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DEVELOPMENT OF HIGH
EFFICIENCY COLLECTOR
PLATES

FINAL REPORT

Teuvo Santala
Ronald Sabol

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ABSTRACT

Composite metal technology was used to manufacture inter-metallic compound (IC) absorption surfaces and to combine them integrally with composite metal tube-in-sheet collector plates.

Five material systems, in which Al was one component metal and Fe, Cr or Ni or their alloy was the other pair, were evaluated. All intermetallic compounds had high solar absorptance $\alpha \approx 0.9$. The AlNi was most promising and $\alpha \geq 0.95$ and $\epsilon \geq 0.3$ were obtained over a broad range of compounding conditions. After eight months exposure in flat plate collector enclosure the characteristic properties of AlNi surfaces remained virtually unchanged.

Only LCS/Cu composite metal tube-in-sheet collector plates could be manufactured successfully. The technical difficulties associated with integrating the intermetallic compound and tube-in-sheet technologies make the manufacturing of composite metal collector plates at the time being economically unfeasible.

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I SUMMARY

The objective of the project was to develop a composite metal solar collector plate in which an intermetallic compound absorption surface is combined integrally with a tube-in-sheet collector plate. The goal for the intermetallic absorption surface was solar absorptance $\alpha \geq 0.9$ and the infrared emittance $\epsilon \leq 0.3$. The goal for the tube-in-sheet collector plate development was to use the composite metals technology to combine materials and use them in quantities and locations which assure the best corrosion resistance and the most economic use of materials.

Al-Fe and Al-Cr intermetallic compounds were shown to have a high solar absorptance $\alpha > 0.95$ but their infrared emittance is also high $\epsilon > 0.55$, resulting in low selectivity.

Aluminum-nickel intermetallic compounds exhibited high solar absorptance and also significant selectivity. To optimize the Al-Ni system the effects of the thickness of the aluminum layer and the temperature, atmosphere, and time of the compounding heat treatment were evaluated. Typical values, obtained under broad compounding conditions, were $\alpha \sim 0.95$ and $\epsilon \sim 0.3$. Under closely controlled process conditions $\alpha \sim 0.95$, $\epsilon \sim 0.20$ and $\alpha/\epsilon \sim 4.75$ have been achieved.

X-ray microprobe was used to determine the surface composition of the aluminum-nickel intermetallic compound, which was shown to be AlNi. AlNi is the most stable compound in this binary system with a melting point of 1638°C (2980°F) making these surfaces suitable for applications where high operation or stagnation temperatures are expected.

Scanning electron microscope (SEM) pictures at 5000x show that the intermetallic compound surfaces have a dendritic or a porous structure with the dimensions of the fine structure in the same range as the wave length of the incident solar radiation. These porous surfaces act as multiple scatter absorption media, in which the surface pores act as black

body cavities.

The exact reason for the lower infrared emittance of the AlNi intermetallic compound surface has not yet been determined, but the fine structure is porous rather than dendritic as it is for the Al-Fe and Al-Cr surfaces. Apparently AlNi surfaces radiate in the infrared wave length region as a smoother surface than either Al-Fe or Al-Cr intermetallic compounds. An effort was made to determine the exact nature of the apparently porous AlNi surface. For that purpose the specimen was shadowed by gold to improve the resolution of the SEM. However, at up to 20000x magnification the surface details uniformly disappeared with increased amount of Au shadowing, indicating that the AlNi surface was covered by a rather continuous film of electron transparent material. Depth profile of Auger electron spectroscopy peak intensities of oxygen, aluminum and nickel show that a layer of approximately 200A aluminum oxide covers the surface.

The porous surfaces were impregnated with thin layers of various polymers such as polyimide and methyl-methacrylate, and with clear glass enamels, which are transparent to solar radiation and generally opaque to infrared radiation, to evaluate if the coatings would cause a "greenhouse" effect and thus influence the selectivity of the absorption surface. The solar absorptance was reduced only by an insignificant amount. The infrared emittance of the impregnated surfaces approached values which were characteristic of those of the impregnating media. Consequently, the selectivity was improved only in the cases where the initial emittance was high.

Samples of unimpregnated Al-Fe, Al-304 SS, Al-430 SS and Al-Ni surfaces have been subjected to environmental testing for eight months in a typical flat plate collector enclosure with one glass pane and for three months in an accelerated durability testing in cyclic humidity chamber where the relative humidity at room temperature is cycled between 10-20% and 100% every eight hours. AlNi intermetallic compounds

have shown good durability, and rather surprisingly a significant improvement of solar absorptance to $\alpha \sim 0.98-0.99$ was observed after both tests. Although small deterioration of the emittance values was observed simultaneously the selectivity of the AlNi specimens has remained virtually unchanged. The absorptance of the Al-Fe, Al-304 SS and Al-430 SS specimens was reduced substantially after the eight months exposure in the flat plate collector enclosure making these surfaces less desirable than AlNi. The durability testing of the intermetallic compound surfaces will be continued beyond the duration of this grant to gain more significant data.

In the second objective of the program, to develop a composite metal tube-in-sheet collector plate and to integrate the manufacturing processes of the intermetallic compound absorption surface and the composite metal collector plate, five material systems were evaluated. Only low carbon steel/copper/copper/low carbon steel could be successfully inflated into tube-in-sheet as an addition to plain low carbon steel.

Aluminum and nickel layers were incorporated into the collector plate material system for the formation of the intermetallic compound absorption surface, and material was bonded to manufacture 11" x 16" test collector plates. However, the incompatibility of the optimum compounding treatment for AlNi and of the tube-in-sheet process heat treatment caused significant difficulties and delay in the completion of this part of the program. Blistering occurred at the copper to copper interface and as an addition necking and rupture of the thin Ni layer adjacent to the Al occurred, resulting in a less desirable mixed Fe_2Al_5 -AlNi intermetallic compound surface on the test collector plate.

Destructive evaluation of the LCS/Cu tube-in-sheet collector plate showed that the copper interliner of the fluid

transfer channel had torn during the tube inflation resulting in the formation of pin holes through the liner. This condition if not corrected would cause very rapid pin hole corrosion through the structural low carbon steel part of the collector plate.

The difficulties to integrate the compounding heat treatment and the process heat treatments of the tube-in-sheet composite metal collector plate has made the economic outlook of a composite metal collector plate dimmer. Although it is expected that the technical difficulties could be overcome, the solutions, like a) increasing the thickness of the nickel layer to eliminate the cracking, b) increasing the copper thickness, using copper alloys or using separator layers to eliminate the pin hole formation, and c) using extended heat treatment to eliminate blister formation, would increase the manufacturing cost to a point where the composite metal collector plates would not be economically competitive.

Although it was recognized that composite metal collector plates would not be feasible at this time, collector plates were installed to evaluate specifically the durability of the intermetallic compound absorption surfaces. The testing will be continued beyond the duration of this grant.

II INTRODUCTION

The initial large scale utilization of solar energy will most probably be for applications in which relatively low grade thermal energy is needed. Largest such uses are space heating and cooling, industrial process heat and hot water supply. Properly designed flat plate collectors are capable of supplying sufficiently high temperatures for space and hot water heating. However, it is generally agreed that to make solar energy harvesting economically justifiable for the most residential uses it has to be able also to provide energy to operate absorption air-conditioning in addition to the space and hot water heating. An efficient operation of absorption coolers requires consistently higher working fluid temperature. Furthermore, for large scale use in permanent installations, high collection efficiency, low initial and maintenance cost and durability become increasingly important.

Although open flow of air⁽¹⁾ or water^(2,3) over the collector plate has been used in actual systems, a collector plate made by brazing or soldering copper tube coils into a copper sheet has been the standard design for commercial hot water solar heaters in the southern U.S. and abroad. However, copper tubing as construction material and brazing and soldering as manufacturing processes are expensive. This construction offers also very few practical choices for fluid flow pattern; and as was shown by Whillier and Saluja⁽⁴⁾ any discontinuity at the brazed joint would impede the thermal flow and diminish the efficiency of the collector.

So called tube-in-sheet structure represents a technologically advanced method to manufacture flat solar collector plates. This structure offers (a) an efficient heat transfer between the plate and the transfer fluid and (b) freedom in channel design. Although tube-in-sheet, made of aluminum, with black painted collection surfaces, has been used in solar

collectors, they have not gained acceptance. Painted surfaces are not selective and do not possess the desired durability; and aluminum, though a good and economical structural material for the plate, is not suitable for hot water tubing, because of the difficulties associated in preventing corrosion on the transfer fluid side^(5,6).

Previous investigation⁽⁷⁾ had shown that some intermetallic compounds, such as Fe_2Al_5 , have a high solar absorptance when they are formed by reacting the component metal layers thermally in solid state. For the collector plate, composite metals technology can be used to combine materials and to use them in quantities and locations which assure the best corrosion resistance and most economic use of materials.

It was then proposed that using the composite metal technology, a solar collector plate could be manufactured in which intermetallic compound solar absorption surface and the tube-in-sheet heat transfer channels are formed integrally. The process is outlined in Figure 1. The component materials for the absorption surface and the structural materials for the composite metal collector plate are metallurgically bonded simultaneously to form a composite. An inflation technique is used to form the array of tubes into collector plate so that a metal with good corrosion resistance forms the lining of the heat transfer fluid channels. After the forming of the tube-in-sheet structure, the collector plate is heat treated to form, in situ, the intermetallic compound absorption surface of two or more selected metals.

A program, supported by ERDA Grant E(11-1)-2600 (initially NSF Grant AER74-09036) and by Texas Instruments Incorporated cost sharing, was initiated to evaluate the feasibility to manufacture intermetallic compound solar absorption surfaces and to develop the manufacturing technology to combine them integrally with composite metal tube-in-sheet collector plate.

Figure 1. Process Outline For Composite Metal Collector Plate.

- 1 and 2 Component metals of the intermetallic compound
- 3 Low carbon steel
- 4 Fluid channel liner material
- 5 Intermetallic compound absorption surface

The objective of this program was to develop a materials system and manufacturing technology to achieve the following technical and economic goals:

1. A thermally stable, selective intermetallic compound surface with $\alpha_{\text{solar}} \geq 0.9$ and $\epsilon_{3-30\mu} \leq 0.3$, in which aluminum is one component metal and commercially available base metals are used as the other component, and which will have a life of 20 years.
2. A collector plate which incorporates the absorption surface and the transfer fluid channel into an integral collector plate assuring efficient thermal energy transfer between the absorption surface and the transfer fluid.
3. A manufacturing technique which will make the above described collector plates available at approximately \$1.50-2.20/sq.ft., in quantities exceeding 1,000,000 sq.ft./year.

To achieve these objectives, the program was divided into three tasks:

Task 1. Development of intermetallic absorption surface.

The variables to be investigated to achieve the objectives for the intermetallic compound surfaces were: a) composition of the intermetallic compounds, b) compounding conditions and c) the effect of impregnation of the porous intermetallic surface with polymers and glasses.

Intermetallic compound surfaces were to be manufactured using composite metal technology.

The impregnated and unimpregnated samples were to be subjected to environmental and accelerated cyclic humidity-temperature testing to establish the criteria for durability.

Task 2. Development of collector material system and geometry

Durable and economical material combinations were to be selected for the composite metal collector plate, and a manufacturing process was to be developed to combine the

intermetallic compound absorption surface technology with an existing tube-in-sheet manufacturing technology.

As a part of this task a simple heat transfer fluid channel pattern was to be developed and a tool built for a 1 sq.ft. tube-in-sheet collector plate to test the heat transfer characteristics and the durability of the composite metal collector plate.

