and a 5 gram load was applied.

III. EXPERIMENTAL RESULTS

A. Diffusional Bonding Phases In The Al-Ni Alloy System

As was reported in the original work⁽¹⁾, metallographic observation of polished and unetched samples of Ni-Al diffusion bonds prepared under pressure revealed the following information:

- (1) Two intermetallic phases were present in samples pressed for two minutes at relatively low pressures (under 11 tsi at a pressing temperature of 500°C). The nickel-rich phase was blue-gray in color and was tentatively identified by X-ray diffraction studies as being Ni_2Al_3 (δ -phase); the aluminum-rich phase was silvery-white in color and was tentatively identified by etching techniques as NiAl_3 (β -phase).
- (2) At sufficiently high pressures (20 tsi at a pressing temperature of 500°C), the formation of Ni_2Al_3 (δ -phase) was completely inhibited, and the NiAl_3 (β -phase) layer was reduced in thickness.

The equilibrium phase diagram for the Al-Ni system is reproduced from the ASM Metals Handbook in Fig. 3. Four intermetallic phases occur at equilibrium, and some of their properties are summarized in Table I. According to the original observations, NiAl (ϵ -phase) and Ni_3Al (ζ -phase) did not form during diffusional bonding. Since NiAl (ϵ -phase) has a relatively wide range of solubility and has an interesting lattice-defect structure which affects diffusion within the phase^(14,15) and which might make the phase pressure sensitive, it appeared desirable to re-check the phase identifications. For this purpose, a specimen was chosen which had been diffusion bonded under pressure and which had fractured during a subsequent atmospheric pressure diffusion anneal along the interface between the two layers. The "d" spacings corresponding to the nickel-rich surface layer were calculated from an X-ray spectrometer trace; subsequently, layers

were removed from the surface by abrasion of the specimen on no. 2-0 emery paper, and successive spectrometer traces were obtained. A positive identification of Ni_2Al_3 (γ -phase) in the nickel-rich layer was made from a comparison of the intensities of the X-ray lines and the appearance of the 4.90 and 3.50 "d" spacings which are unique for this phase (Table II). The possible presence of additional nickel-rich phases was not excluded by the study, since many of the other "d" spacings are common to NiAl (δ), Ni_3Al (ϵ), and nickel. However, this possibility seems unlikely, in view of the fact that the "d" spacings of the Ni_2Al_3 (γ) layer persisted apparently to the nickel, and in view of the metallographic observations which indicated only one nickel-rich layer.

In addition to the X-ray diffraction study, an attempt was made to analyze the nickel-rich layer chemically. Scrapings were obtained from the nickel-rich diffusion layer of each of two diffusion bonded specimens, whose histories were similar to that of the specimen described above, and chemically analyzed. Only minute amounts of material were available (of the order of one milligram); therefore, a colorimetric technique was employed to determine the chemical composition. The results reported are as follows:

<u>Weight Percent Nickel</u>	
<u>Samples</u>	<u>Ni_2Al_3</u>
57	55-60
55	

It is evident that the results of chemical analysis corroborate the X-ray results, and that the nickel-rich phase is Ni_2Al_3 (γ).

Additional X-ray diffraction work is currently being done to identify the aluminum-rich phase; it is expected that the structure will be identified as NiAl_3 (β).

Thus, the identification of the phases which appear during the diffusion bonding of aluminum to nickel is almost completed. Of the two phases which appear metallographically, the nickel-rich phase is Ni_2Al_3 (γ) and the aluminum-rich

phase is probably NiAl_3 (β). The possibility still exists that the NiAl (δ) phase and the Ni_3Al (ϵ) phase are present; if so, they are present in layers of sub-microscopic thicknesses.

B. Growth Of Intermetallic Phases

The thicknesses of the intermetallic layers formed during the bonding of nickel and aluminum have been measured at various diffusion times and temperatures -- for the most part, under atmospheric pressure. The results obtained are tabulated in Table III. A plot of Ni_2Al_3 (γ -phase) layer thickness (mm) versus time (hrs.) for various diffusion temperatures is shown in Fig. 4. It is evident from the data that the Ni_2Al_3 (γ) layer thickness is dependent upon time and temperature. For example, after 96 hours at 450°C , the layer is only 0.03 mm thick, whereas, at 600°C , the layer is 0.33 mm thick -- an increase in thickness by a factor of 11. At the low temperatures, it appears from the slopes of the 400°C and 450°C curves that an incubation period may exist for the formation of the Ni_2Al_3 (γ) layer; however, the data are insufficient at the present time to enable one to decide definitely.

In contrast, the thickness data for the NiAl_3 (β) layer (Table III) are relatively temperature insensitive except possibly at very short diffusion times. The maximum value of the NiAl_3 (β) layer thickness that was recorded is about 0.022 mm and occurs after diffusion for 336 hours at 400°C . The NiAl_3 (β) layer definitely grows with time, however. The maximum rate of growth occurs at the early diffusion times, and then tapers off. The layer appears to grow exponentially with time, but insufficient data are available at the present time to determine the growth law unequivocally.

