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INVESTIGATION OF BONDING IN OXIDE-FIBER
(WHISKER) REINFORCED METALS

By
Willard H. Sutton
March 1963

AMRA CR 63-01/3

Space Sciences Laboratory
Missile & Space Division
General Electric Company
Philadelphia, Penna.

Contract No. DA 36-034-ORD-3768RD
Philadelphia Procurement District, U.S. Army
AMS Code 5010.11.8430051

Department of the Army Project No. 59332008

U. S. Army Materials Research Agency
Watertown 72, Massachusetts

Technical Report AMRA CR 63-01/3
Third Quarterly Report
January 1 to March 31, 1963

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BONDING
CERAMIC FIBERS
COMPOSITE MATERIALS
(METAL-CERAMIC)

AMRA CR 63-01/3

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INVESTIGATION OF BONDING IN OXIDE-FIBER
(WHISKER) REINFORCED MATERIALS

ABSTRACT

Sessile drop experiments were conducted in order to investigate the wetting (contact angle, θ), between pure nickel and single crystal α - Al_2O_3 . Over 16 experiments were conducted in order to evaluate the performance of the apparatus and to establish the most accurate experimental procedure. Of the various factors affecting the contact angle, the impurities in the nickel were found to have the most pronounced effect. A contact angle of 123.5° was recorded for ultra pure Ni at 1500°C . 'Shear' tests were conducted on the solidified Ni drops in order to assess the relative bond strengths, which were found to vary between 510 psi and 9,250 psi. The fracture modes and the chemical etching of the α - Al_2O_3 surfaces by molten nickel are discussed. The results of this investigation will be used ultimately to develop high strength bonds in nickel- α - Al_2O_3 (whisker) composite materials.

I. INTRODUCTION

The purpose of this program is to investigate the major factors affecting the wetting (contact angle) and bonding between two specific materials, namely, nickel and aluminum oxide (α -Al₂O₃). The results of this program will be used ultimately to develop and promote strong interfacial bonding in composites consisting of nickel and α -Al₂O₃ whiskers.

Two areas are currently under study and are listed as follows:

(1) an investigation of factors contributing to the wetting of α -Al₂O₃ with molten nickel, and (2) an investigation of the factors leading to high strength bonds between the two phases once the nickel is solidified. A condition of good wetting is necessary in order to promote complete penetration and contact between the matrix and reinforcing fibers (whiskers) during fabrication, while high interfacial bond strengths are necessary for the achievement of ultra-high strength composite materials. •

This report summarizes the progress of the experimental studies conducted during the third quarter from January 1 to March 31.

II. SESSILE DROP EXPERIMENTS

The wetting and interfacial behavior of molten nickel on single crystal plaques of $\alpha\text{-Al}_2\text{O}_3$ were investigated by the sessile drop method. This method permits direct observation of the contact angle between the two phases under controlled conditions. Since the degree of wetting (contact angle) is extremely sensitive to impurities, the first experiments were directed toward assessing the performance of the sessile drop apparatus and establishing a procedure which would give reliable and precise results. The construction details of the apparatus were described in previous reports (Ref. 1, 2).

In order to evaluate the performance of the apparatus and the experimental procedures, the following factors were investigated:

A. Furnace Materials

- (1) Heating elements; Ta vs. Mo susceptors,
- (2) Thermal radiation shields; graphite vs. Mo.
- (3) Furnace supports; Al_2O_3 vs. BN.

B. Specimens*

- (1) Original Ni geometry
- (2) Ni purity
- (3) Ni drop size
- (4) Amount of Ni vaporized

C. Experimental Procedure

- (1) Specimen levelling and alignment
- (2) Specimen cleaning method

*The specimens of $\alpha\text{-Al}_2\text{O}_3$ were single crystal plaques, 0.375" in dia. and 0.020" thick and were supplied by the Linde Company, Crystal Products Department. The normal to the plaque surface was oriented approximately 60° to the 'c' crystallographic axis, and the surfaces were polished to a smoothness of about 1 micro-inch.

- (3) System bake-out procedure
- (4) Pressure
- (5) Time
- (6) Heating and Cooling rates
- (7) Temperature

A. Furnace Materials

All materials in close proximity to the specimens were considered as being possible sources of contamination. Since the tests were conducted at elevated temperatures (1500° to 1700°C) and under pressures of 10^{-5} to 10^{-4} mm Hg, contamination would result primarily from the evolution of adsorbed gas or from the direct vaporization of the materials themselves. Other sources of contamination, such as oils, greases and adsorbed vapors in other portions of the apparatus were also considered but were not investigated. Special O-rings, rather than vacuum-greased joints were used to seal all removable connections to the apparatus. All parts of the apparatus were cleaned and rinsed in pure acetone or alcohol prior to a test.

The vapor pressures of the refractory metals such as W, Mo, or Ta were sufficiently low under the experimental conditions used in this study, so that they would not ordinarily be considered as contaminants. However, traces of oxygen or moisture can readily oxidize the metals, and thereby liberate the volatile oxides which would then be a definite cause of contamination. Navias (Ref. 3) has shown experimentally that Ta can react with Al_2O_3 by a vapor process under certain conditions, even when the system has been evacuated to a pressure of about 10^{-5} mm Hg at 1600°C for 5 hours.

Since the contact angle (θ) is extremely sensitive to impurities, the effects of contaminants can be detected readily when high purity metals are investigated.

The purpose of the first experiments was to determine the effects of various furnace materials on the contact angle between pure nickel and $\alpha\text{-Al}_2\text{O}_3$. A typical heating system is shown in Figure 1a. This unit consists of a 0.005" thick tube of molybdenum which is shielded by a sheet of 0.040"

thick molybdenum rolled into a scroll. The two end supports used to hold the tube and shield are made of BN. Inside the tube (not shown), a flat Mo-specimen holder with semi-circular ends is centered and holds the plaque of $\alpha\text{-Al}_2\text{O}_3$ supporting a Ni drop. The entire unit is then fitted into a fused silica tube and sealed. Additional construction details of the apparatus were discussed in a previous report (Ref. 1).