Task 3. Tooling and manufacturing of pilot quantities of solar collector plates.

Using information obtained in Tasks 1 and 2 an optimum channel geometry was to be designed and a tool built for manufacturing a limited number of 2 feet by 4 feet tube-in-sheet collector plates for evaluation at Texas Instruments and by other users as designated by ERDA.

Texas Instruments also proposed to sell to prospective users pilot quantities of 2 feet by 4 feet solar collector panels for systems evaluation, but problems which were encountered, and described later, necessitated the elimination of this task.

III SELECTIVE INTERMETALLIC COMPOUND SURFACES

The requirements for an ideal flat plate collector can be summarized as:

- High collection efficiency
- Low cost
- Good durability

The elements of high collection efficiency, which were identified and dealt with earlier by Hottel and Woertz(8), are:

- High solar absorptance
- Low infrared emittance
- Low conduction and convection losses

Solar absorptance and infrared emittance are characteristics of the absorption surface and together with the cost and durability are the major criteria in developing and evaluating collection surfaces. The low conduction and convection losses are determined principally by the collector design and can be influenced only in exceptional cases by the absorption surface.

The need of the high solar absorptance is obvious and all the methods to obtain this property are related to the optical characteristics of the absorber. Low infrared emittance losses on the flat plate collector can be obtained by:

- selective surfaces⁽⁹⁾
- IR reflecting coatings on cover glasses (10,11) or
- geometric trapping and multiple reflection arrangements e.g. (12,13,14).

Of the various methods to reduce the IR emittance, only the first mentioned principle is directly related to the properties of the absorber surface and to the work conducted at Texas Instruments to develop selective intermetallic compound surfaces.

Low cost and good durability have a direct relation to the economic competitiveness and public acceptance of the solar energy collection systems and constituted an important part in selecting the material systems for and assessing the value of the intermetallic compound surfaces.

Three basic methods have been described by J.A. Duffie et al ⁽¹³⁾ to prepare collector plate surface to obtain selectivity:

- a) Coatings with high absorptance for solar radiation and high transmittance for long wave radiation applied to substrate with low emittance.
- b) Interference filters applied to low emittance substrates and
- c) Metallic surfaces, with inherently high reflectance, prepared with a surface morphology designed to make them good absorbers of short wave radiation.

Of the selective surfaces the ones falling under definition

a) have been evaluated most extensively for performance and are also used commercially. However, Tabor ⁽¹²⁾ already indicated that many of these surfaces are not stable in the environment encountered in the flat plate collector, and more recent studies have confirmed this for black copper ⁽¹⁵⁾ and for black nickel ^(15,16). It has also been shown that for surface coatings, in which pigments possessing the characteristics set forth in Item a) above and bonded to a low emittance substrate with a binder, the binders used determine in great degree the performance and durability ^(16,17). Especially, if organic binders are used, the durability of such pigment coatings is severely limited at elevated temperatures.

Decorative electroplated finish of black chrome was shown to have desirable solar selective properties ⁽¹⁸⁾, however, the performance was reported to be determined in significant degree by the type of the nickel underplating and by the thicknesses of the black chrome deposit ⁽¹⁶⁾. The surface of these coatings was shown to be rough ⁽¹⁶⁾ and therefore, it is conceivable that black chrome falls somewhere between type a) and c) in the principle of selectivity. The ChromOnyx ^(R) black chrome was

(R) Registered trade mark of Harshaw Chemical Co.

shown to be stable after extended heat treatment at 300°C in air and under UV-irradiation in air at room temperature⁽¹⁶⁾. The conventional acetic acid-chromic acid black chrome was found to be unstable under UV-irradiation in air⁽¹⁶⁾. Data about the behavior of black chrome exposed to moist atmosphere has not been presented.

Interference filters applied to low emittance substrates have been shown to be efficient and durable at high temperatures⁽¹⁹⁾, however, it is necessary to demonstrate that the manufacturing cost of these surfaces can be made low enough to make them economically attractive for flat plate collectors.

Various manufacturing techniques and metals have been used to manufacture type c) surfaces. The selective characteristics of the gold black has been known for a long time⁽⁹⁾ and they have been re-evaluated recently⁽²⁰⁾. Metal globules and meshes deposited on reflective substrates⁽²¹⁾ as well as vapor deposited In and Sn surfaces with microscopic conical surface morphology⁽²²⁾ have been shown to exhibit selective characteristics. Most of the above mentioned surfaces have severe limitations for the maximum temperature where they can be used because of the low melting point of the metals used or because of the high sintering tendency of the deposits^(9,20). Vapor deposited tungsten has also shown to have a conical surface morphology in microscopic scale, and high solar absorptance and low IR emittance has been demonstrated⁽²³⁾. However, durability data or the projected manufacturing cost of these surfaces have not been made available.

A recent report⁽²⁴⁾ pointed out that absorptance and emittance of these porous or rough surfaces can be very directional, but sufficient data encompassing the various structures is not yet available.

The high absorptance of type c) surfaces has been credited to the multiple scatter of the incoming radiation in the macroscopic irregularities of the absorber plate surface. These so

called multiple scatter absorption media were described and theoretically evaluated by Hottel et al⁽²⁵⁾. Such surfaces can be manufactured by embedding the scattering particles in a third media or by forming a layer of particles overlaying the substrate⁽²⁵⁾ and this method can be a cost-effective approach to obtain selective absorption surfaces. In principle, all porous surfaces should act as multiple scatter absorption media, in which the surface pores act as black body cavities.

Some intermetallic compounds, such as Fe_2Al_5 , exhibit such surface characteristics when they are formed by reacting the component metal layers thermally in solid state. As a result of the crystallographic changes accompanying the compound formation, the formed surface is porous and granular in structure. These intermetallic compound surfaces have been used in large industrial scale in the anodes of the radio tube, (26,28) because they offer a thermally stable emitter surface. Fe_2Al_5 intermetallic compound surfaces were evaluated for use as a solar absorption surface⁽⁷⁾. The results indicated that the absorptance and the emittance were affected by factors like stoichiometry, presence of surface oxides, and the compound forming conditions. However, the changes in the α and ϵ were not directly correlated. Because of the encouraging results obtained with the Fe_2Al_5 surfaces a further study, supported by ERDA Grant E(11-1)-2600 (originally NSF Grant AER74-09036), was conducted to evaluate a family of intermetallic compounds in which aluminum was one of the component metals.

A. SELECTION OF MATERIAL SYSTEMS

Almost an unlimited number of intermetallic compounds can be formed already from simple binary metallic systems and surprisingly little is known or reported about the properties of most of these materials. Although it would have been challenging and intriguing to select a wide variety of intermetallic compounds, the objective of the program was to develop durable and economical alternatives to the existing selective solar absorption surfaces. Therefore, the materials to be used had to be available in large quantities, be inexpensive and suitable for use with existing mass manufacturing technologies.

Each binary system of aluminum with chromium, copper, iron and nickel has several intermetallic compound phases⁽²⁹⁾, therefore, the probability that a suitable surface morphology can be formed does exist. All above mentioned materials are commonly available as commercially pure metals and in a wide assortment of alloys and they do meet the basic requirements of economics and manufacturability. Therefore, the investigation was limited to those metals.

Material combinations listed in Table I were selected for the initial evaluation.

Aluminum with:

- 1006 Low Carbon Steel
- Chromium
- 430 SS (83% Fe - 17% Cr)
- 304 SS (74% Fe - 18% Cr - 8% Ni)
- Nickel
- Copper

TABLE I Material Systems Evaluated for Formation
of Intermetallic Compound Absorber Surfaces

Binary intermetallic compounds or compound mixtures will be formed between Al-LCS, Al-Cr, Al-Ni and Al-Cu, but it is obvious that the pairs Al-430 SS and Al-304 SS do not produce binary but potentially ternary and quasiternary compounds respectively.

B. INITIAL SCREENING OF COMPOUNDS

Previous work has shown⁽⁷⁾ for Fe-Al compounds, that solar absorptance and infrared emittance are affected by factors like stoichiometry, presence of surface oxides, the compound forming conditions and the thickness of the formed compound layer. The same parameters are expected to influence other compound systems in which Al is one of the component metals. Although it is possible that desired intermetallic compound surfaces can be formed if either of the component metals is on the outside, past practice has shown that more consistent results are obtained if the aluminum is the outside component. This practice was followed through the whole program.

For specimen compounded to completion the thickness of the intermetallic compound is determined by the amount of the component metals available for compound formation, and therefore, in the case where the Al was the outside member, by the thickness of the Al layer. The other component metal, as an addition to participating in the compound formation, was also used as the substrate. To evaluate the effect of the thickness, compound thickness from 0.0005" (12 μm) to 0.002" (50 μm) was desired and to achieve this three aluminum thicknesses 0.0004" (10 μm), 0.0008" (20 μm) and 0.0012" (30 μm) were used.

Minor alloying elements in the aluminum were not expected to affect the morphology of the intermetallic compound, however commercially pure (1100) aluminum and aluminum - 1.5% silicon alloy (4022) were used. Silicon additive is known to retard the onset of compound formation in Al-Fe system, and it was expected that in integrating the intermetallic compound absorption surface technology with the composite metal tube-in-sheet collector plate technology, intermediate anneals might be necessary and therefore, as high as possible compounding temperatures might be desirable.

Samples for screening were produced by roll bonding the respective component metals and subsequently rolling them to 0.020" (0.5 mm) overall thickness without intermediate anneals. The only exception to this process was the Al-Cr pair which could not be manufactured by rolling technology because chromium is not available in ductile form. In this case 0.0008" (30 μ m) chromium was electroplated onto 0.031 (0.8 mm) thick 430 SS substrate and 0.0003" (8 μ m) high purity aluminum was electron beam vapor deposited onto the chromium.

Despite the significant effect which temperature and time can have in determining the type of compound which is formed, only 816°C (1500°F) for 30 minutes was used for screening. The only exception for this was the Al-Cu pair, which was compounded at 566°C (1050°F) because of the low melting eutectic which is formed on the aluminum rich side. 816°C (1500°F) is clearly over the melting point of aluminum, but investigations of Fe-Al system in hot stage microscope have shown that the melting of the aluminum is not a prerequisite nor a hindrance to the formation of a certain surface morphology of the intermetallic compound surface.

Three commercially available atmospheres, air, exothermic base gas (cracked city gas, CC) and dissociated ammonia (cracked ammonia, CA) were used. It was realized, that at the time when compounding commences, an oxide layer is always present at the surface of the aluminum, however, the thickness of the oxide layer determined by the atmosphere. The use of a reducing atmosphere was desired to protect the component metals of the collector plate in the latter part of the program.

Because of the large number of variables, it was not feas-

ible to evaluate all possible permutations. Table II lists the selected combinations.

Material Pair	Atmosphere		
	Air	CC	CA
0.0004" 4022 Al/LCS	X	X	X
0.0008" 4022 Al/LCS	X	X	X
0.0012" 4022 Al/LCS	X	X	X
0.0008" 1100 Al/LCS	X	X	X
0.0004" 4022 Al/430 SS	X	X	
0.0008" 4022 Al/430 SS	X	X	
0.0012" 4022 Al/430 SS	X	X	
0.0012" 4022 Al/304 SS	X	X	
0.0004" 4022 Al/201 Ni	X	X	
0.0008" 4022 Al/201 Ni	X	X	
0.0012" 4022 Al/201 Ni	X	X	
0.0004" 1100 Al/Cu		X	
0.0004" HP Al/0.0008"Cr/ 0.031" 430 SS	X	X	X

Table II. Material and Process Variable Combinations for Screening Compound Surfaces.