Fig. 5 is a plot of log thickness of the Ni_2Al_3 (γ) layer versus log time for various diffusion temperatures. A family of curves is obtained which are definitely asymptotic at the higher temperatures, the asymptotic line having a slope equal to $1/2$. Thus, at the higher temperatures and at sufficiently long diffusion times, the thickness of the Ni_2Al_3 (γ) layer obeys a parabolic

growth law of the form:

$$x = kt^{1/2}$$

It is interesting to note that the slopes of the curves tend to reach the asymptotic value, $1/2$, at a Ni_2Al_3 (γ) layer thickness of about 0.025 to 0.030 mm.

The effect of pressure upon the growth of the Ni_2Al_3 (γ) layer is currently being determined. The available data are summarized in Table III and plotted in Fig. 5. A pressure of 5 tsi reduces the thicknesses of the layers obtained at various times. Tentatively, it appears that the slopes of the curves still approach the asymptotic value of $1/2$.

The $NiAl_3$ (β -phase) layer growth data at 5 tsi indicate that pressure reduces the layer thickness slightly (Table III); sufficient information is not yet available to determine the effect of temperature.

C. Other Studies

A number of other studies have been initiated fairly recently, and the results obtained to date although incomplete, are mentioned briefly below.

- (1) The movement of markers during the diffusion bonding process is being investigated. It appears from the photomicrograph (Fig. 6) that the markers remain at the $NiAl_3$ (β) - Ni_2Al_3 (γ) interface but this is not certain, as yet.
- (2) The hardnesses of the intermetallic phases and of the nickel and aluminum adjacent to the interfaces have been determined for a few specimens; two typical photomicrographs and a hardness plot are shown in Figs. 7 and 8. Since the data collected to date are not complete, the following results are considered tentative:
 - (a) The hardness of the nickel adjacent to the Ni_2Al_3 (γ) interface seems to remain constant, while the hardness of the aluminum adjacent to

the NiAl_3 (β -phase) remains constant at the lower temperatures but seems to increase as the temperature is raised.

(b) The Ni_2Al_3 (γ -phase) is harder than the NiAl_3 (β -phase), but the variations in hardness of the two phases with temperature is not yet clear.

(3) The variation of composition in the Ni_2Al_3 layer as a function of depth is being obtained by means of a colorimetric technique. No results are available as yet.

IV. DISCUSSION OF RESULTS

During the past year, some progress has been made towards an understanding of the diffusional bonding process in the Ni-Al system and the effect of pressure upon the process; however, a number of points remain to be clarified.

A. Appearance Of Phases During Diffusional Bonding

It now seems reasonably clear that the NiAl (δ -phase) and the Ni_3Al (ϵ -phase) do not form in microscopically perceptible thicknesses during the diffusion bonding of aluminum to nickel, even though they are thermodynamically stable phases as evidenced by the equilibrium phase diagram. Two possible explanations exist for their absence:

- (1) For reasons not yet clear, the nucleation of these phases does not take place under the conditions of the test.
- (2) The phases do nucleate, but their rate of growth is so slow in comparison with the rate of growth of the Ni_2Al_3 (γ) layer, that the phase cannot grow to any perceptible thickness in competition with the Ni_2Al_3 (γ) layer.

Sufficient data are not yet available to distinguish between these two alternatives. The first is obviously consistent with the observations; some supporting data

can be assembled to show that the second alternative is also plausible. The value of the diffusion coefficient of Co^{60} in 47.3 a/o NiAl can be estimated from the data of Berkowitz, Jaumot, and Nix⁽¹⁵⁾ as being in the vicinity of $10^{-15} \text{ cm}^2/\text{sec}$ at 600°C , and the activation energy for diffusion is of the order of 55,000 cal./mol. By making suitable assumptions, one can calculate (at least roughly) a value for the chemical diffusion coefficient and the heat of activation for diffusion in the Ni_2Al_3 (δ) layer from layer growth data; the details of the calculations are taken up in the Appendix. A value of $0.7 \times 10^{-10} \text{ cm}^2/\text{sec}$ is obtained for the diffusion coefficient at 600°C , and the heat of activation is estimated to be about 32,000 cal./mol. Thus, even if the chemical diffusivity in the NiAl (ϵ) layer is 100 times greater than the diffusion coefficient of Co^{60} (which should approximate the self diffusion coefficient of Ni in NiAl), it will still be less by almost three orders of magnitude than that in the Ni_2Al_3 (δ) layer. It is also of interest to note that the diffusion coefficient of aluminum has been measured in a dilute solution of aluminum in nickel⁽¹⁶⁾; the estimated value of the coefficient at 600°C is about $1.2 \times 10^{-15} \text{ cm}^2/\text{sec}$. Thus, it seems reasonable to conclude that the Ni_2Al_3 (δ) layer will grow much faster than the NiAl (ϵ) layer at the relatively low diffusion temperatures employed in the present study; a similar argument is advanced for the comparative rates of growth of the Ni_2Al_3 (δ) and Ni_3Al (ϵ) layers.