The following materials were used and investigated separately:

(1) Mo and Ta susceptors, (2) BN and Al_2O_3 end supports, and (3) Mo and graphite radiation shields. The graphite radiation shield, which is shown in Figure 1b, consisted of a matt of graphite cloth wound around the susceptor tube and tied with graphite yarn. It was an excellent radiation shield, but out-gassed continually at the elevated temperatures so that pressures below 10^{-4} mm Hg could not be attained easily. Baking the graphite at 2000°C in vacuo to remove all volatile matter rendered the matt too weak for handling. For this reason, Mo was used as the shield material. The substitution of tantalum for molybdenum parts, and the substitution of Al_2O_3 for BN supports had no measurable effects on the contact angle.

B. Specimens

Pure nickel in the form of 0.040" thick wire and superpurity nickel in the form of 0.125" rods were used. The spectrographic analysis of these materials is shown in Table I.

The nickel wire was cut and then twisted in a small spiral and placed on an $\alpha\text{-Al}_2\text{O}_3$ plaque prior to melting as shown in Figure 2a. Figure 2b shows a melted Ni drop. The specimens made from the high purity nickel rod were ground to small truncated cones. The weights of the specimens varied from 0.2 to 0.4 grams which corresponded to drop diameters of about 0.1 to 0.2 inches. The nickel was melted so that molten metal advanced across the plaque surface before the drop shape came to equilibrium. However, no differences in contact angle were detected for receding or advancing drop movements which resulted from changes in temperature and from volatilization of nickel during test. In one case as much as 50% of the nickel was volatilized during a prolonged test (50 minutes) at temperatures above 1650°C . The weight loss of the nickel would usually vary from 5% to 30% of the original drop weight.

(a)



(b)



Figure 1. Heating Units Used in Sessile Drop Experiments
(a) Mo-Tube Susceptor, Mo-Scroll Radiation Shield and BN End Support
(b) Mo-Tube and Graphite Cloth Radiation Shield

TABLE I. Purity of Nickel Specimens Used in Sessile Drop Experiments

Sample	Major Impurity (ppm)	Elements not Detected
Nickel wire 99.34%	2600 Mn 1300 Co 1100 Fe 580 Cu 310 Mg 280 Si 220 Ti 60 Al < 50 Pb < 50 Cr < 20 B < 20 S <u>< 10 Ca</u> < 6600 ppm Total	
Super purity Nickel Rod 99.999% Ni	5 Si 2 Cu 2 Fe 2 Mg 1 Al 1 Cu 1 Na < 1 Mn <u>< 1 Ag</u> < 15 ppm Total	As, Au, B, Ba, Be, Be, C, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mo, Nb, O, P, Pb, Pt, Rh, Re, Ru,*Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

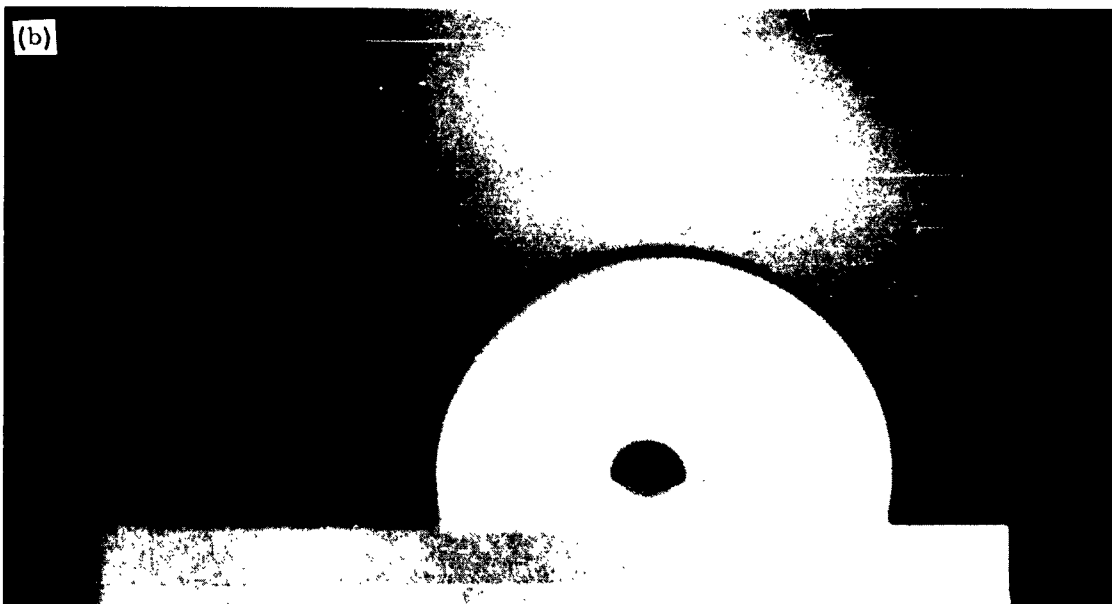
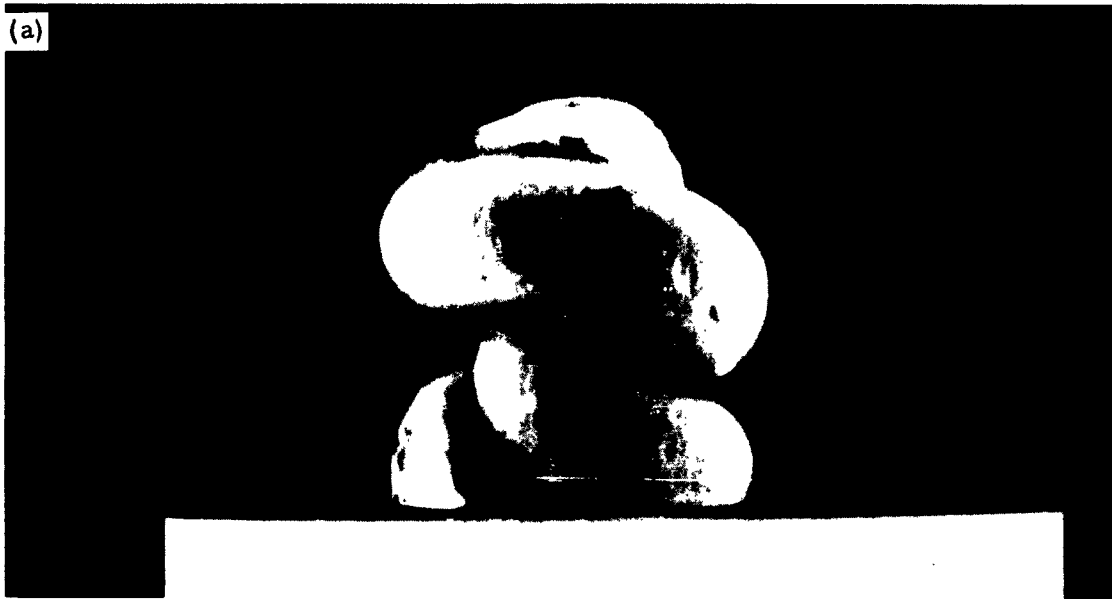