The measurement of solar absorptance and infrared emittance was used as a sole evaluation criteria for the screening samples. The absorptance was measured by a calorimetric comparison technique. Specimens were subjected to a simulated solar radiation provided by a Aerospace Controls Solar Simulator adjusted to supply an incident flux of 100 mW/cm². The heating rate of the unknown sample was compared to the heating rate of the same sample coated with Nextel Black Velvet Coating No. 101-C10 manufactured by the Reflective Products Division of 3M. The hemispherical emittance in the 3-30μ wave length range was measured with Lion Research Corporation Model 25B Emissometer,

using flat black laquer, $\epsilon = 0.97$ and aluminum foil $\epsilon = 0.04$ as calibration standards. More detailed description of the measuring methods is in Appendix A.

Results of the first evaluation matrix are shown in Table III. The measured values of α and ϵ show that all evaluated intermetallic compounds have a high solar absorptance. The aluminum-nickel system is the most interesting because it has significantly lower infrared emittance than the other compound systems. Aluminum-copper pair could not be compounded to form an acceptable surface structure, therefore, α and ϵ were not measured.

The results indicate that addition of chromium and nickel as alloying elements to iron, in quantities they are used for 430 and 304 stainless steels, does not significantly alter the solar absorptance or infrared emittance characteristics of the basic aluminum-iron system. The atmosphere has an insignificant effect. For the 4022 Al/201 Ni material system 0.0004" (10 μ m) aluminum thickness is not sufficient to form a desired intermetallic compound structure.

Selected intermetallic compound surface specimens of this evaluation series were subjected to durability testing in a flat plate collector enclosure (Chapter III E).

Because of the substantially lower infrared emittance and consequently significantly better selectivity of the Al-Ni intermetallic compounds, the aluminum-nickel material system was selected for an optimization study.

C. OPTIMIZATION OF Al-Ni COMPOUNDS

The most important factor omitted in the screening of the intermetallic compounds was the effect of the temperature. The purpose of the optimization of the Al-Ni compounds, therefore, was specifically to evaluate the effect of the temperature, rather than variables like alloy compositions, pre- or post-treatments of the surfaces and like, which all could

Material Combination	Al Thickness	Compounding Atmosphere					
		Air		Exothermic-Base		Dissociated Amm	
		α	ϵ	α	ϵ	α	ϵ
4022 Al/LCS	0.0004	0.99	0.55	0.95	0.56	0.98	0.55
	0.0008	0.99	0.65	0.94	0.58	0.95	0.55
	0.0012	0.93	0.53	0.90	0.67	0.91/0.93	0.60/0.58
1100 Al/LCS	0.0008	0.93	0.54	0.93	0.72	0.90/0.97	0.66/0.56
4022 Al/430 SS	0.0004	0.98	0.51	0.82	0.58		
	0.0008			0.44	0.61		
	0.0012	0.90	0.52	0.96	0.67		
4022 Al/304 SS	0.0012	0.89	0.47	0.90	0.66		
4022 Al/201 Ni	0.0004	0.64	0.32	0.87	0.26		
	0.0008	0.91	0.30	0.91	0.29		
	0.0012	0.94	0.30	0.90	0.33		
HP Al/Cr	0.0004	0.90	0.62	0.97	0.60	0.94	0.48

Table III α and ϵ of Selected Intermetallic Compounds Compounded at 816°C (1500°F) for 30 min.

affect the surface morphology and consequently the solar absorptance and the infrared emittance.

Samples for the evaluation were prepared from 4022 aluminum and 201 nickel by roll bonding. Only two thicknesses of aluminum, 0.0008" (20 μ m) and 0.0012" (30 μ m), were used because the first evaluation series indicated that 0.0004" (10 μ m) thick aluminum is not sufficient to form the desired compound surface structure. The three atmospheres for the compounding heat treatment were retained as variables. The temperature of compounding and the time at temperature were added as variables. The measurement of solar absorptance and infrared emittance was used as sole evaluation criteria.

The parameters of the first optimization matrix and the measured values of α and ϵ are shown in Table IV. The results verified those obtained during the screening in that aluminum-nickel system exhibited considerable selectivity. It is significant to note that the specimen with 0.0008" of 4022 aluminum and compounded for 60 minutes at 732°C (1350°F) in partially combusted natural gas had $\alpha = 0.99$ and $\epsilon = 0.27$ and therefore, met the set objectives of the project without need of any additional surface treatments. Table IV also shows that more favorable results were obtained at the lowest temperature and at the shortest time of compounding heat treatment. Consequently, it was possible that the optimum compounding conditions were outside of this first optimization matrix.

Additional set of samples was prepared to extend the temperature region of the evaluation. At this point, the compounding conditions had been refined to the extent that it was possible to see if the silicon additives in the 4022 aluminum alloy would have the expected retarding effect on the onset of the compounding. Also, maximum workability of the component metals was desirable from the manufacturing standpoint, therefore, a second set of samples was prepared using commercially

Atmosphere	Time & Temp Al Thickness	732°C(1350°F)				816°C (1500°F)				899°C (1650°F)			
		15 min		60 min		7.5 min		30 min		5 min		20 min	
		α	ε	α	ε	α	ε	α	ε	α	ε	α	ε
Air	0.0008"	0.93 x	0.32 x	0.86 *	0.28 *	0.85 x	0.32 x	0.86 x	0.35 x	0.79 x	0.36 x	0.79 x	0.35 x
	0.0012"	0.93 *	0.26 *	0.96 *	0.32 *	0.96 *	0.27 *	0.78	0.32	0.80 x	0.32 x	0.74 x	0.39 x
Exothermic Base Gas	0.0008"	0.92 *	0.31 *	0.99 *	0.27 *	0.89 *	0.27 *	0.91 *	0.30 *	0.90 x	0.35 x	0.86 x	0.30 x
	0.0012"	0.96 *	0.32 *	0.90 x	0.40 x	0.90 *	0.30 *	0.83 x	0.37 x	0.86 *	0.27 *	0.85 x	0.29 x
Dis- sociated Ammonia	0.0008"	0.94 *	0.27 *	0.92 *	0.30 *	0.87 *	0.27 *	0.85 x	0.29 x	0.84 *	0.27 *	0.86	0.31
	0.012"	0.89 *	0.27 *	0.86 x	0.33 x	0.82 x	0.31 x	0.81 x	0.31 x	0.78 x	0.33 x	0.76 x	0.32 x

Table IV First Evaluation Matrix to Optimize
Al-Ni Intermetallic Compounds

4022 Aluminum on 201 Nickel

* Denotes samples placed in environmental testing

x Denotes samples placed in accelerated testing

pure (1100) aluminum and 4022 aluminum alloy with high purity nickel 270 in place of 4022 Al/201 nickel used in the first optimization study of Al-Ni system. Only 0.0008" thickness of aluminum was used because Table IV indicated that it gave the highest and most consistent absorptance values. Samples compounded in air and in dissociated ammonia exhibited generally lower absorptance values than the respective samples compounded in exothermic base gas, therefore, only the exothermic base gas was used as compounding atmosphere in preparation of the second set of Al-Ni samples.

The second evaluation matrix to optimize the process and the material parameters for the Al-Ni system and the measured values of α and ϵ are shown in Table V.

Figure 2 combines all the results for the Al-Ni system from Tables III, IV and V. Figure 2 shows that high absorptance $\alpha \geq 0.9$, and infrared emittance $\epsilon \sim 0.3$ can be obtained over a wide range of compounding conditions when either aluminum alloy is used. The best compounding range for Al-Ni compounds formed with 4022 Al is from $\sim 650^{\circ}\text{C}$ ($\sim 1200^{\circ}\text{F}$) to $\sim 750^{\circ}\text{C}$ ($\sim 1380^{\circ}\text{F}$) and for compounds formed with 1100 Al from $\sim 600^{\circ}\text{C}$ ($\sim 1100^{\circ}\text{F}$) to $\sim 750^{\circ}\text{C}$ ($\sim 1380^{\circ}\text{F}$). For specimens made with 4022 Al and compounded at 612°C (1150°F) for 15 min. the ϵ is reduced to 0.12 but the absorptance is also reduced to $\alpha \sim 0.81$ negating all the benefits obtained by reduced emittance. For the compounds formed using the commercially pure 1100 aluminum the absorptance and emittance values remain unchanged through the lower temperature range, indicating that the compounding has proceeded to completion, confirming the effect of silicon as a retardant for compound formation in the aluminum nickel system.

The specimens from the first optimization series identified with an asterisk in Table IV, were placed into environmental testing and specimens identified with x in Table IV were placed in the accelerated cyclic humidity test (Chapter III E).

Material Combination	Aluminum Thickness	Compounding Temperature and Time					
		621°C (1150°F)		677°C (1250°F)		732°C (1350°F)	
		15 min.	60 min.	15 min.	60 min.	15 min.	60 min.
4022 Aluminum/ 270 Nickel	0.0008"	0.81 0.13	0.90 0.33	0.97 0.29	0.91 0.38	0.94 0.29	0.95 0.28
1100 Aluminum/ 270 Nickel	0.0008"	0.95 0.29	0.95 0.30	0.93 0.30	0.97 0.30	0.97 0.30	0.99 0.30

Table V Second Evaluation Matrix to Optimize
Al-Ni Intermetallic Compounds.
Exothermic Base Gas Atmosphere

Figure 2 Effect of Compounding Temperature on Absorptance and Emittance of Aluminum-Nickel Intermetallic Compounds

Specimens from the second optimization series were placed both into the environmental and into the accelerated cyclic humidity test.

Ultrasonic cleaning was used on some of the samples before they were introduced into the accelerated cyclic humidity test. The measured values of α and ϵ before and after the cleaning are shown in Table VI.

Material	T _{comp} °C (°F)	t _{comp} min	Atm.	Before Cleaning		After Cleaning	
				α	ϵ	α	ϵ
4022 Al/ 270 Ni	621 (1150)	15	CC	0.81	0.13	0.85	0.17
	732 (1350)	60	CC	0.95	0.28	0.95	0.25
1100 Al/ 270 Ni	621 (1150)	15	CC	0.95	0.29	0.99	0.21
	732 (1350)	60	CC	0.99	0.33	0.99	0.32
4022 Al/ 201 Ni	732 (1350)	60	Air	0.88	0.32	0.94	0.27

Table VI Effect of Ultrasonic Cleaning
on α and ϵ of some Al-Ni
Compound Surfaces

Except for the first sample which was not completely compound-
ed the results in Table VI show that ultrasonic cleaning can
improve the performance of Al-Ni intermetallic compounds. In some
cases the improvement is marginal, but especially for the sample
compounded in air the improvement in α and ϵ values is
significant. The evaluation of the ultrasonic cleaning was too
brief to draw any conclusions. It only indicates that post
treatments alter the solar absorptance and the infrared emittance
of the compounded surfaces.

D. SURFACE MORPHOLOGY OF INTERMETALLIC COMPOUNDS

Earlier investigation⁽⁷⁾ has shown that the high solar absorptance of Fe_2Al_5 is due to the surface morphology. Aluminum-nickel intermetallic compounds were presumed to be selective by virtue of having highly porous surface structure with pore dimensions of the same order as the wave length of solar radiation. These surfaces absorb as cavities, yet radiate in the infrared wave length region as flat surfaces⁽³⁰⁾.

Scanning electron microscope SEM pictures were taken of the various intermetallic compound surfaces with 1000x and 5000x magnification. The aluminum-iron, Figures 3 and 4, and aluminum-chromium surfaces, Figure 5, show a dendritic structure with the dimensions of the fine structure in the same range as the wave length of solar radiation. When chromium is added as alloying element into the Fe as in 430 stainless steel, Figure 6, both the surface morphology and the α and ϵ values changed very little. When chromium and nickel are added into iron as alloying elements as in 304 stainless steel, Figure 7, a small change in the surface morphology is noted. However, the properties of interest are still the same as for aluminum-iron intermetallic compounds.