B. Kinetics Of Layer Growth

The interpretation of the Ni_2Al_3 (δ) layer growth data as a function of time is not yet satisfactory. One can conclude from the data in Fig. 5 that volume diffusion in the Ni_2Al_3 (δ -phase) becomes the rate controlling factor after a minimum thickness of the order of 0.025 to 0.030 mm is reached; however, the rate controlling factor during the earlier stages of growth is not yet clear. It is possible that some of the rapid growth observed during the early stages is more apparent than real. It will be noted in Table III that the thickness of the Ni_2Al_3 (δ) layer formed at heating times considerably under 3 hours at 450°C and under 7 hours at 400°C

is less than the precision of the measurement; the NiAl_3 (β) layer under the same conditions is much thicker. The possibility cannot be ignored that the Ni_2Al_3 (γ) layer requires an incubation period to nucleate; if so, the initial curvatures of the slopes of the curves in Fig. 5 will be exaggerated. In Fig. 9, various incubation times are assumed for Ni_2Al_3 (γ) at temperatures of 500°C and 450°C. It will be noted that some tendency exists for the curvature to become less pronounced. Nevertheless, it is not possible, even with the assumption of maximum incubation times consistent with the data, to straighten the curves out to the point where the slopes have a constant value of 1/2 for all times and temperatures. Layer growth must proceed during its early stages at a rate more rapid than would be expected from bulk diffusion considerations. A number of possibilities exist, including the following:

- (1) Diffusion of atoms through short circuiting paths of some kind may be rate controlling during the early stages of growth, when the layers are relatively thin.
- (2) The stress systems existing at the interfaces may influence diffusion rates throughout the entire Ni_2Al_3 (γ) layer, until the layer thickness exceeds a minimum value.

At the present time, it is not possible to say much about either of these possibilities which is not almost purely speculative. Grain boundary diffusion, for example, may play a role in determining the kinetics of layer growth during the early stages; metallographic evidence is too incomplete to assess the possible importance of this mechanism. The microhardness data are not sufficiently complete to indicate whether hardening effects occur because of the presence of interfaces. (Interpretation of such data once obtained will be difficult at best, since the data will have been taken at room temperature rather than at the diffusion temperature.) Satisfactory explanations of the kinetics of layer growth at short diffusion times must await further analysis of present data and the accumulation of more metallographic, diffusional, and microhardness data. Although data on the effect of pressure upon the kinetics of layer growth are incomplete at this stage, one tentative conclusion can be drawn. It appears that pressure exerts its effect during

the latter stages of layer growth by decreasing the value of the bulk diffusion coefficient in the Ni_2Al_3 (γ) layer; for example, it is estimated that a pressure of 5 tsi lowers the 600°C diffusion coefficient by 33% (see Appendix). It is not yet clear whether pressure changes the heat of activation for diffusion or the entropy of activation; also, the effects of pressure during the early stages of growth are not known as yet. More data are needed.

C. Future Work

In view of the results and the discussion above, it is convenient to think of layer growth in the Al-Ni system in terms of the "transient" period (the initial period of growth during which the rate controlling factors are not clear) and the "steady state" period during which the growth rates obey the classical diffusion equations. The future work program will be directed towards a study of the mechanisms which might be operating during each or both of these periods. A more careful study will be made of the phases appearing during the initial stages of diffusion bonding to determine if submicroscopically thick layers of the missing phases are actually present. X-ray diffraction, electron diffraction, and electron microscopy techniques will be utilized. Metallographic studies (if possible, cathodic vacuum etching techniques) will be made to determine the extent, if any, to which grain boundary diffusion, recrystallization, nucleation of voids, etc., influence the course of layer growth, particularly during the transient period. Microhardness studies of layers will be continued, and the results obtained will be compared with the hardnesses of the bulk intermetallic phases in an attempt to gain some understanding of the mechanical properties of the layers. In this connection, dimensional changes during the course of diffusion bonding will also be ascertained. The chemical diffusivity in the Ni_2Al_3 (γ) layer and the effect of pressure thereupon will be investigated in the diffusion bonded samples. If possible, the intrinsic diffusivities will also be determined through marker movement (incremental diffusion couples may have to be used). It is hoped that the many-pronged attack outlined above will succeed in clarifying the nature of the diffusional bonding process and the role played by

pressure.

V. CONCLUSIONS

1. Diffusion bonding in the Al-Ni alloy system in the temperature range 400-625°C occurs by the formation and growth of the Ni_2Al_3 (σ) and the NiAl_3 (β) layers. Other phases are either not present or occur in submicroscopically thin layers.
2. The growth of the Ni_2Al_3 (σ) layer in the temperature range 400-625°C is controlled by volume diffusion in the Ni_2Al_3 (σ -phase) once a minimum layer thickness of the order of 0.025 to 0.030 mm has been reached; prior to this, the layer grows more rapidly than volume diffusion considerations would predict.
3. Tentatively, the chemical diffusivity in the Ni_2Al_3 (σ -phase) has been calculated to be of the order of $0.7 \times 10^{-10} \text{ cm}^2/\text{sec.}$ at 600°C; the heat of activation is in the vicinity of 32,000 cal./mol. over the temperature range 400 to 625°C.
4. The NiAl_3 (β -phase) grows at a much less rapid rate than does the Ni_2Al_3 (σ -phase); also, the growth of the former is relatively temperature insensitive in the range 400 to 625°C.
5. Pressure decreases the rate of growth of the Ni_2Al_3 (σ) layer. Tentatively, it appears that one effect of pressure is to lower the chemical diffusivity in the Ni_2Al_3 (σ -phase); it is estimated that a pressure of 5 tsi lowers the 600°C diffusion coefficient by 33%.