Figure 2. Nickel Wire on an α - Al_2O_3 Plaque (a) Prior to, and
(b) After Melting (9X)

C. Experimental Procedure

Several experimental factors that can affect the contact angle or its measurement were investigated so that the experimental errors could be determined. One of the first variables studied was the levelling and alignment of the nickel and α - Al_2O_3 plaque in the furnace. This was made difficult by the inaccessibility of the specimen inside the Mo susceptor. A transit gage was used to level* the plaque in a left-to-right direction within one or two degrees. However, the level of the front portion with respect to the back portion of the plaque was more difficult to achieve, since the view was along the line-of-sight of the transit gage. Several techniques were used, including focussing on front and back surfaces, water-levels, and back lighting techniques. It was found that if care was taken the plaque surface could be levelled to the extent that the normal to the plaque surface passed through the center of the drop. Contact angles were measured on the left and right side of the drop which agreed within 0.5 degrees.

Since all sources of contamination are detrimental to the accurate determination of contact angle, several cleaning procedures were investigated. The α - Al_2O_3 plaques were cleaned by using various cleaning solutions (dichromate, HCl, or detergents), or by ultrasonic methods and were then rinsed in distilled water and then in pure acetone or alcohol. The nickel wire and rod were cleaned by acid treatment (HNO_3 , HCl) or by ultrasonic methods and were then rinsed in distilled water which was followed by an acetone or alcohol rinse. No differences could be observed in the contact angle due to the various cleaning procedures. It appears that these procedures resulted in sufficiently clean surfaces. Since the cleaning procedure does not rid the surfaces of adsorbed (and absorbed) gases, the specimens were heated in vacuo at elevated temperatures for short periods of time. However, in order to insure maximum cleanliness, the effects of bake-out periods of several

*Levelling was accomplished by three screws, arranged in a triangular fashion, located under the sessile drop apparatus.

hours at 1000°C in vacuo will be investigated further.

Several sessile drop tests have been conducted under conditions of pressures varying from 10^{-5} to 10^{-3} mm Hg; of temperatures varying from 1500°C to 1725°C; and of periods varying from 3 to 52 minutes. The results of these tests are summarized in Section III. In general, the measured contact angles were found to be reproducible for a given set of experiments. It was found that the rates of heating and cooling the specimens were important. During the heating cycle, release of adsorbed gases could be detected when heating was rapid. On cooling, it was found that slow rates would tend to cause cracking of the α -Al₂O₃ plaques in the region under the nickel drop. This is discussed further in Section IV.

If the photographic prints of the sessile drops were in good focus and exhibited a high contrast, the contact angles* could be measured with a precision of 1.5°, which can be compared to estimated accuracy of 2° to 5° reported by others. If the prints were not clear, however, due to motion of the drop or fogging of the sight windows, the precision was of the order of 2° to 4°.

The procedure now used to conduct the sessile drop experiments is sufficiently precise to detect the effects on the contact angle of minor amounts of specific elements added to the nickel. The effects will be used to evaluate both the wetting and bonding of the Ni to α -Al₂O₃.

*The contact angle (θ) is defined as the interior angle between the tangent to the surface of the drop at the point of contact with the substrate and the substrate surface. This is further defined in Reference 2.

III. EXPERIMENTAL RESULTS

Sixteen sessile drop tests were conducted in order to evaluate the performance of the equipment and to evaluate the effects of various procedures used. After the tests were completed, the solidified drops of Ni on the α -Al₂O₃ plaques were subjected to 'shear' tests in order to determine the relative adherence of the metal to the substrate. Although several variables have been studied, a few relationships were observed and will be discussed along with the results.

A. Sessile Drop Experiments

One of the first problems to be solved was the illumination of specimens and the choice of an optical system used to photograph the drop image. At temperatures below 1000°C, back lighting was necessary for the levelling and alignment of the specimens. At high temperatures, the radiation was sufficiently intense to provide the necessary illumination. A 35 mm camera was attached to a telemicroscope which would provide a magnification of approximately 10X at working distance of 18 inches. However, the photographic images were not clear until the standard 10X eyepiece was replaced by a 14X orthoscopic eyepiece. In Figure 2, a nickel wire is shown before and after melting; the latter case being a sessile drop of nickel resting on an α -Al₂O₃ disc. If the sessile drop in Figure 2b is compared with those shown in Figure 3, the improvements due to better lighting and use of the orthoscopic eyepiece can be seen in the latter photographs.