The surface morphology of the aluminum-nickel intermetallic compounds compounded at 732°C (1350°F) is significantly different, Figures 8 and 9. Rather than being dendritic it is porous and spongelike. The dimensions of the fine structure are still in the same range with the wave length of the solar radiation. The absorptance values $\alpha = 0.95$ for the 4022 Al/270 Ni compound and $\alpha = 0.99$ for the 1100 Al/270 Ni compound are high and the respective emittance values $\epsilon = 0.28$ and $\epsilon = 0.33$ are characteristic of the aluminum nickel intermetallic compounds. When the temperature of compounding is increased to 816°C (1500°F), Figure 10, the dimensions of the fine structure increase and the solar absorptance decreases. Further increase in the temperature to 899°C (1650°F), Figure 11, coarsens the fine structure which now dimensionally exceeds the wave length range of the solar

a) 1000x

b) 5000x

Figure 3 Scanning Electron Microscope pictures of 4022 Al (0.0008")/Low Carbon Steel compounded at 816°C (1500°F) for 30 minutes in dissociated ammonia.
 $\alpha = 0.98$ $\epsilon = 0.55$

a) 1000x

b) 5000x

Figure 4 SEM pictures of 1100 Al (0.0008")/
LCS compounded at 816°C (1500°F)
for 30 minutes in $\alpha = 0.93$ $\epsilon = 0.72$
exothermic base gas

a) 1000x

b) 5000x

Figure 5 SEM pictures of evaporated HP Al (0.0004") on electroplated chromium (0.0008") on 430 SS compounded at 816°C (1500°F) for 30 minutes in exothermic base gas.
 $\alpha = 0.99$ $\epsilon = 0.59$

a) 1000x

b) 5000x

Figure 6 SEM pictures of 4022 Al (0.0012")/
430 SS compounded at 816°C (1500°F)
for 30 minutes in exothermic base
gas. $\alpha = 0.96$ $\epsilon = 0.67$

a) 1000x

b) 5000x

Figure 7 SEM pictures of 4022 Al (0.0012")/
304 SS compounded at 816°C (1500°F)
for 30 minutes in air.
 $\alpha = 0.89$ $\epsilon = 0.47$

a) 1000x

b) 5000x

Figure 8 SEM pictures of 4022 Al (0.0008")/
270 Ni compounded at 732°C (1350°F)
for 60 minutes in exothermic base
gas. $\alpha = 0.95$ $\epsilon = 0.28$

a) 1000x

b) 5000x

Figure 9 SEM pictures of 1100 Al (0.0008")/
270 Ni compounded at 732°C (1350°F)
for 60 minutes in exothermic base
gas. $\alpha = 0.99$ $\epsilon = 0.33$

a) 1000x

b) 5000x

Figure 10 SEM pictures of 4022 Al (0.0008°)/
201 Ni compounded at 816°C (1500°F)
for 30 minutes in exothermic base
gas. $\alpha = 0.91$ $\epsilon = 0.30$

a) 1000x

b) 5000x

Figure 11 SEM pictures of 4022 Al (0.0008")/
201 Ni compounded at 899°C(1650°F)
for 20 minutes in exothermic base
gas. $\alpha = 0.86$ $\epsilon = 0.30$

a) 1000x

b) 5000x

Figure 12 SEM pictures of 4022 Al (0.0008")/
270 Ni compounded at 677°C(1250°F)
for 15 minutes in exothermic base
as. $\alpha = 0.97$ $\epsilon = 0.29$

a) 1000x

b) 5000x

Figure 13 SEM pictures of 4022 Al (0.0008")/
270 Ni compounded at 621°C (1150°F)
for 15 minutes in exothermic base
gas. $\alpha = 0.81$ $\epsilon = 0.13$

radiation, thus the slowly declining value of α with increasing temperature of the compounding.

When the compounding temperature is reduced to 677°C (1250°F), Figure 12, the surface still has the characteristic appearance, high absorptance and a typical emittance of aluminum-nickel intermetallic compounds. Further reduction in the temperature and time at the temperature results only in partial compounding of the 4022 Al/270 Ni system, Figure 13. The surface is a mixture of intermetallic compound and uncompounded aluminum, and the reduced values of α and ϵ confirm this. The emittance value $\epsilon = 0.13$ for sample compounded at 621°C (1150°F) is apparently the weighted average of the intermetallic compound and metallic aluminum surfaces. The corresponding absorptance $\alpha = 0.81$ is higher than would be expected, but the presence of Al_2O_3 oxide layer might have an effect.

The resolution of the scanning electron microscope (SEM) pictures taken at 1000x and 5000x, Figures 8-12, is not sufficient to give a clear indication of the nature of the apparently porous surface of the aluminum-nickel intermetallic compounds. An effort was made to determine the exact nature of this apparently porous surface and for that purpose the surface of a specimen compounded at 732°C (1350°F) was shadowed by gold to improve the resolution of the SEM. However, at up to 20000x magnification in original size, Figure 14, the surface details uniformly disappeared with increased amount of gold shadowing indicating that Al-Ni compound surface is covered by a rather continuous film of electron transparent material.

An Auger electron spectroscopy was used to determine qualitatively the composition of several intermetallic compound surfaces and all of them showed only aluminum and oxygen as major elements at the surface. In none of the samples was the other component metal of the intermetallic compound, Ni, Fe, or Cr present. Due to the high temperatures and the types of atmospheres used in compounding an Al_2O_3 layer will always

a) 5000x

b) 20000x

Figure 14 SEM pictures of 4022 Al/201 Ni
 surface compounded at 732°C (1350°F)
 for 60 minutes in dissociated ammonia,
 shadowed with Au
 $\alpha = 0.92$ $\epsilon = 0.30$

Figure 15 Depth profile of Auger Electron Spectroscopy peak intensities of Oxygen, Aluminum and Nickel for AlNi surface

be present on the aluminum surface at the beginning of the compound formation. This oxide layer is evidently ductile enough to form at least locally continuous film over the intermetallic compound surface.

The surface of 4022 Al/270 Ni, Figure 8, compounded at 1350°F for 60 min. in exothermic base gas atmosphere was sputtered in the Auger electron spectroscopy to remove the surface layer. The oxygen, aluminum and nickel were continuously scanned. Although the distance scale of the abscissa of Figure 15 is only very approximate, it shows that nearly 200Å thick layer of aluminum oxide covers the intermetallic compound surface. Below the initial oxide layer, the relative values of Al, O and Ni change only gradually because the surface is exceedingly uneven and, as an example, layers of aluminum oxide can penetrate deep into the structure.

The results of Auger electron spectroscopy could not be readily used to determine the composition of the intermetallic compound below the oxide layer. X-ray microprobe was used to determine the surface composition of the aluminum-nickel intermetallic compound, which was shown to be AlNi. AlNi is a most stable compound in this binary system with melting point of 1638°C (2980°F) making these surfaces suitable for applications where high operation or stagnation temperatures are expected.

E. DURABILITY TESTING

The evaluation of the intermetallic compounds was divided in two parts. The measurement of α and ϵ was used to categorize and to select the best intermetallic compound systems and process parameters. Durability testing was conducted to evaluate the effect of the environmental conditions, encountered in the flat plate collector enclosure, on the absorptance and emittance of the compound surfaces and on the corrosion characteristics of the surfaces and of the composite metal collector plate. The degradation of the absorption surface and the collector plate can be due; to electrochemical corrosion caused by humidity and air borne pollutants; due to physical changes

caused by the solar irradiation; due to thermal stresses caused by temperature fluctuations or by temperature gradients within the plate; or due to structural changes caused by thermal diffusion.

Because the interest in materials for solar collectors is rather recent and because of the possible interactions of many and unique variables, accelerated testing procedures in simulated environment were not available. Therefore, two different procedures were used to evaluate the durability of the surfaces and the composite metal collector plate materials:

- a) Environmental testing in a flat plate collector enclosure and
- b) Accelerated testing in a cyclic humidity chamber.

Measurements of α and ϵ before and after the exposure were used as performance criteria in both tests. Standardized method of color photography was used to record the changes in the visual appearance of the specimens. As an addition the steady state temperature of selected specimens in the collector enclosure was measured to compare the stagnation temperatures of the various specimens to see if the relative changes in α and ϵ values could be detected.

a) Environmental Testing

Two inch by six inch specimens of material which were manufactured for screening of various intermetallic compounds (Chapter III B) and for optimization of the aluminum nickel intermetallic compounds (Chapter III C), were placed into a flat plate collector enclosure.

Figure 16 shows the schematic cross section of the construction of the collector frame. The overall dimensions of the frame are 63" x 63" x 5" and the module is divided into four quarters approximately 29" square. Three inches of Owens Corning type 703 fiber glass, $K = 0.23$ @ 24°C (75°F), is used as thermal insulation. A single sheet of 1/8" thick, double strength, clear PENVERNON^R glass (solar transmittance ~ 85%)

R PENVERNON registered trade mark PPG

Figure 16 Schematic cross section of collector frame for the durability evaluation of intermetallic compound surfaces.

is used as a cover plate. The air gap between the glass and the samples is 5/8 inches. The glass is sealed with a U-shaped rubber and all corners are additionally caulked with silicon rubber. The whole collector module is secured to a steel frame and it can be tilted manually to be normal to the sun at solar noon.

The test frame is on a platform built onto the roof of an unoccupied single family dwelling with one floor, full basement and a gabled roof. The environment at the test site is industrial-rural.

The collector module was oriented to geographical south using the method described by Harrison⁽³¹⁾. The orientation device is permanently attached to the test frame.

An Epply pyranometer (No. 8-48) is used to measure the total incident solar radiation. The pyranometer is also attached to the frame of the test module and, therefore, the plane of the pyranometer is oriented perpendicular to the incident solar radiation at solar noon.

Adjacent to the collector is an instrument shelter to measure and record temperature and the relative humidity. A hot wire anemometer is used to measure wind velocity. Strip chart recorders are used to record the solar insolation, air temperature, relative humidity and the specimen temperatures. The level of atmospheric pollutants was not measured.

The temperature of selected samples is measured with 24 AWG copper-constantan thermocouples which is soldered to the back of the 2" x 6" samples.