REFERENCES

1. S. Storchheim, J. L. Zambrow, and H. H. Hausner, "Solid State Bonding of Aluminum and Nickel", Trans. A.I.M.E. 200, 1954, pp. 269-274.
2. S. Storchheim, "Uranium-to-Nickel Solid State Bonding", (SEP-156), April 28, 1954, pp. 1-19.
3. S. Storchheim, "Some Studies of Aluminum-Copper and Aluminum-Zirconium Solid State Bonding", (SEP-164), June 7, 1954, pp. 1-21.
4. S. Storchheim, "Solid State Bonding and Canning of Thorium With Aluminum", Nuclear Science and Technology, TID-2508, 1A, Issue 3, December 1955, pp. 395-407.
5. H. D. Vasileff and R. Smoluchowski, "Two and Three-Phase Intermetallic Diffusion", Carnegie Institute of Technology (Unpublished manuscript).
6. W. Jost, "Bemerkung zur Mathematischen Behandlung Komplizierter Diffusions-problems", Zeitschrift fur Physik 127, pp. 163-167 (1950).
7. B. Lustman and R. F. Mehl, "Rate of Growth of Intermediate Alloy Layers in Structurally Analogous Systems", Trans. A.I.M.E. 147, pp. 369-395 (1942).
8. J. H. Kittel, "Layer Formation by Interdiffusion Between Some Reactor Constructional Materials", (ANL-4937) June 17, 1949, pp. 1-29.
9. N. H. Nachtrieb, J. H. Weil, E. Catalano, and A. W. Lawson, "Self-Diffusion in Solid Sodium. II. The Effect of Pressure", J. Chem. Phys. 20, No. 8, pp. 1189-1191, (1952).
10. N. H. Nachtrieb and A. W. Lawson, "Effect of Pressure on Self-Diffusion in White Phosphorus", J. Chem. Phys. 23, pp. 1193-1195, (1955).

11. T. Liu and H. H. Drickamer, "The Effect of Compression and of Hydrostatic Pressure on the Diffusion Anisotropy of Zinc", J. Chem. Phys. 22, pp. 312-319, (1954).
12. F. J. Radavich and R. Smoluchowski, "Influence of Pressure on Intermetallic Diffusion", Phys. Rev. 65, pp. 62, 248, (1944).
13. F. S. Buffington and M. Cohen, "Self-Diffusion in Alpha Iron Under Uni-axial Compressive Stress", Trans. A.I.M.E. 194, pp. 859-860, (1952).
14. A. J. Bradley and A. Taylor, "X-ray Analysis of the Nickel-Aluminum System", Proc. Roy. Soc. (London) A159, pp. 56-72, (1937).
15. A. E. Berkowitz, F. E. Jaumot, Jr., and F. C. Nix, "Diffusion of Co^{60} in Some Ni-Al Alloys Containing Excess Vacancies", Phys. Rev. 95, pp. 1185-1189, (1954).
16. R. A. Swalin and A. Martin, "Solute Diffusion in Nickel Base Substitutional Solid Solutions", presented at the Annual Meeting, I.M.D., A.I.M.E., N.Y., February 21, 1956.

TABLE I - DATA FOR PHASES IN THE Al-Ni SYSTEM

Phase	Formula	Density (g/cc)	Melting or Decomposition Temperature (°C)	Solubility Range at 600°C (a/o Ni)	Diffusion Coefficient at 600°C
α	Al	2.70	660 (m)	negligible	unknown
β	NiAl ₃	3.98	854 (d)	negligible	unknown
γ	Ni ₂ Al ₃	4.78	1132 (d)	36-41	unknown
δ	NiAl	5.95	1640 (m)	43-60	10^{-15} cm ² /sec. *
ϵ	Ni ₃ Al	7.49	1395 (d)	71-75	unknown
ζ	Ni	8.90	1455 (m)	88-100	2×10^{-15} cm ² /sec. **

* Estimated self-diffusion coefficient of Co⁶⁰ in NiAl (δ) from data of Berkowitz et al(15).

** Estimated chemical diffusivity from data of Swalin et al(16).

TABLE II - "d" SPACINGS OF Ni-Al PHASES

Ni_2Al_3 (γ)	NiAl (δ)		Ni_3Al (ϵ)	Ni (α)
(1)	(1)	(2)	(2)	(1)
4.90				
3.50				
2.85	2.86			
2.01	2.02	2.03	2.07	2.03
1.86				
1.75			1.79	1.76
1.65	1.65			
1.48				
1.42	1.43	1.44		
1.32				
1.27	1.28		1.27	1.25
1.22				
1.19				
1.16	1.17	1.18		
1.13				
1.05			1.08	1.06
1.03			1.03	
1.01	1.01	1.02		1.02
0.90			0.90	
0.847				0.88
0.824			0.82	0.81
0.764			0.80	0.79

(1) ASTM Card Index.