The greatest contact angle (θ) measured was 123.5° between the high purity Ni (99.999%) and α -Al₂O₃ at about 1500°C. Theoretical values for the θ vary from 123° to 128°, depending on the values chosen for the interfacial energies and the surface tension of molten nickel. The greatest single factor in lowering the contact angle is the impurity content in the nickel. This is illustrated in Figure 3. The results of the sessile drop tests are summarized in Table II.

It can be seen in the Table that the greatest measured values of θ were 106° and 123.5° for the 99.34% and 99.999% nickel samples, respectively.

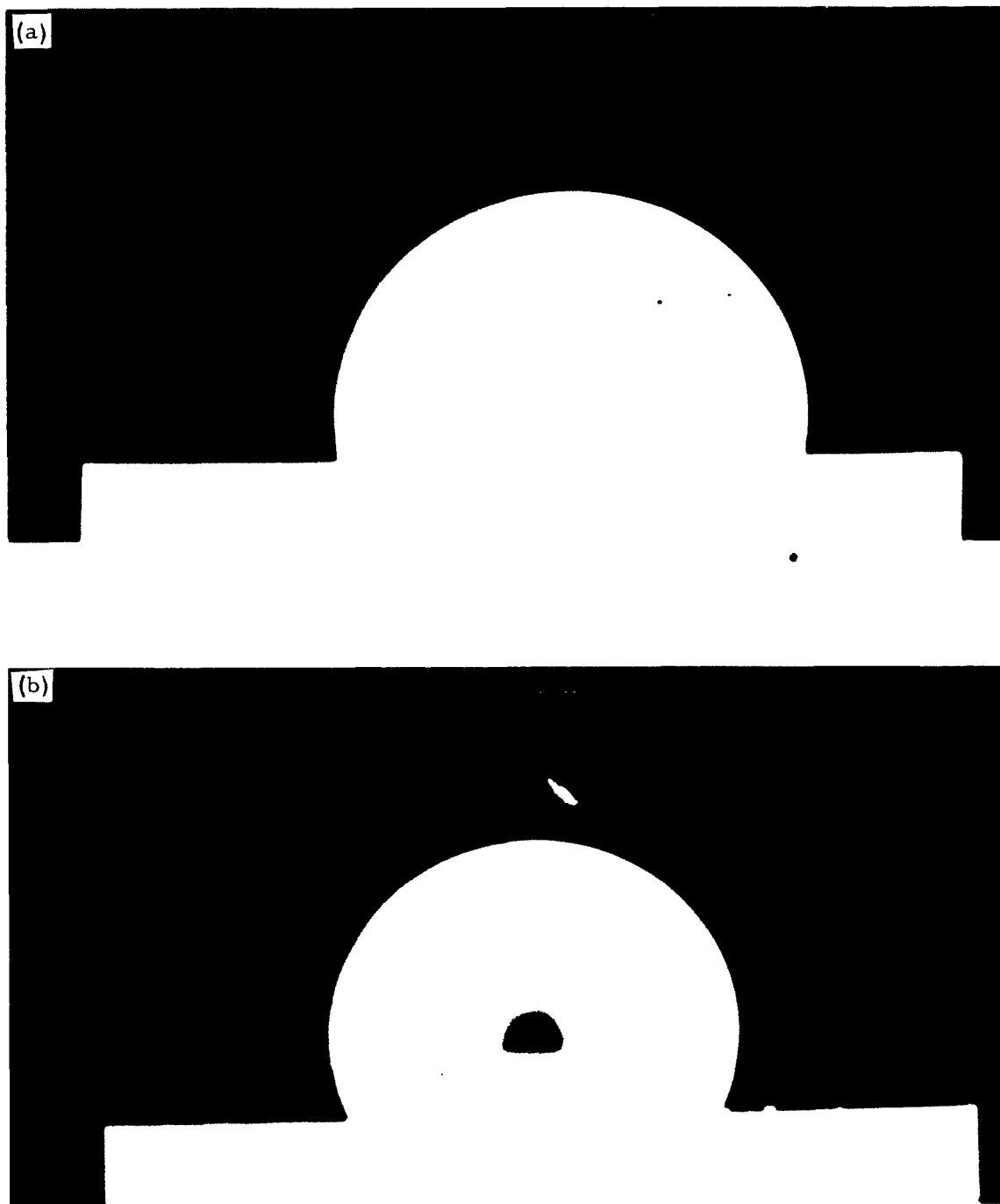


Figure 3. Effect of Nickel Purity on the Contact Angle (θ) at 1500°C
(a) 99.34% Ni, $\theta = 103^\circ$ (9X)
(b) 99.999% Ni, $\theta = 123.5^\circ$ (9X)

Substitution of graphite matt for the Mo radiation shield lowered the contact angle by 4 to 8°. This is presumed to be a result of contamination due to the adsorbed gases evolving from the graphite. It was also more difficult to get pressures below 10^{-5} mm Hg when the graphite shield was used.

B. 'Shear' Strength Tests

In order to determine the relative adherence of the solidified nickel drops to the α - Al_2O_3 plaques, a special 'shearing' jig, which is shown in Figure 4, was used. The sessile drop specimen is carefully and tightly fitted into a contoured slot in the jig which is then placed into an Instron Testing machine. The load is applied at a cross-head movement rate of 0.02 inches/minute. The shearing arm, which fits over the drop is located about 0.001" above the α - Al_2O_3 plaque so that the load is applied to the drop near the interface. The 'shear' stress is determined by dividing the applied load by the original cross-sectional area of the bead at the interface. The results of the shear tests and contact angle measurements are also summarized in Table II.