The test specimens of the various intermetallic compound surfaces were retrieved after 8 months. Table VII shows the initial values of α and ϵ and the values after exposure. It is immediately apparent that the absorptance values of the aluminum-low carbon steel pairs have decreased significantly, and the same is true for the thin 4022 Al on 430 SS and 4022 Al on 304 SS. But more significant and rather surprising is the fact that the absorptance of the aluminum-nickel inter-

			Air		Exothermic-Base Atmosphere	
			A	B	A	B
4022 Al/LCS	0.0004	α	0.99	0.74	0.95	0.72
		ϵ	0.55	0.54	0.56	0.54
	0.0008	α	0.99	-	0.94	0.76
		ϵ	0.65	-	0.58	0.58
	0.0012	α	0.93	0.82	0.90	0.79
		ϵ	0.53	0.66	0.67	0.61
1100 Al/LCS	0.0008	α	0.93	0.84	0.93	0.75
		ϵ	0.54	0.57	0.72	0.70
4022 Al/430 SS	0.0004	α	0.98	0.82	0.82	0.76
		ϵ	0.51	0.53	0.58	0.61
	0.0012	α	0.90	0.99	0.96	0.99
		ϵ	0.52	0.54	0.67	0.69
4022 Al/201 Ni	0.0004	α	0.64	0.99	0.87	0.99
		ϵ	0.32	0.32	0.26	0.28
	0.0008	α	0.91	0.99	0.91	-
		ϵ	0.30	0.36	0.29	-
	0.0012	α	0.94	0.99	0.90	0.99
		ϵ	0.30	0.34	0.33	0.38
4022 Al/304 SS	0.0012	α	0.89	0.62	0.90	0.65
		ϵ	0.47	0.42	0.66	0.65

Table VII α and ϵ of Various Intermetallic Compound Surfaces after 8 Months Exposure in Flat Plate Collector

A - Original Data

B - Eight Month Environmental Data

Compounding Temp			732°C (1350°F)				816°C (1500°F)				899°C (1650 °F)	
Compounding Time			15 min		60 min		7.5 min		30 min		5 min	
Atm.	Al Thick.		A	B	A	B	A	B	A	B	A	B
Air	0.0008	α ϵ	0.93 0.32	- -	0.86 0.28	0.99 0.31	0.85 0.32	- -	0.86 0.35	- -	0.79 0.36	- -
	0.0012	α ϵ	0.93 0.26	0.99 0.32	0.96 0.32	0.99 0.33	0.96 0.27	0.99 0.37	0.78 0.32	- -	0.80 0.32	- -
Cracked City	0.0008	α ϵ	0.92 0.31	0.99 0.33	0.99 0.27	0.99 0.33	0.89 0.27	0.99 0.30	0.91 0.30	0.99 0.29	0.90 0.35	- -
	0.0012	α ϵ	0.96 0.32	0.99 0.26	0.90 0.40	- -	0.90 0.30	0.99 0.31	0.83 0.37	- -	0.86 0.27	0.99 0.32
Cracked Ammonia	0.0008	α ϵ	0.94 0.27	0.99 0.31	0.92 0.30	0.99 0.41	0.87 0.27	0.99 0.30	0.85 0.29	- -	0.84 0.27	0.95 0.29
	0.0012	α ϵ	0.89 0.27	0.99 0.32	0.86 0.33	- -	0.82 0.31	- -	0.81 0.31	- -	0.78 0.33	- -

Table VIII α and ϵ of Aluminum-Nickel Intermetallic
Compound Surface After 5 Months Exposure
in Flat Plate Collector
A - Original Data; B - Five Month Environmental Data

metallic compound surfaces has increased significantly. The emittance values of all of the samples have remained practically the same.

Table VIII summarizes the original and remeasured values of α and ϵ of aluminum-nickel intermetallic compounds which were subjected to the environmental testing for 5 months. At the time of the expiration of this grant the testing data was available only for the samples from the first optimization matrix. Again a significant increase in the absorptance can be observed in the cases where the original values were low. Although some specimens show an increase in the infrared emittance the changes are less consistent and a reduction in the emittance values is observed in some cases.

The time of exposure for both sets of samples is too short to establish the durability of the various intermetallic compounds. Obviously the intermetallic compounds in which iron is one of the component metals do not possess the necessary durability in collectors where moisture is present. In the case of aluminum-nickel intermetallic compounds, it is necessary to show that the solar absorptance and the infrared emittance will stabilize on an acceptable level, and the testing of the samples is continued.

b) Accelerated Testing

A cyclic humidity test described by A.J. Opinsky et al⁽³²⁾, has been used for the accelerated corrosion testing. The method was modified, by eliminating the dipping of the specimens into a dilute chloride-acid solution after each 24 hour period, because such a dipping simulates conditions which are completely unrelated to the conditions existing in a flat plate collector. The testing is done at room temperature and the relative humidity is cycled between 10-20% and 100% every eight hours. Test data for aluminum-nickel intermetallic compounds after 3 months exposure is shown in Table IX. Again the increase in the solar absorptance was noticed. Because the con-

Comp Temp	Comp Time Min.	Meas.	4022 Al/270 Ni			1100 Al/270 Ni		
			α	ϵ	α/ϵ	α	ϵ	α/ϵ
621°C (1150°F)	15	A	0.81	0.13	6.2	0.95	0.29	3.3
		B	0.84	0.15	5.6	0.89	0.29	2.9
		C	0.99	0.35	2.8	0.99	0.37	2.3
	60	A	0.90	0.33	2.7	0.95	0.30	3.2
		B	0.86	0.31	2.7	0.97	0.32	3.2
		C	0.93	0.36	2.6	0.99	0.43	2.7
677°C (1250°F)	15	A	0.97	0.29	3.3	0.93	0.30	3.1
		B	-	-	-	-	-	-
		C	0.99	0.29	3.4	0.99	0.37	2.9
	60	A	0.91	0.35	2.6	0.97	0.30	3.2
		B	0.93	0.32	2.6	0.89	0.34	2.6
		C	0.99	0.35	2.8	0.99	0.34	2.7
732°C (1350°F)	15	A	0.94	0.29	3.2	0.97	0.30	3.2
		B	-	-	-	0.91	0.32	2.8
		C	0.99	0.33	3.0	0.99	0.36	3.0
	60	A	0.95	0.28	3.4	0.99	0.33	3.0
		B	-	-	-	0.89	0.37	2.4
		C	0.99	0.31	3.2	0.99	0.33	2.8

Table IX α and ϵ of Aluminum-Nickel Intermetallic Compound Surfaces After 3 Months Exposure In Cyclic Humidity Chamber.

A - Original data

B - Remeasured values of unexposed samples

C - After 3 months exposure

sistent high values of α were rather surprising and unexpected, the absorptance and emittance was retested on samples which were made at the same time with the exposed samples but stored in plastic envelopes in an office. The remeasured values are also shown in Table IX. Although the initial and remeasured α and ϵ of the unexposed samples show some scatter, the increase in α seems to be real.

Samples compounded at lowest temperature show a significant increase in the infrared emittance. Although no investigation was conducted to find out the reason for the increase on the partially compounded samples it is apparently due to the formation of aluminum oxide or aluminum hydroxide. The fully compounded samples show insignificant changes.

Data was available only after 3 months exposure, therefore, it is not possible to determine if and at what level the absorptance and emittance values would stabilize. However, the results support the findings made in the environmental testing.

The accelerated testing of aluminum-nickel and other intermetallic compounds is continued and next withdrawal of samples is planned after 9 months exposure.

F. EFFECT OF IMPREGNATION

Previous report⁽⁷⁾ showed that the infrared emittance of Fe_2Al_5 surface was reduced, without affecting the solar absorptance, by impregnating the porous surface with clear lacquer, such as KRYLON^R. It was assumed that the porous surface acts as a multiple scatter absorption media in which the surface pores act as black body cavities and impregnating or covering the pores with polymers or glasses which are transparent to solar radiation but opaque to infrared radiation, would cause a "greenhouse effect" and thus influence the selectivity of the absorption surface.

To evaluate this rationale, two intermetallic compound surfaces were selected for impregnation studies: one with high α

R - KRYLON registered trade mark of Borden Inc.

and ϵ (Al-Fe) and the other with high α and low ϵ (Al-Ni). Three polymers - PYRE-ML^R, clear TEFLON^R and methyl-methacrylate were selected for impregnation studies. Clear glass enamel was obtained from Mr. Clifford Ruderer of Ferro Corporation, Cleveland, Ohio. The polymers were selected to obtain as wide a selection of optical characteristics as possible, not because they were expected to possess the most desirable characteristics. The impregnation could be done successfully with PYRE-ML, methyl-methacrylate and the glass enamel. Clear TEFLON was used in foil form and it could not be fused successfully to the intermetallic compound surfaces.

The PYRE-ML solution was applied to the surfaces by doctor blading. The polyimide was cured at 250°C in air for one hour. One, two and three mil layer thicknesses were produced.

The enamel frit was applied by dipping the intermetallic compound surface samples into the slurry and smoothing the deposit by wiping. Samples were dried at 120°C in air and fired at 760°C for 4 minutes in air and cooled in air. Approximately 0.001" enamel layers were obtained by this process.

The methyl-methacrylate lacquer was obtained by dissolving ground sheet in acetone. The obtained "lacquer" was applied by doctor blading onto aluminum-nickel intermetallic compound surface and cured at 100°C in air. One and three mil layers were manufactured.

The materials and the α and ϵ values before and after coating are listed in Table X. The results clearly show that thin layers of polymer or glass, which are predominantly transparent to solar radiation, do not significantly alter the solar absorptance of intermetallic compound surfaces. It also appears that thin layers of glass or polymers which are opaque to infrared radiation do not block the IR radiation from the inter-

R - PYRE-ML and TEFLON registered trade marks of DuPont

Material Combination	Surface Coating	α	ϵ	α/ϵ
4022 Al/LCS (A)	Compound	0.99	0.61	1.62
	0.001 Pyre ML	0.99	0.77	1.29
	0.002 Pyre ML	0.93	0.89	1.04
	0.003 Pyre ML	0.97	0.83	1.17
	0.001 Enamel	0.96	0.91	1.35
	0.001 Enamel	0.98	0.78	1.26
4022 Al/201 Ni (B)	Compound only	0.92	0.32	2.88
	0.001 Enamel	0.86	0.52	1.65
4022 Al/201 Ni (C)	Compound only	0.83	0.33	2.52
	0.001 Enamel	0.91	0.51	1.72
4022 Al/270 Ni/LCS (D)	Compound only	0.99	0.30	3.3
	0.001 methyl- 0.002 methacrylate	0.99	0.33	3.0
		0.99	0.33	3.0
	Pore-Free Enamel	0.99	0.31	3.2
	0.002 Enamel	0.99	0.79	1.3

Table X Effect of Impregnation on α and ϵ of Various Intermetallic Compound Surfaces

A - 0.0008" Al 816°C (1500°F) for 30 min. in Diss.

Ammonia

B - 0.0008" Al 899°C (1650°F) for 20 min. in Diss.

Ammonia

C - 0.0012" Al 816°C (1500°F) for 30 min. in Air

D - 0.0008" Al 704°C (1300°F) for 45 min. in Exoth.

Base Gas

metallic surface and cause the "greenhouse effect". At least under conditions prevailing in the emissometer the temperature of the impregnating media very rapidly approaches the temperature of the intermetallic compound absorption surface and subsequently the emittances of the impregnated surfaces are more characteristic to those of the impregnation media. The only exception were the samples coated with the methyl-methacrylate, where only insignificant increase in ϵ value was noted. Reduction of emittance could then be possible in the cases where the initial value of ϵ is high, as an example for some Fe_2Al_5 surfaces, but ϵ is increased in the cases where the initial value is below the infrared emittance of the impregnating media, as an example for AlNi surfaces.

It is expected that the behavior of the impregnated samples is similar at higher temperatures under actual operating conditions of a flat plate solar collector. However, because the impregnation might have a beneficial effect with respect to the atmospheric durability of the intermetallic compound surfaces, specimens of the impregnated surfaces have been incorporated into the environmental testing in a flat plate collector enclosure and into the accelerated testing of the cyclic humidity chamber.

IV COMPOSITE METAL COLLECTOR PLATES

A. SELECTION OF MATERIAL SYSTEMS

The objective of this part of the program was to select a durable and economical material combination for the composite metal collector plate, and to develop a manufacturing process which combined the technique to produce the selective inter-metallic compound absorption surface with the existing tube-in-sheet technology. The development of a low cost collector plate material system has been lagging behind the development of the absorber surfaces. Because aluminum possesses desirable characteristics like high thermal conductivity, low weight, easiness of manufacturing (excluding soldering or brazing) and low cost, it has been extensively used in demonstration projects. However, it is an accepted fact that corrosion problems associated with aluminum, in systems where fluid is used as the heat transfer medium, have not been solved completely. Meticulous care has to be used in designing the collector system to eliminate all metallic contact between the aluminum and other metals like copper, stainless steel, etc., and all heavy metal ions have to be excluded from the aqueous heat transfer fluids to prevent pitting corrosion, or organic heat transfer fluids have to be used ^(5,6). When all these constraints, and the difficulty of joining are considered, the apparent advantages of using aluminum are lost and copper collectors are used or specified increasingly for demonstration projects.