(2) Calculated from data in ASM Metals Handbook.

TABLE III - SUMMARY OF LAYER THICKNESS DATA

Number		Diffusion		Ni ₂ Al ₃ Layer		Total Layers		NiAl ₃ Layer	
Samples	Al-Ni Inter-faces	Temp. (°C)	Time (min.)	Average Thickness (mm)	Standard Deviation (mm)	Average Thickness (mm)	Standard Deviation (mm)	Average Thickness (mm)	Standard Deviation (mm)
ATMOSPHERIC PRESSURE									
3	3	400	420	0.0001	-	0.0032	±0.0001	0.0030	±0.0002
3	6		1050	0.0010	±0.0002	0.0046	±0.0009	0.0055	±0.0004
1	2		1200	0.0007	±0.0002	0.0098	±0.0002	0.0071	-
1	2		2400	0.0046	±0.0001	0.0133	±0.0011	0.0091	-
2	3		20160	0.0126	±0.0017	0.0336	±0.0026	0.0221	±0.0002
3	4	450	200	0.0007	±0.0002	0.0051	±0.0003	0.0039	±0.0001
6	10		420	0.0028	±0.0007	0.0096	±0.0001	0.0066	±0.0004
1	1		960	0.0076	-	0.0127	-	0.0070	-
3	8		2880	0.0165	±0.0018	0.0268	±0.0005	0.0109	-
3	8		5760	0.0326	±0.0040	0.0453	±0.0007	0.0162	0.0023
2	2	500	15	0.0005	±0.0001	0.0038	±0.0004	0.0034	-
2	3		30	0.0014	±0.0001	0.0055	±0.0005	0.0045	±0.0003
2	7		60	0.0042	±0.0001	0.0090	±0.0001	0.0051	±0.0002
2	7		180	0.0100	±0.0001	0.0169	±0.0005	0.0067	±0.0001
2	5		420	0.0185	±0.0002	0.0258	±0.0005	0.0080	-
1	3		960	0.0334	±0.0001	0.0408	±0.0007	0.0080	±0.0004
1	2		2880	0.0555	±0.0032	0.0631	-	-	-
1	1		5760	0.0825	-	-	-	-	-
2	4	550	15	0.0034	±0.0001	0.0068	±0.0001	0.0039	±0.0001
2	3		30	0.0082	±0.0002	0.0125	±0.0008	0.0054	±0.0008
3	4		60	0.0128	±0.0002	0.0176	±0.0010	0.0046	-
2	2		180	0.0249	±0.0004	0.0303	±0.0001	0.0061	-
1	2		420	0.0398	-	0.0436	-	-	-
3	3		960	0.0635	±0.0016	0.0704	±0.0006	0.0085	±0.0011
3	4		5760	0.1494	±0.0019	0.1614	±0.0057	0.0186	±0.0003
2	4	600	15	0.0094	±0.0001	0.0130	±0.0002	0.0038	0.0000
3	9		30	0.0167	±0.0005	0.0214	±0.0005	0.0055	0.0006
2	5		60	0.0304	±0.0002	0.0348	±0.0012	0.0051	0.0003
2	8		180	0.0535	±0.0010	0.0583	±0.0006	0.0061	0.0001
2	8		420	0.0798	±0.0011	0.0874	±0.0015	0.0067	-
2	3		960	0.1219	±0.0011	0.1289	±0.0052	0.0103	-
1	2		5760	0.2907	±0.0007	0.3071	±0.0010	0.0171	-
2	4	625	15	0.0144	±0.0001	0.0178	±0.0005	0.0035	±0.0001
2	8		30	0.0259	±0.0000	0.1099	±0.0003	0.0044	±0.0002
2	7		60	0.0343	±0.0005	0.0377	±0.0008	0.0051	0.0002
2	6		180	0.0582	±0.0010	0.0637	±0.0022	0.0080	0.0014
2	4		420	0.0959	±0.0022	0.1044	±0.0057	0.0117	0.0002
3	7		960	0.1319	±0.0012	0.1383	±0.0119	0.0097?	-
5 TSI PRESSURE									
1	2	450	960	0.0048	±0.0001	0.0107	±0.0000	0.0061	±0.0002
1	3	500	180	0.0103	±0.0002	0.0151	±0.0010	0.0045	±0.0001
1	2		420	0.0161	±0.0002	0.0219	±0.0001	0.0058	±0.0000
1	3		4320	0.0591	±0.0014	0.0717	±0.0019	0.0136	±0.0005
1	4		5760	0.0714	±0.0005	0.0843	±0.0004	0.0134	±0.0006
1	2	550	960	0.0480	±0.0002	0.0562	±0.0002	0.0082	±0.0001
1	2	585	960	0.0805	±0.0005	0.0900	±0.0002	0.0095	±0.0000
1	2	600	5760	0.2500	±0.0063	0.2561	±0.0001	0.0150	±0.0003

250X

Unetched

Fig. 1a Spot Welded Sample Before Diffusion.