TABLE II. Results of Sessile Drop Experiments and Shear Tests of Ni on α - Al_2O_3 Plaques

Sample	Ni Purity	Heating Unit	Temperature (°C)	Pressure mm Hg	Contact Angle (°)	Cooling Rate*	Ni-drop Diameter (inches)	'Shear' Strength (psi)	Fracture
X-1	99.34%	(1)	1640	0.7atm Ar	105.5°	Fast	0.195	1050**	Across Al_2O_3 Plaque
X-2	99.34%	(1)	1645	0.7atm Ar	106.0°	Fast	0.137	1630	Across Al_2O_3 Plaque
1	99.34	(2)	1550	1x10 ⁻⁴	~100°	Fast	0.130	9250	Across Al_2O_3 Plaque
2	99.34	(3)	1550	1x10 ⁻⁴	~100°	Fast	0.195	510**	In Al_2O_3 Plaque***
3	99.34	(3)	1550	1x10 ⁻⁴	~103°	Fast	0.155	700**	In Al_2O_3 Plaque***
4	99.34	(3)	1550	1x10 ⁻⁴	~100°	Fast	0.182	590**	In Al_2O_3 Plaque***
5	99.34	(3)	1550	5x10 ⁻⁵	103.5°	Fast	0.167	1515	Between Ni and Al_2O_3
6	99.34	(3)	1550	5x10 ⁻⁵	99.0°	Fast	0.147	3820	In Al_2O_3 Plaque***
7	99.34	(3)	1550	5x10 ⁻⁴	102.0°	Fast	0.170	5820	Across Al_2O_3 Plaque
8	99.34	(3)	1550	5x10 ⁻⁴	100.7°	Fast	0.184	980**	Across Al_2O_3 Plaque
9	99.34	(4)	1725	4x10 ⁻⁴	103.4°	Fast	0.167	8950	Across Al_2O_3 Plaque
10	99.34	(4)	1535	4x10 ⁻⁴	103.1°	Slow	0.188	**	Al_2O_3 badly cracked
11	99.34	(5)	1535	2x10 ⁻⁴	102.4°	Fast	0.196	1270	Between Ni and Al_2O_3
12	99.34	(6)	1535	5x10 ⁻⁵	105.7°	Slow	0.174	1640	Between Ni and Al_2O_3
13	99.999	(4)	1500	5x10 ⁻⁵	115.6°	Slow	0.161	2100	Across Al_2O_3 Plaque
14	99.999	(6)	1500	1x10 ⁻⁵	123.5°	Slow	0.121	4440	Across Al_2O_3 Plaque
15	99.999	(7)	1500	1x10 ⁻⁵	114.7°	Slow	0.180	2520	Across Al_2O_3 Plaque
16	99.999	(7)	1500	1x10 ⁻⁵	119.3°	Slow	0.141	2820**	Across Al_2O_3 Plaque

*Slow = 20°/min, Fast = 200°/min.

** Al_2O_3 Plaque cracked on cooling.

***Concave section removed from plaque, still adhering to Ni.

(1) = Ta-susceptor

(2) = Mo-susceptor, Mo shield, BN holders.