Copper possesses all the technological attributes necessary to make it the most desirable collector plate material. It has high thermal conductance, is easy to manufacture and has good corrosion characteristics which can be improved by alloying. The major drawback of copper is its price, which, although presently relatively low due to the global recession

economy, is very volatile. And even with the recently low cost of \$0.63 per pound (8/10/75 U.S. producer ingot price), the raw material cost of a square foot of .020" thick collector plate is already \$0.60 without any labor or provision for heat transfer fluid channels. Using comparative prices for aluminum and low carbon steel one square foot of 0.020" thick collector plate will cost \$0.12/sq.ft. and \$0.10/sq.ft. respectively.

Low carbon steel is used as collector plate material,⁽³³⁾ however, due to its electrochemical characteristics, the corrosion problems associated with steel are similar to those of aluminum.

It is recognized that copper has substantially higher thermal conductivity than steel. However, if so-called tube-in-sheet method is used or in the cases where the collector plate is not fully supported, structural requirements, rather than thermal conductivity will determine the plate thicknesses. Tube-in-sheet approach is used here as a criteria because it seems to offer the best technology for large scale manufacturing.

To benefit from the high thermal conductance of copper, minimum plate thickness has to be used to reduce the raw material cost, consequently, tubular heat transfer fluid channels have to be soldered, brazed, welded or glued to the collector plate. However, now the material cost of the plate becomes insignificant and the total cost of the complete collector plate is determined by the cost of heat transfer fluid tube per unit length, the cost of manifolding parallel conduits and the cost of joining the tubes into the plate. As an example, the price of 3/8 O.D. copper tubing, with 0.030" wall is \$0.14/linear foot (8/10/75) when purchased in car lot quantities, and it can be assumed that at least two feet of conduit, costing \$0.28, is required per square foot of collector. After adding the labor and material cost of the manifolding and

the joining of the tubes to the plate, this type of structure is not necessarily less expensive than a tube-in-sheet structure, even if it apparently offers a method to make copper collector plates equal in price to low carbon steel plates with equal thermal conductance.

To reduce the raw material cost of the collector plate, Texas Instruments proposed to develop a composite metal tube-in-sheet collector plate in which inexpensive metals would be used as the structural material and copper would be used as the liner in the heat transfer fluid channels and only in quantities which offer sufficient corrosion protection and durability. The following criteria were used to select the materials:

- compatibility with intermetallic compound absorber surface materials
- corrosion resistance to heat transfer fluid and ambient atmosphere
- Suitability for large scale tube-in-sheet manufacturing technology
- material cost and
- availability

To meet the selling price target of \$1.50 to \$2.20 per sq. ft. only inexpensive materials which met all the technical criteria were considered. Table XI lists the cost per sq. ft. of the prime candidate materials for this work at the time of the initiation of the work in November 1973.

ALLOY	DENSITY LB/IN ³	COST PER LB	SQUARE FOOT OF COLLECTOR	
			WEIGHT LBS	METAL VALUE *
COPPER ETP	0.324	\$.77	2.10	\$ 1.62
STAINLESS STEEL 304	0.284	\$.51	1.84	\$.94
STAINLESS STEEL 430	0.284	\$.39	1.84	\$.72
CARBON STEEL 1006AK	0.284	\$.10	1.84	\$.18
ALUMINUM 1100	0.0975	\$.33	0.63	\$.21

* METAL VALUE DOES NOT INCLUDE YIELD LOSSES OR BONDING AND OTHER PROCESSING COSTS.

Table XI
Flat Plate Collector Material
Cost

Because of the high temperatures required to form the inter-metallic compound absorption surfaces and because of other metallurgical restrictions, aluminum was not a desired structural material for the composite metal tube-in-sheet collector plate. Low carbon steel was, therefore used, and stainless steels and copper and copper alloys were evaluated as possible liners for the heat transfer fluid channel. Table XII lists the material combinations which were selected for initial evaluation.

Low Carbon Steel (LCS)/Low Carbon Steel (LCS)
LCS/401 Monel/401 Monel/LCS
LCS/80-20 Cupronickel/80-20 Cupronickel/LCS
LCS/430 SS/430 SS/LCS
LCS/Copper/Copper/LCS

Table XII Material Combinations Evaluated for
Composite Metal Tube-in-Sheet Collector Plate

Each material combination was processed by bonding, rolling, annealing and slitting to 0.040" thick overall by 2" wide x 12"-18" long test samples. The ratios of the 4 layer materials at final gage were 0.015"/0.0015"/0.005"/0.015". Samples were inflated into a straight tube-in-sheet pattern shown in Figure 17.

Figure 17. LCS/Cu/Cu/LCS Tube-in-Sheet
Test Segment

Of the five combinations, only LCS/LCS and LCS/Cu/Cu/LCS material systems could be successfully inflated. For the other either the original bond was too strong, so that the materials could not be separated at the bond interface using gas pressures up to 4000 psi, or the bond was too weak, so that after inflation the materials separated at the bond interface. As a result the LCS/Cu/Cu/LCS material system was selected for the development of the 11" x 16" test collector plates.

B. MANUFACTURING OF 11" x 16" TEST COLLECTOR PLATES

The purpose of the small test collector plates was to provide information to:

- evaluate the durability of intermetallic compound absorption surfaces in actual flat plate environment
- evaluate the durability of composite metal collector plates
- determine the efficiency of collector plates with intermetallic compound absorption surfaces and
- provide information for the design of the full size composite metal collector plates.

It was expected that relatively numerous material systems would be evaluated and that long time exposure would be desirable, to provide information on the relative changes of the performance with time rather than on the absolute instantaneous performance. Therefore, approximately one square foot collector plate size was selected to keep the size of the testing facilities within a reasonable limit, despite the inaccuracies which would be caused by the edge effects.

Maximum 12 inches wide material was available for small lot bonding, therefore, 11 inch x 16 inch collector plate size was selected.

When the manufacturing of test collector plates was initiated aluminum-nickel intermetallic compound was known to be the best of the evaluated material systems. Therefore, it was selected to be used as the absorption surface.

An existing prebonded three layer material system of 15% extra low phosphorous (XLP) copper/80% low carbon steel (LCS)/5% nickel was used for fabrication of the collector plates. Aluminum alloy 4022 was bonded with two layers of the above material system, Figure 18a, to a 0.040" final thickness giving a combination of 0.001" Al/0.001" Ni/0.0165" LCS/0.003" XLP Cu/0.003 XLP Cu/0.0165" LCS/0.001" Ni, Figure 18b. The aluminum-nickel pair was for the formation of the intermetallic compound absorption surface while the Ni layer on the opposite side had no functional purpose - it was there as a result of a simplified small lot bonding run. The 0.003" thick copper pair would form the tube lining in the tube-in-sheet forming operation.

Because the data generated by the 11" x 16" collectors were to be used for designing the 2' x 4' collector plates, the fluid channel center to center dimensions were selected to most nearly simulate those which would be needed on the larger plates. Temperature gradients could be measured across the plates with greater ease to determine the optimum tube spacing. A corner to corner entry-exit configuration was used to alleviate the problem of obtaining balanced flow in a small pattern and it also offered advantages for manufacturing and installation. A tool was built to inflate the tube pattern shown in Figure 19. A 75 ton press was used to provide the hold down pressure for the dies and inflating of the pattern was done with bottled nitrogen.

To obtain a sufficient fluid channel cross section it was necessary to inflate the channels up to 0.100" height. However, because of the cold work already present in the bonded material, a successful pattern could be achieved only if the tube height did not exceed 0.020". At the higher inflation heights a cracking took place along the edges of the tube. Ultimately, the inflation of the 0.100" high by 0.750" wide channel was accomplished in two steps. First, inflation was done only for

Figure 18. Process Outline for Composite Metal Tube-in-Sheet Collector Plate

1. Aluminum
2. Nickel
3. Low Carbon Steel
4. Copper
5. Intermetallic Compound Absorption Surface

Figure 19 11" x 16" Test Collector Plates
Tube-in-sheet Pattern

the purpose of separating the bond. This first inflation was followed by a heat treatment at 1300°F to 1350°F in exothermic base gas to simultaneously form the intermetallic compound absorption surface and to sinter the copper to copper bond. The plates were subsequently second inflated to a tube height of 0.100".

Compounding heat treatment, unfortunately, exposed the potentially serious problem of blistering at the copper/copper interface, Figure 20. The blistering could not be eliminated by changing the heat treatment temperature and time within the confines set by the requirements of successful compounding of aluminum-nickel system. It was felt that pre-heat treatment after the first inflation at low temperature for a long period of time would eliminate or minimize the gas evolution at the copper to copper interface. To find the proper temperature-time-atmosphere combination for successful tube inflation and compounding the conditions listed in Table XIII were evaluated. The bonded plates were first inflated to 0.015" - 0.020" high x 0.700" wide pattern. First inflation after the low temperature heat treatment was not possible.

As can be seen from the results in Table XIII, three evaluation criteria had to be used to determine the best time-temperature combinations.

Low temperature pre-treatment, even for long periods of time, is not sufficient to permit second inflation to the final height of 0.100" prior to the compounding heat treatment. Blistering at the copper to copper interface was eliminated when long temperature heat treatment times were 16 hours or longer. However, the preheat-treatments also delayed the onset of compounding, so that complete compounding was obtained only after 45 minutes at 705°C (1300°F).

Figure 20 Blistering of 11" x 16" test collector plate.

Pre Heat Treatment \ Compounding Heat Treatment	None	650°C(1200°F) 22 min EB Gas	650°C(1200°F) 45 min EB Gas	705°C(1300°F) 22 min EB Gas	705(1300°F) 45 min EB Gas
None	1	2	2	2	2
370°C (700°F) 16 hrs in air	1	3	3	3	④
370°C (700°F) 24 hrs in air	1	3	3	3	④
425°C (800°F) 4 hrs in air	1	2	2	2	2
425°C (800°F) 8 hrs in air	1	2	2	2	2
425°C (800°F) 16 hrs in air	1	3	3	3	④
480°C (900°F) 4 hrs in air	1	2	2	2	2
480°C (900°F) 8 hrs in air	1	2	2	2	2

Table XIII Evaluation Matrix to Eliminate Blistering at Cu/Cu Interface

Code: 1. Plate cracked at second inflation
 2. Blisters at Cu/Cu interface
 3. No blisters, incomplete compounding
 4. No blisters, compounding completed.

The pre heat-treatment for 16 hours at 425°C (800°F) and compounding for 45 min. at 705°C (1300°F) gave the best results for reducing blistering at the Cu/Cu interface; only some small blisters were evident along one edge. The results also indicate that with further studies, a process could be developed which would eliminate blistering altogether.

The following process was established for the 11" x 16" test collectors:

- First-inflate tube pattern to 0.015" height x 0.700" width
- Pre heat-treat for 16 hours at 800°F in inert gas
- Compound for 45 minutes at 1300°F in Cracked city
- Second-inflate tube pattern to 0.100" height to 0.705" width

This process resulted in a well compounded surface and only occasional blistering along one edge of the plate.