250X

Unetched

Fig. 1b Spot Welded Sample After Diffusion for One Hour at 625°C.

Fig. 2 HOT PRESSING APPARATUS

Fig. 3 THE ALUMINUM-NICKEL PHASE DIAGRAM

Fig. 4 Ni_2Al_3 LAYER THICKNESS VS. DIFFUSION TIME

Fig. 5

$N_{12}Al_3$ LAYER THICKNESS VS. DIFFUSION TIME — LOG PLOT

250X

Unetched

Fig. 6 - Marker Movement in Specimen Diffused at 5 tsi and 500°C for 96 hours.

250X

Unetched

Fig. 7 - Knoop Hardness Impressions in Sample
Diffused at 5 tsi and 500°C for 96
hours.

Fig. 8 HARDNESS TRAVERSE THROUGH DIFFUSION ZONE

Fig. 9 EFFECT OF ASSUMED INCUBATION PERIOD ON LAYER GROWTH CURVES

Fig. 10 DETERMINATION OF ACTIVATION ENERGY FOR DIFFUSION IN Ni_2Al LAYER

APPENDIX

Calculation of Heat of Activation for Diffusion in the Ni_2Al_3 Layer.

A. Assumptions

1. The Ni_2Al_3 (γ -phase) lies between the NiAl_3 (β -phase) and a nickel-rich solid solution; the concentrations at the interface boundaries remain constant with time and temperature.
2. The displacement ratio, $F_{\gamma\text{Ni}}(T)/F_{\beta\gamma}(T)$, is constant and independent of temperature.
3. The chemical diffusion coefficient (D) in the Ni_2Al_3 (γ -phase) is independent of concentration.
4. The chemical diffusion coefficients in the NiAl_3 (β -phase) and in the nickel-rich solid solution are very much smaller than the chemical diffusion coefficient in the Ni_2Al_3 (γ -phase).

B. Notation

1. $C_{1\beta\gamma}$ = concentration of Ni in NiAl_3 (β -phase).
2. $C_{2\beta\gamma}$ = concentration of Ni in Ni_2Al_3 (γ -phase) at the β -phase boundary.
3. $C_{1\gamma\text{Ni}}$ = concentration of Ni in Ni_2Al_3 (γ -phase) at the γ -Ni phase boundary.
4. D = chemical diffusivity of the Ni_2Al_3 (γ -phase).
5. t = time.
6. T = absolute temperature
7. $F_{\beta\gamma}$ = position of the β - γ interface.
8. $F_{\gamma\text{Ni}}$ = position of the γ -Ni interface.

C. Analysis

1. The general solutions of the three-phase inter-metallic diffusion problem by Vasileff and Smoluchowski⁽⁵⁾ are applied as follows:

$$0 = \frac{\sqrt{\pi}}{2} (C_{1\beta\gamma} - C_{2\beta\gamma}) \frac{F_{\beta\gamma}}{\sqrt{t}} + \frac{(C_{2\beta\gamma} - C_{1\gamma N_1}) D_{\gamma}^{1/2} \exp(-F_{\beta\gamma}^2/4D_{\gamma}t)}{\operatorname{erfc}(F_{\beta\gamma}/2\sqrt{D_{\gamma}t}) - \operatorname{erfc}(F_{\gamma N_1}/2\sqrt{D_{\gamma}t})} \quad (1)$$

$$\frac{(C_{2\beta\gamma} - C_{1\gamma N_1}) D_{\gamma}^{1/2} \exp(-F_{\beta\gamma}^2/4D_{\gamma}t)}{\operatorname{erfc}(F_{\beta\gamma}/2\sqrt{D_{\gamma}t}) - \operatorname{erfc}(F_{\gamma N_1}/2\sqrt{D_{\gamma}t})} = \frac{\sqrt{\pi}}{2} (C_{1\gamma N_1} - C_{2\gamma N_1}) \frac{F_{\gamma N_1}}{\sqrt{t}} \quad (2)$$

2. Dividing equation (1) by equation (2):

$$\left(\frac{C_{1\beta\gamma} - C_{2\beta\gamma}}{C_{1\gamma N_1} - C_{2\gamma N_1}} \right) \left(\frac{F_{\beta\gamma}}{F_{\gamma N_1}} \right) = - \exp \left[- (F_{\beta\gamma}^2 - F_{\gamma N_1}^2) / 4D_{\gamma}t \right] \quad (3)$$

or $K_1 = \exp \left[- (F_{\beta\gamma}^2 - F_{\gamma N_1}^2) / 4D_{\gamma}t \right] \quad (4)$

where $K_1 \equiv - \left(\frac{C_{1\beta\gamma} - C_{2\beta\gamma}}{C_{1\gamma N_1} - C_{2\gamma N_1}} \right) \left(\frac{F_{\beta\gamma}}{F_{\gamma N_1}} \right) \quad (5)$

3. Since:

$$(F_{\beta\gamma}^2 - F_{\gamma N_1}^2) = (F_{\beta\gamma} + F_{\gamma N_1}) (F_{\beta\gamma} - F_{\gamma N_1}) = C F_{\beta\gamma} (F_{\beta\gamma} - F_{\gamma N_1}) \quad (6)$$

where $C \equiv F_{\beta\gamma} / F_{\gamma N_1}$

if a constant value of thickness is selected it is evident that $(F_{\beta\gamma}^2 - F_{\gamma N_1}^2)$ will be a constant independent of temperature.