(3) = Mo-susceptor, graphite shield, BN holders

(4) = Ta-susceptor, graphite shield, BN holders

(5) = Ta-susceptor, graphite shield, Al_2O_3 holders

(6) = Ta-susceptor, Mo shield, BN holders

(7) = Ta-susceptor, Mo shield, Al_2O_3 holders

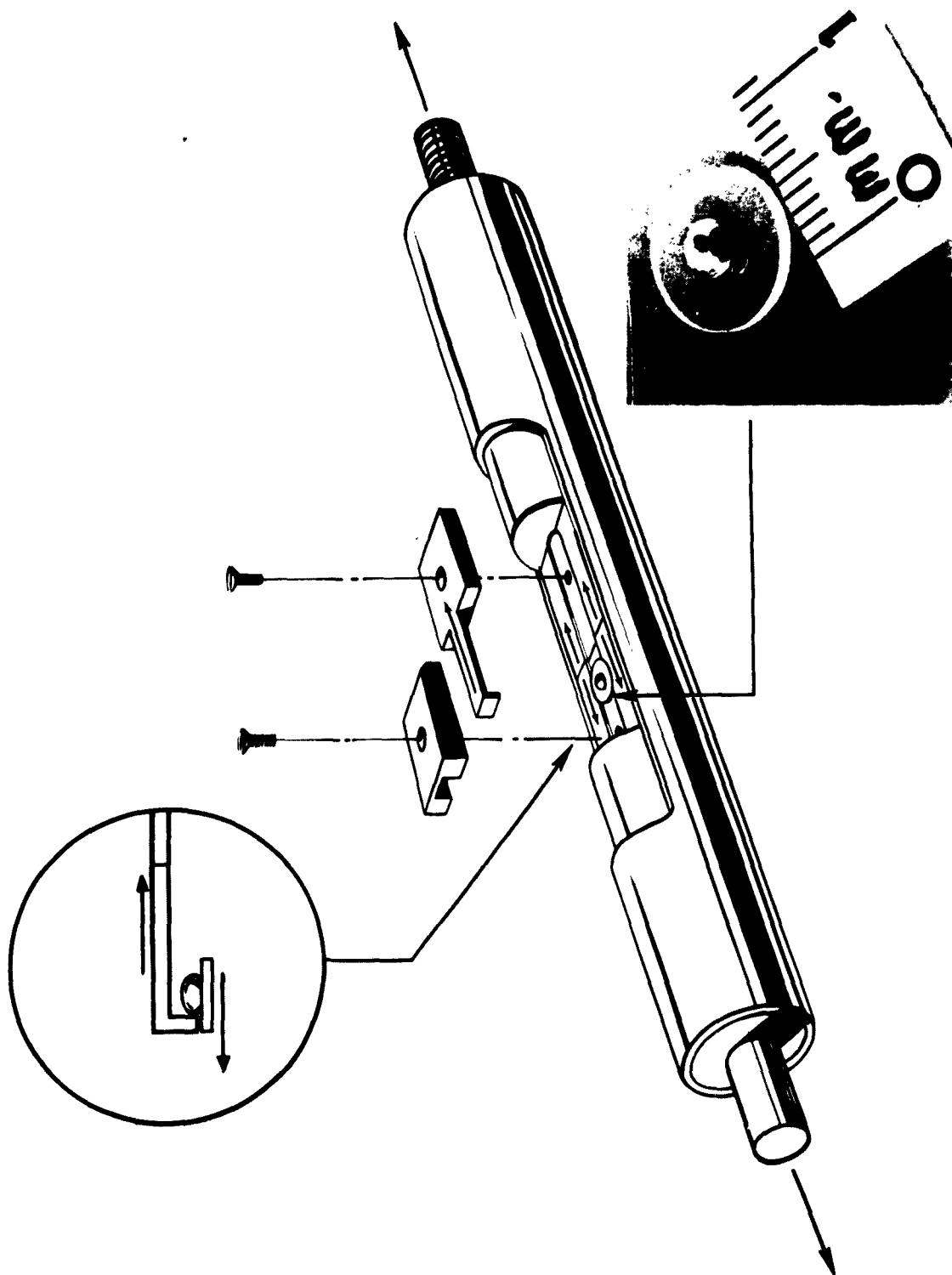


Figure 4. Schematic Diagram of Device Used for Determining Sessile Drop 'Shear' Strength. INSET: Photograph of Solidified Metal Drop on α - Al_2O_3 Plaque

IV. DISCUSSION

The purpose of the adherence tests of the Ni to α - Al_2O_3 was to, (1) provide some data on the magnitude of the bond stresses between the two materials, (2) make correlations, where possible, with the experimental conditions, and (3) determine the effect of specific additives on the bond strengths. While these tests are qualitative, they do provide a good basis for comparison*. For example, in Table II it can be seen that all low strength values can be explained by the fact that there were cracks initiated in the α - Al_2O_3 under the nickel drop during cooling. It is most likely that these originated from thermal stresses arising from a mismatch of the thermal coefficients of expansion. This view is further substantiated by the fact that cracks always occurred (1) when the drop size was relatively large, viz., dia. >0.18 inches, (2) when the drop was located away from the edge of the plaque, and (3) when slow cooling rates were employed. While the magnitude of these residual stresses probably will not be as great for the α - Al_2O_3 whiskers because of size and geometry considerations, it is important to note that the stresses are sufficiently large to cause cracks in the α - Al_2O_3 plaques under the conditions of the present experiments. When the diameters of the nickel drops were less than 0.18 inches, cracking occurred in only one experiment.

The bond strengths which are given in Table II represent low values since most of the fractures occurred in the α - Al_2O_3 . This does not necessarily mean that the interfacial bond strengths are stronger than the strength of the α - Al_2O_3 ; it is more likely that stress concentrations occur in the α - Al_2O_3 during the period that the load is applied. It was further noted that even though the Al_2O_3 fractured in different modes, each had a common geometry with respect to the direction of the applied load. The stress distribution in the nickel drop is being further investigated analytically.

*The maximum bond strength of Ni- α - Al_2O_3 was 9,250 psi, which can be compared with a maximum of 1780 psi for silver- α - Al_2O_3 , (Ref. 4) and 870 psi for gold- SiO_2 (Ref. 5).

Essentially three types of failure occurred when the nickel drops were 'sheared' from the $\alpha\text{-Al}_2\text{O}_3$ substrate. These are shown schematically in Figure 5. The wedge types failures (Figure 5b) occurred the most frequently and also resulted in the greatest 'shear' strengths. The lens type failures (Figure 5c) resulted from specimens where circumferential cracks at the drop interface were observed prior to testing. These failures resulted in the lowest shear values, vis. 510-700 psi. Complete separation of the bead from the $\alpha\text{-Al}_2\text{O}_3$ substrate (Figure 5d) occurred only in three cases, and the Ni surface appeared to be dull. This latter fracture mode occurred only for the 99.34% Ni specimens.

The most significant factor affecting the 'shear' strength is the quality of the contact between the nickel and $\alpha\text{-Al}_2\text{O}_3$ (whisker) composites. It was observed that poor contact resulted when the molten Ni-drop moved over the surface of the $\alpha\text{-Al}_2\text{O}_3$ during an experiment, and further that the reactive area was always concentrated at the edge of the drop. As the drop moved, it would leave a series of reaction rings on the $\alpha\text{-Al}_2\text{O}_3$ surface. These rings were less pronounced in the purer nickel (99.999%) specimens. The reaction zone is illustrated in Figure 7, where an under-side view of a $\alpha\text{-Al}_2\text{O}_3$ plaque is shown with a nickel drop on the opposite surface. It can be seen in Figure 7a that the drop had moved from the center of the plaque to its present position where some back and forth motion occurred. The region of poor contact (light area) under the nickel corresponds to the region where the drop was originally. The region on the surface of the $\alpha\text{-Al}_2\text{O}_3$ where the Ni passed over is shown in Figure 7b. Since the reaction zone is of importance to the bond strength, it is being further investigated. Electron micrographs of the $\alpha\text{-Al}_2\text{O}_3$ surface, which was under the Ni drop prior to fracture, were taken and also revealed that some chemical reaction had occurred. Figure 8 shows some of the etching of the $\alpha\text{-Al}_2\text{O}_3$ which occurred under the Ni drop. It appears that reaction occurs between Ni and $\alpha\text{-Al}_2\text{O}_3$ at temperatures of 1500°C , but that most of the reaction is concentrated at the rim of the Ni drop, i.e., at the three-phase boundary.