In evaluating the inflated and compounded 11" x 16" test collector plates, a striated surface structure was observed on the intermetallic compound indicating some type of periodic inhomogeneity. This type of surface appearance was known to be caused in other composite metals by rupture of layers below a thin overlay. Metallographic cross section of the surface of the collector plate before compounding, Figure 21, shows that the nickel layer adjacent to the aluminum had necked and ruptured during the rolling processes. The underlying reason for this behavior, although not completely explained, is the difference in the work hardening characteristics of the aluminum and nickel and in the process parameters⁽³⁴⁾. It is not caused by the properties of the nickel, because the nickel at the back surface does not show any cracking, although it has the same process history as the nickel between the aluminum and the low carbon steel.

This discontinuity of the nickel has an adverse effect, because during the compounding heat treatment both AlNi and Fe₂Al₅ intermetallic compounds are formed, Figure 22, and previous tests have shown that aluminum-iron intermetallic

Figure 21 Photomicrograph (200x) of Al/Ni/LCS composite showing the rupture of the Ni layer.

Figure 22 Photomicrograph (200x) of compounded Al/Ni/LCS composite showing alternate formation of AlNi and Fe_2Al_5 intermetallic compounds.

compounds have substantially higher infrared emittance. Consequently, the emittance of the mixed AlNi-Fe₂Al₅ surface would be expected to have an inferior emittance when compared to pure AlNi intermetallic compound surface.

Although it was not possible to form the most desired intermetallic compound surface eight 11" x 16" collector plates were manufactured for installation in the test facility to obtain information about the durability of the materials in a flat plate collector environment.

Porosity in the form of pinholes or cracks constitutes the most critical type of defect in the copper interliner of the transfer fluid channel. To obtain early information about the continuity of the copper interliner several collector plates were cut open. Several pinholes in which the copper layer had been torn loose from one surface and transferred to the opposite side, were found along the length of the tube, Figures 23 and 24.

This type of defect is formed when, in localized areas, the bond between the copper and the low carbon steel is substantially weaker than the copper to copper bond. This condition if not corrected would cause a very rapid pinhole corrosion through the low carbon steel structural plate. Several methods can be used to eliminate the pinholes. The most obvious way is to improve the copper to steel bond, but increasing the copper thickness or use of copper alloys with better mechanical strength, or using separator layers at the copper to copper interface, would also reduce the formation of pin holes caused by tearing.

Figure 23 Pinhole in copper lining

Figure 24 Cross section of pinhole
formed by tearing of copper

C. DURABILITY TESTING

1. Testing Facilities

Flat plate collector enclosure and circulating system was built to test up to sixteen 11" x 16" test collector plates simultaneously. The National Bureau of Standards draft of the proposed standard - "Method of Testing for rating Solar Collector based on Thermal Performance" dated November 1, 1974 was used as a guideline in designing the collector system. The construction of the flat plate collector enclosure is similar to that used for the testing of the dry intermetallic compound surface samples, Figure 16, and the collectors are adjacent to each other. Manual adjustment is used to orient the plane of the circulating collector module to be perpendicular to the sun at solar noon.

Figure 25 shows the schematic layout and the significant technical data of the circulating system. Although the collector enclosure was designed to accept initially only sixteen 11" x 16" collector plates, the circulating system is sufficiently large to handle up to 80 sq. ft. total collector area.

Two constant temperature baths supply heat transfer fluid at controlled temperatures to the collectors. The inlet temperature for all collectors is kept uniform and constant. The temperature and flow rate of the transfer fluid exiting from each collector is measured and subsequently the fluid passes through a heat exchanger to dump excess heat before it is returned to the constant temperature baths. Because of the locality of the testing facility, water-ethylene glycol mixture will be used as a circulating fluid to permit year around operation. The properties, especially the viscosity and density of this cooling fluid mixture are influenced by the temperature, therefore, the flow from each flow-meter can be directed into a weighing container so that each instrument can be calibrated frequently.

Figure 25 Schematic lay-out of the circulating system for testing experimental collector plates.

2. Testing and Test Results

Five 11" x 16" composite metal collector plates with intermetallic compound absorption surface and one 48" long Corning evacuated tubular base line collector also with intermetallic compound collector plate were installed for performance and durability testing. The inlet and exit temperature and flow rate of each collector are monitored. In addition a matrix of 9 thermocouples was soldered into the back side of one 11" x 16" collector plate to measure the temperature distribution for the purpose of obtaining design data for full size collector plates.

Due to the delays caused by the previously described difficulties in the manufacturing of the collector plates, the testing started very late in the program and only a very limited amount of performance data was collected. All the data was collected during the calibration of the instrumentation and the circulation system, therefore, the performance was measured only with the inlet temperature at or near the room temperature. In these initial tests water was used as the circulating fluid. Obviously the test period was much too short to obtain any durability data, but because of the pinholes, which were observed in the copper liner, it is expected that early failure of the collector plate will take place due to pitting corrosion.

The instantaneous efficiency of one of the 11" x 16" collector plate in the test collector with one cover glass is shown in Table XIV for one four-hour test period. The efficiency η is calculated using equation

$$\eta = \frac{(T_{f,e} - T_{f,i}) \cdot \dot{m} \cdot C_p}{H}$$

In which the

$T_{f,e}$ = temperature of the fluid leaving the collector

$T_{f,i}$ = temperature of the fluid entering the collector

$\dot{m}$ = mass flow rate of the transfer fluid

Time EDST	T _a °C (°F)	T _{f,i} °C (°F)	T _{f,e} °C (°F)	H BTU/sq ft/hr	η
10:00 AM	13 (55)	31 (88)	53 (127)	205	0.69
10:30	14 (57)	33 (91)	57 (135)	224	0.69
11:00	15 (59)	34 (93)	61 (142)	245	0.71
11:30	15.6 (60)	35 (95)	63 (145)	260	0.69
12:00	16 (61)	36 (97)	66 (151)	268	0.72
12:30 PM	17 (63)	37 (99)	67 (153)	274	0.70
1:00	18 (64)	37 (99)	68 (154)	275	0.72
1:30	18 (64)	37 (99)	70 (158)	272	0.78
2:00	18 (64)	38 (100)	69 (156)	260	0.76

Table XIV Performance of 11" x 16" test collector plate

Testing date: September 10, 1975

Collector area: 1.195 Sq.Ft.

Transfer fluid: Water $\dot{m} = 32$ cc/min

Figure 26 Efficiency vs $((T_{f,e} + T_{f,i})/2 - T_a)/H$ of 11" x 16" experimental collector.

C_p = specific heat of the transfer fluid

H = total solar energy flux incident upon the plane
of the collector

In evaluating results it should be remembered that the purpose of the collector testing was to obtain durability data of collector plates rather than to evaluate and develop collectors for maximum performance. Therefore, the relative changes in performance as a function of exposure time are more important than the relative performance of the various collector plates or collectors at a particular time. The duration of the test has been much too short to give any useful data in this respect. But even so it is gratifying to note that the instantaneous efficiencies of $\eta \sim 0.68-0.78$ for the flat plate collector compare favorably with published data of other types of collector plates.

In Figure 26 the efficiencies are shown as a function of $((T_{f,e} + F_{f,i})/2 - T_a)/H$, in which T_a is the ambient temperature. Because the temperature of the water entering the collector was varied very little during the test period. The efficiency was determined for very narrow range of operation conditions. Therefore, it is not possible to determine the slope of the efficiency curve nor the zero efficiency intercept point.

A 48" long Corning evacuated tubular base line collector with intermetallic compound absorption surface was tested during the same period. The collector consisted of a flat-plate absorber housed in a four inches diameter evacuated glass tube. This particular collector plate was 48" long made of 0.015 thick low carbon steel with AlNi intermetallic compound absorption surface, $\alpha = 0.92-0.95$, $\epsilon = 0.30-0.35$, Figure 27. 0.250 outside diameter by 0.030" wall copper tubing heat transfer fluid channel was joined to the back side of the collector plate. The copper tube inlet and outlet are located at one end of the glass tube to allow for thermal expansion and to provide ease in manifold-
ing. The back side of the steel collector plate was cleaned

with #600 emery paper to reduce the infrared emittance. Measured ϵ_{IR} was 0.1-0.2, unfortunately the solar absorptance was not measured.

The collector was mounted horizontally on the front of the lower portion of the test collector enclosure, Figure 27. For the same test period, which was used for the 11" x 16" test collector plates, efficiencies from 0.82 to 0.91 were obtained for the 48" long Corning evacuated tubular base line collector with the AlNi intermetallic compound absorption surface. The efficiency calculation is based on the collector plate area not on the outside diameter of the tube. Even so, these efficiencies are 0.1 to 0.15 higher than calculations based on the measured α and ϵ values, indicate. This discrepancy is thought to be due to the mounting of the tubular collector above the polyethylene sheet covered Corning-Owens #703 fibre glass insulation, which would be expected to reflect some of the solar radiation to the back side of the collector plate.

Figure 27. Schematic cross section of 48" long Corning evacuated tubular base line collector with AlNi intermetallic compound absorption surface. Mounting for test.

V DISCUSSIONS AND CONCLUSIONS

The development of an intermetallic compound solar absorption surface has shown that suitable surface morphology can be obtained by compounding two commercially available wrought metals or alloys in situ. The process of forming intermetallic compound surfaces is well known and extensively used for the manufacturing of radio tube anodes, in which these surfaces are used as thermally stable emitters. This work, supported by ERDA Contract E(11-1)-2600, has shown that the surface morphology of these intermetallic compounds, formed in situ, is sensitive to the basic material combination, starting geometry, and the conditions of the compounding heat treatment.

For the solar absorption surfaces, where the selectivity is based on the surface morphology, the homogeneity of the structure is very important. Although mechanically manufactured systems, like meshes, spheres, gratings, etc. can be used to form the required surface morphology, such methods become expensive when the periodicity of the surface has to be in the range of the wave length of solar radiation. Compounding of two specific, intimately bonded metal layers does provide suitable dimensions and homogeneity of structure of an exceptionally high solar absorptance $\alpha \approx 0.95-0.99$ Table III, IV and V. This property can be obtained with wide variety of commercially available and inexpensive materials and the materials and processes are well suited for large scale mass manufacturing.

The second important property of a good solar absorption surface is low infrared emittance. Although $\epsilon \approx 0.3$ was obtained with the AlNi surfaces, this value is still substantially higher than $\epsilon \approx 0.1$ which has been demonstrated with other selective surfaces such as black copper, black nickel and especially black chrome. In the case of intermetallic

compound surfaces where the selectivity is presumably based strictly on the surface morphology, it has not been possible, within the scope of this work to determine the basic requirements which are prerequisite for a low emittance. To obtain the desired selectivity of high absorptance accompanied with low infrared emittance, it is assumed that the morphology must be such that in the scale of the wave length of visible light the surface is very rough but in the scale of the wave length of infrared radiation the surface is smoother. Although significant selectivity was observed it is obvious from Figure 3-13 that the intermetallic compounds are also rough in the 3-30 μ scale. This is clearly apparent for the Fe_2Al_5 and Al-Cr intermetallic compound surfaces Figures 3-5, and these surfaces also exhibited the highest infrared emittances.

Accepting the principle that the intermetallic compound surfaces formed in situ absorb as a multiple scatter media in the visible light region and radiate as "smooth" surfaces in the infrared region, it is to be expected that materials and process conditions could be found which would improve the selectivity from the values obtained in this work. This was already implied by the brief test, in which intermetallic compound surfaces were cleaned ultrasonically, resulting in reduced infrared emittance. The reduction of the emittance is not surprising because the scanning electron microscope and Auger electronspectroscopy work did show an oxide film on the AlNi surface and processes like ultrasonic cleaning, etching, etc. would be expected to influence the absorptance and emittance values.