Then: $K_1 = \exp \left[- K_2 / 4D_{\gamma}t \right] \quad (7)$

where $K_2 \equiv F_{\beta\gamma}^2 - F_{\gamma N_1}^2$ is a function of the layer thickness.

4. Taking logarithms, equation (7) becomes:

$$\ln K_1 = - K_2/4D_{\gamma}t \quad (8)$$

$$\text{and } D_{\gamma} = - K_2/4t \ln K_1 = K_2/4t \ln 1/K_1 \quad (9)$$

5. Since $D_{\gamma} = D_{\gamma_0} \exp (- Q_{\gamma}/RT)$:

$$D_{\gamma} = D_{\gamma_0} \exp (- Q_{\gamma}/RT) = \frac{K_2}{4 \ln 1/K_1} 1/t \quad (10)$$

$$\ln 1/t = \ln(4 \ln 1/K_1)/K_2 + \ln D_{\gamma_0} - Q_{\gamma}/RT \quad (11)$$

Thus if the logarithm of the reciprocal of the time required for the Ni_2Al_3 (γ) layer to reach a constant thickness is plotted as a function of the reciprocal of the absolute temperature, a straight line whose slope is equal to $- Q/R$ is obtained. The heat of activation, as determined from the plot of the data in Fig. 10, is approximately 32,000 cal./mol.

Calculation of Diffusion Coefficient at 600°C

The assumptions and notation are the same as for the previous section. In addition, it is assumed that the concentrations $C_{1\beta\gamma}$, $C_{2\beta\gamma}$, and $C_{1\gamma\text{Ni}}$ are equilibrium concentrations which may be obtained from the Al-Ni equilibrium phase diagram, and that $C_{2\gamma\text{Ni}}$ is equal to 88 a/o.

A. Values of Parameters for 96 Hour Run at 600°C (Atmospheric Pressure)

1. $F_{\beta\gamma} = 0.0177 \text{ cm.}$
2. $F_{\gamma\text{Ni}} = 0.0113 \text{ cm.}$
3. $t = 3.46 \times 10^5 \text{ sec.}$
4. $C_{1\beta\gamma} = 25 \text{ a/o}$
5. $C_{2\beta\gamma} = 36 \text{ a/o}$
6. $C_{1\gamma\text{Ni}} = 41 \text{ a/o}$
7. $C_{2\gamma\text{Ni}} = 88 \text{ a/o}$

B. Calculations

Substitution of numerical values in the formula:

$$\frac{C_{1\beta\gamma} - C_{2\beta\gamma}}{C_{1\gamma N_1} - C_{2\gamma N_1}} = - \exp \left[- (F_{\beta\gamma}^2 - F_{\gamma N_1}^2) / 4 D_{\gamma} t \right] \quad (3)$$

$$\left(\frac{25-36}{41-88} \right) \left(- \frac{0.113}{0.177} \right) = - \exp \left[- (.0064) (.0290) / 4 D_{\gamma} (3.46 \times 10^5) \right]$$

$$- \frac{(.0064) (.0290)}{4 \times 3.46 \times 10^5} = D_{\gamma} \ln \left(\frac{11}{47} \right) \left(\frac{0.113}{0.177} \right)$$

$$\text{and } D_{\gamma} = \frac{(.0064) (.0290)}{(4 \times 3.46 \times 10^5) \ln \left[\frac{(.47) (.177)}{(.11) (.0113)} \right]} = \frac{1.34 \times 10^{-10}}{\ln 6.70}$$

$$D_{\gamma} = 0.7 \times 10^{-10} \text{ cm}^2/\text{sec.}$$

A similar calculation with the results from one 5-tsi pressure run for 96 hours at 600°C indicates that the diffusion coefficient is reduced to 2/3 of the above value.

CHIEF ENGINEER
B KOPELMAN
N ZAFFT, SECY

PLANT AND SHOP SERVICES

S J VAIANA, FOREMAN
M ZUCCHELLI, SECY

EQUIPMENT MAINTENANCE
AND CONSTRUCTION
C GARBY, SUPERVISOR
2—ELECTRICIANS
2—WELDERS
1 GROUP LEADER
1—PIPEFITTER
2—MECHANICS

ACCOUNTABILITY, SHIPPING
RECEIVING, FILES AND STOCK
W J DONOHUE, SUPERVISOR
5—CLERKS
1—EXPEDITER
1—COURIER
G DUNDREA, CENTRAL FILES
2—CLERKS