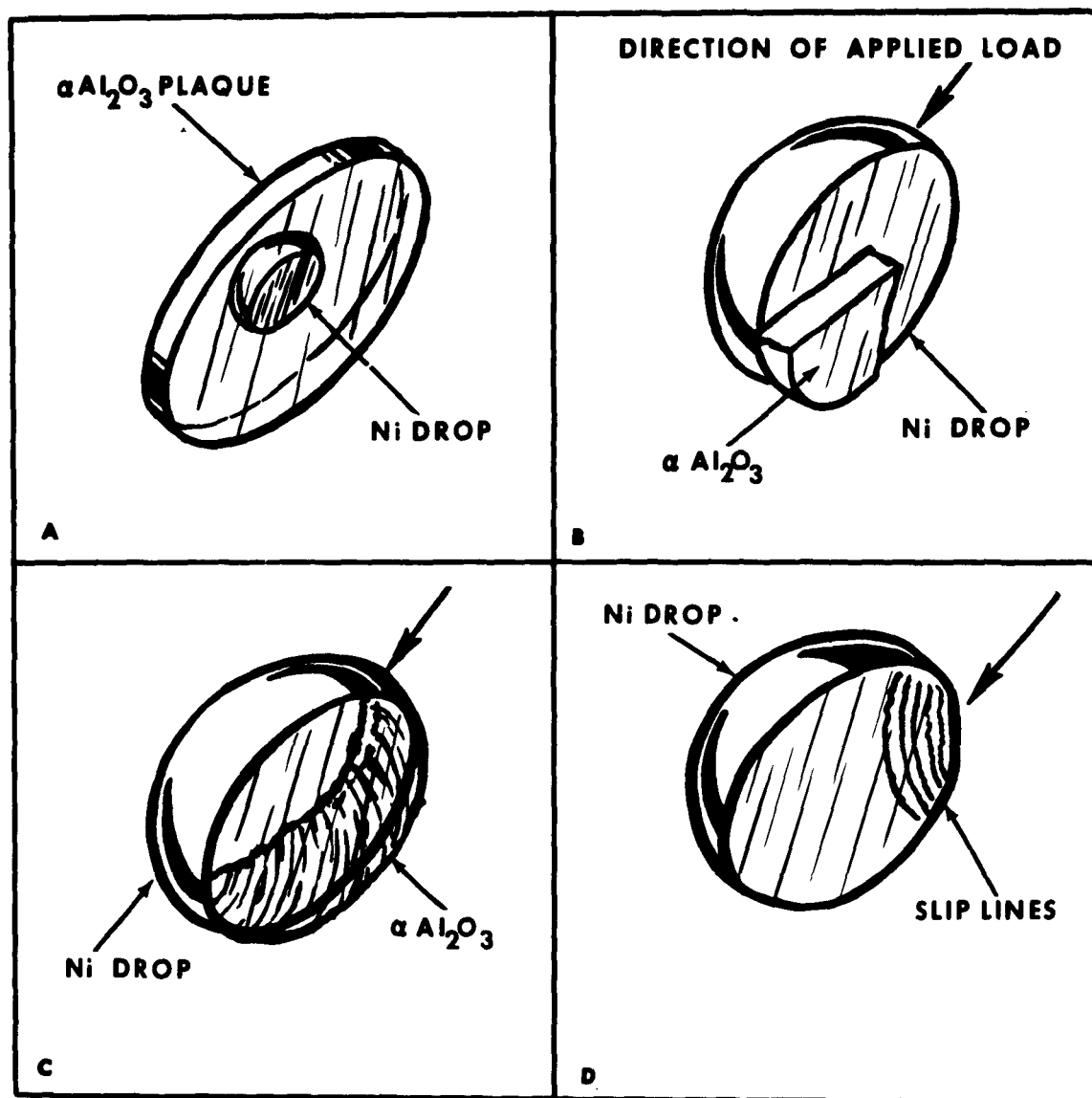


Figure 5. Fracture Modes in 'Sheared' Ni - $\alpha\text{-Al}_2\text{O}_3$ Specimens

- (a) View Thru $\alpha\text{-Al}_2\text{O}_3$ Showing Contact Region with Ni Prior to Test.
- (b) Ni-Drop with Wedge of $\alpha\text{-Al}_2\text{O}_3$ Attached After Rupture
- (c) Ni-Drop with Convex Lens of $\alpha\text{-Al}_2\text{O}_3$ Attached After Rupture
- (d) Complete Separation of $\alpha\text{-Al}_2\text{O}_3$ From Ni Drop

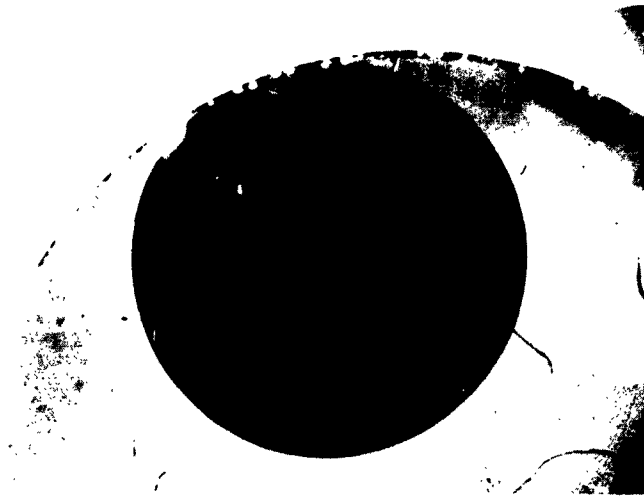


Figure 6. Contact Area Between Ni Sessile Drop and α -Al₂O₃ Plaque
(a) Good Contact, Strong Interfacial Bonding (12X)
(b) Poor Contact, Weak Interfacial Bonding (12X)