In general, the project was too limited in scope and short in duration to thoroughly investigate this new family, and concept of manufacturing, of selective surfaces and to make final assessment of the value of the intermetallic

compound surfaces as solar absorbers. Only very few material combinations were investigated, although the investigation covered the most promising areas especially if the cost and the availability of the starting materials is considered. The processing conditions were investigated thoroughly, within practical limits, only for the AlNi surfaces.

The short duration of the project did not permit accumulation of sufficient information about the durability of intermetallic compound surfaces. Early indications are that Fe_2Al_5 does not have sufficient resistance to atmospheric corrosion. The solar absorptance of AlNi surfaces increased during the durability testing, but based on information obtained in the accelerated cyclic humidity testing, the possibility exists that the emittance also might be increased after long exposures in the flat plate collector environment.

An effort to improve the selectivity by coating the intermetallic compound surfaces with polymers or glasses was unsuccessful. Because of technological and economical reasons only very thin layers could be used. The impregnation layers were in intimate contact with the absorption surface and the heat transfer was controlled by conductance through the impregnation layer and by the characteristic emittance of the impregnation layer. Consequently, it is expected that further work in this area would not bring significant improvements and therefore, the only contribution of the impregnation would be in improved durability, but only with substantial sacrifice in selectivity.

Intermetallic compounds, like Fe_2Al_5 and especially AlNi have a high melting point. The use of Fe_2Al_5 in its present successful application as anode surface in radio tubes requires a good thermal stability for long periods of time at temperatures which are estimated to be 400-500°C. In a normal flat plate collector stagnation temperature is not expected to exceed 150-200°C, therefore, the thermal stability of these

surfaces is more than adequate for this application. In evacuated flat plate collectors of the Corning type stagnation temperatures of 250-500°C are conceivable, but even here the thermal stability would be sufficient especially because any concern of failure by oxidation is eliminated due to the vacuum environment. Because of the high melting point and good thermal stability of the intermetallic compound surfaces, they might be considered as viable candidates for focusing collectors.

During the completion of this project additional information has become available on the selective black chrome coating. Because of its properties and apparent thermal stability up to 300°C it is in direct competition with the AlNi surfaces. Although the intermetallic compound surface seems to have higher solar absorptance the emittance $\epsilon \sim 0.1$ of the black chrome is substantially lower. A commercial process does exist for the black chrome and, provided that a good durability is demonstrated in a flat plate collector environment, it has to be considered at this time to be the favored candidate for flat plate collector applications.

Although it was possible to manufacture low carbon steel/copper/copper/low carbon steel tube-in-sheet collector plates, the results were only moderately successful. The development was delayed by the unanticipated difficulty to integrate the compounding heat treatment and the process heat treatments of the composite metal tube-in-sheet collector plate and it was not possible to resolve the critical pinhole problem within the allotted time or resources. As was pointed out earlier pinholes in the copper will cause an early failure of the collector plate, therefore, their elimination is a prerequisite for a successful composite metal collector plate where more noble metal is used as liner for the heat transfer fluid channel.

The cracking of the nickel layer below the aluminum, resulting in a less desirable mixed compound surface can be

avoided with proper selection of material geometry and rolling parameters.

It is expected that the technical difficulties in manufacturing of the composite metal tube-in-sheet collector plate can be overcome, but the solutions, like: a) increasing the thickness of the nickel layer to eliminate the cracking b) increasing the copper thickness, using copper alloys or using separator layers to eliminate the pinhole formation, and c) using extended heat treatments to eliminate blister formation, will increase the manufacturing cost. Therefore, although substantial savings can still be made in the material cost even if the above mentioned corrective actions are taken, the increase in manufacturing cost make it more difficult to see how the target price of \$1.50 to 2.20/sq.ft could be achieved, making the economic outlook of a composite metal collector plate dimmer.

But because the major cost of the flat plate collector plate is in the material cost of the plate and the heat transfer fluid channels rather than in the selective surface, any technological innovation reducing the basic material cost is important. The development work of composite metal tube-in-sheet collector plate can be considered successful because it indicated that, in principle, potentially substantial material savings can be obtained by the use of the composite metal technology, without a sacrifice in technical performance. Therefore, the development of composite metal collector plate should be continued and a thorough economic analysis should be conducted to determine the viability of the principle.

The following conclusions can be drawn from the work completed with the support of ERDA Contract E(11-1)-2600:

- Intermetallic compound surfaces formed in situ offer a technologically viable alternative as absorber surfaces for solar collectors.

- High solar absorptances $\alpha > 0.9$ can be achieved with Al-Fe, Al-Cr and Al-Ni intermetallic compounds.

- Moderate selectivity, $\alpha \geq 0.95$, $\epsilon \sim 0.3$ and $\alpha/\epsilon > 3.0$ can be achieved with Al-Ni intermetallic compounds.
- The broad range of processing conditions, under which $\alpha \geq 0.95$ and $\epsilon \sim 0.3$ is obtained for AlNi intermetallic compound surfaces, make them suitable for mass manufacturing of collector plates.
- Although the AlNi surfaces have shown good stability in flat plate collector environment the 10 months testing time is too short for conclusive assessment of durability.
- Impregnation of porous intermetallic compound surfaces with thin layers of polymers or glasses, which are transparent to solar radiations and opaque to infrared radiation, does not improve selectivity. Because the absorptance of the intermetallic compounds is not reduced by the application of the glass enamels, the impregnation could be used, if necessary, to improve the durability of the intermetallic compound surface, but with a sacrifice in selectivity.
- Of the competitive selective coatings for flat plate collectors, black chrome is in many respects comparable with the AlNi surfaces. However, the black chrome has to be considered at this time to be more favorable technologically and economically because of its lower infrared emittance and because a commercial process is available for its application to varied substrates. The economic advantages of the AlNi intermetallic compound, formed in situ, can be utilized only if the manufacturing processes of the absorption surface can be integrally combined with the manufacturing steps of the collector plate, however, the development work has not yet progressed sufficiently to achieve this.
- Only a limited number of various combinations of composite metal tube-in-sheet collector plates can be manufactured

due to the technological limitations set by the applied process. Low carbon steel/copper composite, in which the low carbon steel is used as the structural material and copper as the heat transfer fluid channel liner is the best evaluated alternative. However, a substantial amount of additional development work is required to eliminate the detrimental pinhole formation in the copper liner.

- The economic outlook is unfavorable at this time for the composite metal tube-in-sheet collector plate with AlNi intermetallic compound absorption surface because of the complex process steps required to make it technologically sound.

VI RECOMMENDATIONS FOR FUTURE WORK

1. Testing of the dry intermetallic compound specimens should be continued both in the collector enclosure and in the cyclic humidity chamber to obtain more conclusive data about the durability of the intermetallic compound absorption surfaces.
2. Testing and evaluation of the existing 11" x 16" composite metal collector plates should be continued to obtain performance and durability data especially for the intermetallic compound surfaces under actual operating conditions, but also to evaluate the performance of the composite metal tube-in-sheet collector plates, even if an early failure is expected due to the pinholes in the copper liner.
3. The development of the intermetallic compound absorption surfaces should be continued to evaluate other families of materials which might offer lower infrared emittance without substantial sacrifice in the solar absorptance.
4. Intermetallic compound surfaces especially AlNi should be evaluated for their suitability in the focussing collectors where high operation and stagnation temperatures are expected.
5. Careful economical analysis with emphasis in the future raw material costs should be conducted to assess the value of composite metal collector plates. Although the obtained results were less than satisfactory, the potential benefit in reducing the material cost of the collector plate is sufficient to warrant further study.
6. Provided that the economic outlook for the composite metal collector plate is promising, further work should be conducted to find out if the technical difficulties, especially the pinholing, can be resolved within the boundaries set by the economic requirements.

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IX APPENDIXES

APPENDIX A MEASURING METHODS OF α AND ϵ

Engineering & Automation Services
Mechanical Engineering Technology
Memorandum No. 74-50-016

3 October 1974

TO: Ron Sabol

FROM: Sam Rea

SUBJECT: Characterization of Intermetallic Surfaces

MEASUREMENT TECHNIQUES

Emittance

Emittance was measured with a Lion Research Corporation Model 25B Emissometer (Lion is located in Newton, Ma, telephone: (617) 969-4710). This equipment measures the total hemispherical emittance of samples near room temperature using a thermopile radiating to its enclosure which is cooled by a thermoelectric cooler. The thermopile "sees" the sample as well as the cooled enclosure and comes to an equilibrium temperature somewhere between the sample and enclosure temperatures. This equilibrium temperature is proportional to the sample emittance.

The emissometer is calibrated before and during sample testing against known samples (flat black surface and aluminum foil). The emittance values in the preceding table are the average of 4 readings. Accuracy of the unit is estimated at $\pm 5\%$.

Absorptance

The technique used to estimate absorptance is not so straightforward as the emittance measurement. Basically, a calorimetric approach is used in which the temperature response (heating rate) of a sample is measured when the sample is exposed to a solar radiation flux. The solar flux is supplied by an Aerospace Controls Solar Simulator adjusted to supply an incident flux of about 0.1 W.cm^2 . This solar flux corresponds approximately to that of the United States at ground level.

Copper-constantan thermocouples were soldered to the backs of the samples. Each sample was then placed under the shuttered simulator. The shutter was opened and the resultant temperature rise of the sample was plotted with a Hewlett-Packard Model 7000A X-Y Recorder. The signals from the thermocouples were referenced against the ice point by feeding them through an Acromag Incorporated Model 325 Thermocouple Reference. The output trace on the recorder in millivolts could then be converted easily to temperature.

Each sample was tested as-received and was then painted on the coated side with Nextel Black Velvet Coating No. 101-C10 manufactured by the Reflective Products Division of 3M. After painting, the samples were again exposed to the solar flux and the temperature response measured. The ratio of the temperature response, dT/dt , before painting to that after painting multiplied by the paint absorptance (assumed 0.99) gives the apparent solar absorptance of the samples.

The attached figure shows the thermocouple response for sample 1-K-04-A. The dashed lines are the eyeballed temperature slopes at $t = 0$. This particular sample exhibited a rather low absorptance as evidenced by the large variation in slopes. Typical heating rates of the samples were in the 0.3 to 0.4 C/sec range.

The absolute accuracy of this absorptance measuring technique is difficult to determine. The thermocouple measures the back side temperature so the surface exposed to solar energy is somewhat hotter than the thermocouple indicates. Thin samples will minimize this error. Also, the presence of the black paint introduces a thermal resistance which will slow the response of the back side. Care was exercised to minimize the paint thickness but, nevertheless, an error is present and the sign of the error is such that the true absorptance value is somewhat lower than that reported. Since all the samples were treated alike, the relative values of absorptance reported should be valid although a variance of 0.01 - 0.03 in the reported values is not believed significant.

DISCUSSION

The Lion Emissometer is responsive primarily in the 3-30 micron spectral region. A surface at room temperature will have 89% of its radiated energy in this spectral region and at 327 C (600 K) 94% of its emitted energy will be in this region. Since the measured absorptances are based on the solar spectrum the net result is that the α/ϵ values should accurately reflect solar collector performance assuming no significant surface

property changes with temperature. In this regard, it appears that the K - series surfaces, C22 Al/201 Ni, offer promise as solar collector materials.

Two samples of B-08-N were tested and α/ϵ varied from 1.4 to 1.7. This seems to indicate that the α/ϵ values are repeatable within ± 0.2 although results based on one sample should not be generalized too widely.

Sam Rea

SR:ed

SAMPEL: 1-K-04-A

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