MACHINE SHOP
J SIKULA, SUPERVISOR
2—DEVELOPMENT
MACHINISTS
3—MACHINISTS

BLDG MAINT & SERVICES
G BURKLE, SUPERVISOR
2—PIPEFITTERS
1—MILLWRIGHT
4—CUSTODIANS

PROCESS METALLURGY
AND CHEMISTRY

J L ZAMBROW, MGR
H BANNIETTIS, SECY
M DEVINE, SECY

CLADDING AND POWDER
METALLURGY SECTION
H McCULLOUGH—HEAD
I SHEINHARTZ—ENG CHG
SR ENG J FUGARDI
R KING
J MITILINEOS
R WITT
ENG V ADLER
J NYLIN
J GRUBESSICH
C ROMERO
R SILVERMAN
F TEPPER
E VEIL
TECHNICIANS
J CAULFIELD
F KLIMUCK
H KOERNER
K MCCUSKER
J MONTAGNINO
C PAOLINI
J RUDOLPH
G SCHMIDT
L SIRIGNANO
E WELSH
A ZARNOWSKI

CHEMISTRY SECTION
C WHITMAN—HEAD
ADV RES ENG T BAURER
SR ENG R POWERS
O BLABER
N FUHRMAN
L VIELAND
B KRAKOW
R KURTZ
TECHNICIANS
S AZZARELLO
A HASAPIS
J MATHERN
T PAUL
R ZEIN

PHYSICAL METALLURGY
AND CERAMICS

H P KLING, MGR
J KURTZ, SECY
P BARTELS, SECY

FUNDAMENTAL METALLURGY
SECTION
L SEIGLE, HEAD
L CASTLEMAN—ENG SPEC
ADV RES ENG H MINDEN
A OPINSKY
C TUFTS
SR ENG A LIBOFF
A PRANATIS
ENG J BLACK JR
J OREHOTSKY
R RESNICK
TECHNICIANS
A CALVANO
J GITTO
J GUY
F MERKERT
E NOVAK
J PACHER
R SMITH
G WERBER

REFRACTORY METAL
SECTION
H BENDER, HEAD
SR ENG B BRODWIN
H HOFFMAN
L SAMA
ENG E DALDER
A GREEN
A MACHONIS
TECHNICIANS
L JOHRDEN
W KELLER
G McCLUSKY
D MELONE
G PEPINO
T PRIZZIA
E TRIOLA

CERAMIC SECTION
R HOLDEN, HEAD
SR ENG K LANGROD
H SHAPIRO
ENG A GETTO
J BURKERT
TECHNICIANS
J ANSELMO
T HENZE
A MALLILO

METAL FABRICATION
AND ASSEMBLY

H S KALISH, MGR
J ROSS, SECY
L WICHROWSKI, SECY

METAL WORKING SECTION
W LIDMAN, HEAD
E MAZZA, ENG CHG
SR ENG R HANNA
R RUBINO
W WEINBERGER
ENG R HARMON
F PIANKI
TECHNICIANS
J BLACK SR
F BUCHERATI
A CULEN
J CIRILLO
M DOWNEY
M FESTA
W KNAPP
N MADY
F ROLDAN
E RYAN
J SZELWACH

ALLOYS AND MIXTURES
SECTION
F BOWMAN, ENG SPEC
ADV RES ENG H RAIKLEN
SR ENG S MEGERF
R WITTMAN
ENG J BARA
A EISS
N KOENIG
TECHNICIANS
B ALBERT
R COPPOLA
R KRIZEK JR
G MCGINNESS
F SCIMECA

TECHNICAL SERVICES

R S STEWART, MGR
V REUL, SECY

DESIGN AND TESTING
SECTION
N GROSSMAN, HEAD
SR ENG E KRINICK
A PFIZENMAIER
S PRICEMAN
E SISGOREO
TECHNICIANS
O HAINES
R MODENA
DRAFTSMEN
F KORZEKOWSKI
W BRANDT

CHEMICAL AND METALLURGICAL
SERVICES
R CAMPBELL, ENG IN CHG.
ANALYTICAL CHEMISTRY
C GREGG, ENG IN CHG.
ENG C C CLEMENCY
C V CLEMENCY
J PATTI
TECHNICIAN B HAINES

METALLOGRAPHY
H WOODS, SUPERVISOR
ENG G AUSTIN
J GROSS
W SEETOO
TECHNICIANS
E KULESZ
M PIANKI

STANDARD FABRICATION
TECHNICIANS
A DALEY
J HENN
R SICHLER

ADMINISTRATIVE SERVICES

Y CAVALLARO, ENGINEER
S LAZLO, ASST TECH EDITOR
M MORRIS, DOCUMENT CUSTODIAN
D DIETRICH, LIBRARIAN
I ZAVARINE, TECH ABTRACTOR
2—SENIOR CLERKS

SAFETY AND SECURITY

R D EARLY, SAFETY ENG.
J GILDEA, TECHNICIAN
L TORTOSA, SECY
R KRIZEK, SGT GUARD FORCE
II GUARDS

MANPOWER AND ORGANIZATION
CHART

GENERAL ENGINEERING
LABORATORIES
ATOMIC ENERGY DIVISION
SYLVANIA ELECTRIC PRODUCTS
INC
BAYSIDE, N Y

AUGUST 1, 1956