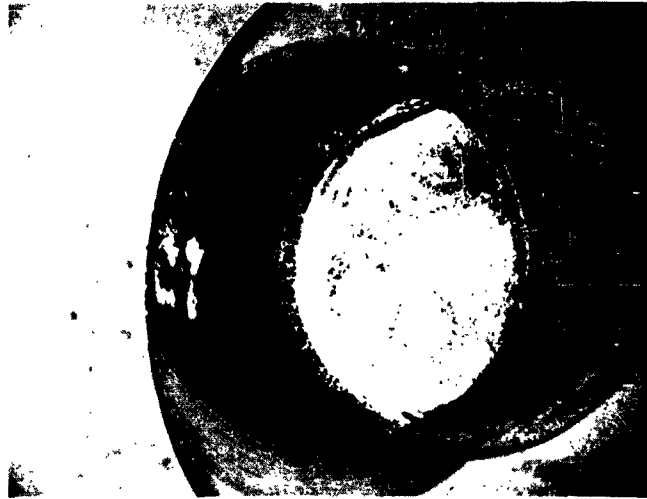


Figure 7. Photographs Showing Reaction Rings Between Ni and α -Al₂O₃

- (a) Rings Showing Movement of Molten Ni Drop During Experiment (12X)
- (b) Detail of Reaction Ring (120X)

This indicates that the chemical activity between the Ni and $\alpha\text{-Al}_2\text{O}_3$ is enhanced at the vapor interface. For example, if oxygen is available, NiO can readily form and react with $\alpha\text{-Al}_2\text{O}_3$ at above 900°C to form nickel spinel⁽⁶⁾. Presumably most of this reaction would occur right at the meniscus of the Ni-drop.

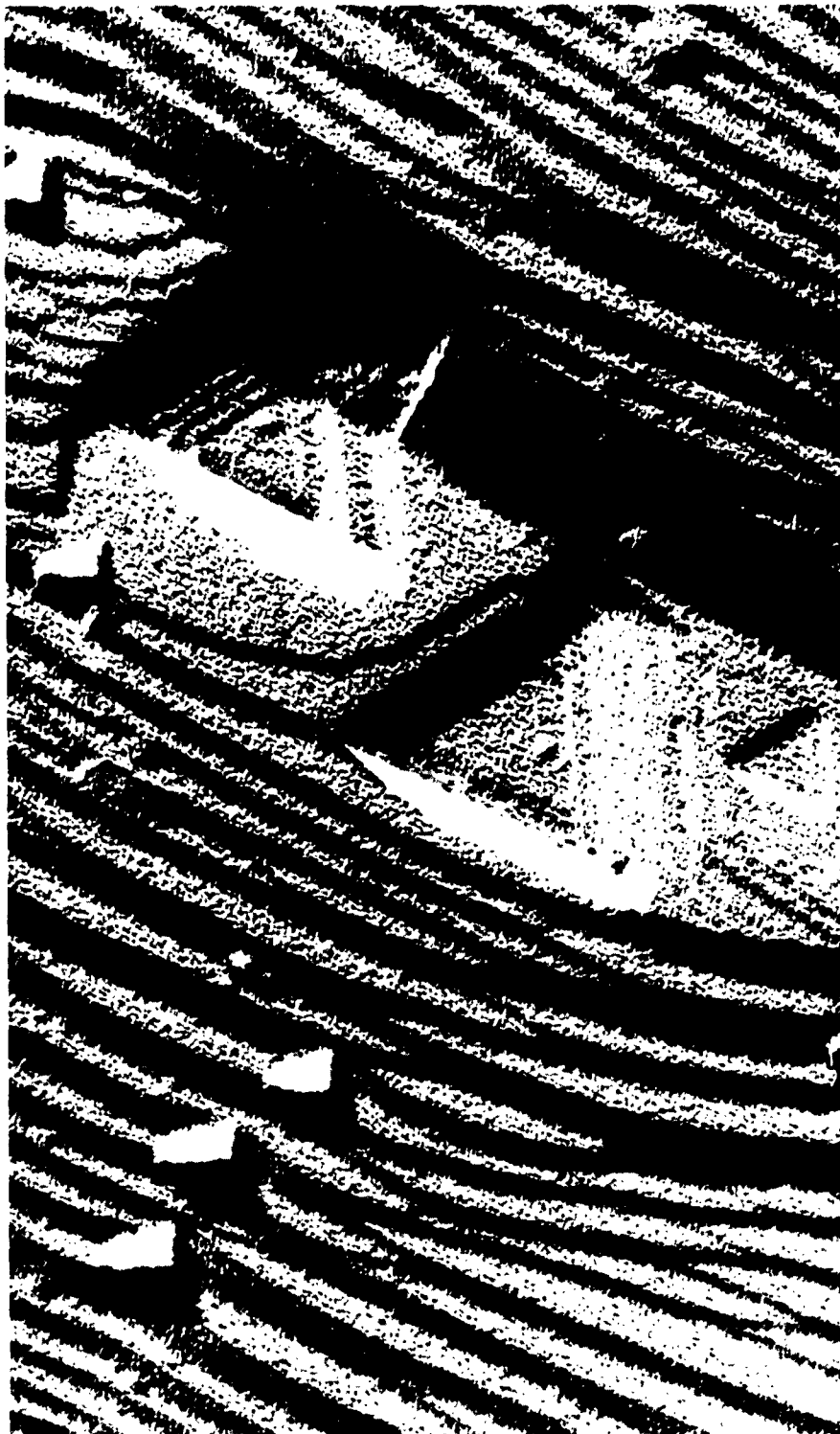


Figure 8. Electron Micrograph of α - Al_2O_3 Surface
Previously Under Ni Sessile Drop (60,000X)

V. FUTURE WORK

The emphasis in future work will be directed towards the effects of specific additives, viz., Cr and Ti, on the wetting (contact angle) and the bonding between Ni - α -Al₂O₃ sessile drop specimens. The Cr and Ti will be added directly to the Ni in small percentages and also will be applied as vapor deposited metals to the α -Al₂O₃ surface. It is also planned in the near future to conduct other types of tests which will quantitatively measure the bond strength between Ni, Ni-alloys and α -Al₂O₃.

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