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## Hypereutectic Heat Storage Alloy Final Report: Silicon Shell Integrity in Molten Al-Si Eutectic

M. R. Bennett  
J. Braunstein

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HYPEREUTECTIC HEAT STORAGE ALLOY

FINAL REPORT: SILICON SHELL INTEGRITY IN MOLTEN Al-Si EUTECTIC

M. R. Bennett  
J. Braunstein

Chemistry Division  
Oak Ridge, TN 37831

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## HYPEREUTECTIC HEAT STORAGE ALLOY

### FINAL REPORT: SILICON SHELL INTEGRITY IN MOLTEN Al-Si EUTECTIC

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#### ABSTRACT

As a part of a program to evaluate the feasibility of using silicon encapsulated spheres of aluminum-silicon eutectic for thermal energy storage at temperatures near 650°C, experiments were done to test the dimensional stability of the interface between silicon and the eutectic to thermal cycling. Cycled samples were sectioned and examined by optical micrography and by electron microscopy (SEM/EDX) techniques. Little or no degradation of the interface was observed at 600°C (eutectic temperature 577°C) while catastrophic degradation occurred at 700°C. At 650°C interpenetration of 0.1-0.2 mm was observed between the silicon and the eutectic alloys, with occasional larger (3-4 mm) intrusions.

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#### 1. INTRODUCTION

This report summarizes results of experiments designed to evaluate the stability of the interface between silicon metal and a eutectic alloy of aluminum and silicon to thermal cycling between temperatures at which the alloy (and the silicon) is solid and temperatures (up to 650°C) at which the molten alloy is in contact with solid silicon.

Mobley and Rapp (1980) have pointed out the potential advantages of metallic alloys as phase change heat storage materials for recovery of industrial waste heat. In particular, they proposed the development of methods to encapsulate aluminum-silicon alloy shot in an integral silicon shell intended to contain the heat storage alloy during repeated cycles of melting and freezing of the eutectic core. Their initial proposal was to form silicon encapsulated shot by cooling a molten aluminum-silicon mixture of hypereutectic, or silicon rich, composition. Hence the designation Hypereutectic Heat Storage (HHS).

The HHS concept may be illustrated with reference to the aluminum-silicon equilibrium phase diagram shown in Fig. 1. The silicon encapsulated shot would have an overall composition (core and shell) as indicated by the line A-B in the phase diagram, somewhat richer in silicon than the eutectic composition. If heated to temperatures above that of point B, a homogeneous liquid solution would result. On cooling the melt, silicon would precipitate as the temperature fell between  $T_B$  and  $T_D$  while the equilibrium composition of the melt within the solid silicon shell changed from  $X_B$  to  $X_D$  along the liquidus line. As the temperature continued to fall, between  $T_D$  and  $T_F$ , additional silicon would precipitate; the composition of liquid would be further depleted in silicon until the composition  $X_{eut}$  was reached at temperature  $T_{eut}$ . Here the melt is saturated with both Si and Al. On further heat removal the eutectic of Si and of Al-rich solid solution will precipitate in the fixed, eutectic, ratio, with no change in composition (or temperature) of the remaining liquid until no more liquid remains. The latent heat evolved in the solidification is the basis of the energy storage. The

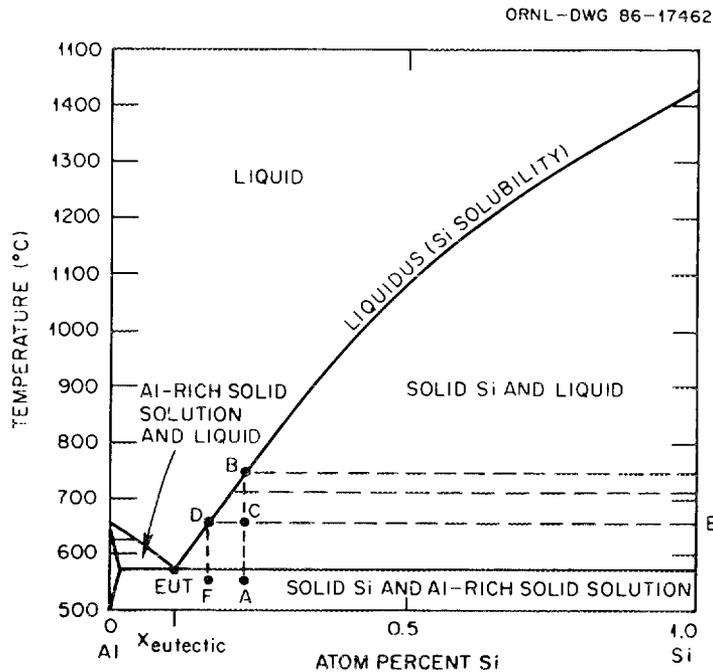


Fig. 1. Al-Si Phase Diagram (adapted, with Permission of McGraw-Hill, from Hansen (1958)).

temperature of the solid phase will then fall as further heat is removed.

If the shot is reheated to  $T_B$ , or above, it will liquefy. If however, as in the intended application, the shot is heated only to some lower temperature,  $T_C$ , some solid silicon will remain, which could form an integral shell surrounding the core of eutectic composition. As the shot is heated from  $T_A$  to  $T_{eut}$  no melting occurs. At  $T_{eut}$  the eutectic core melts, the relative amounts of solid silicon and of liquid eutectic being in the ratio  $(X_A - X_{eut})/(1-X_A)$ . On further heating, the composition will change along the liquidus curve. At  $T_C$  the ratio of solid to liquid will have decreased to  $(X_A - X_D)/(1-X_A)$ , but a solid silicon shell could conceivably remain, under proper conditions, if the temperature remained below  $T_B$ . The phase diagram, however, indicates only the relative amounts of the two phases at equilibrium. It does not indicate their spatial distribution. Therefore, if a mechanism exists for the precipitating silicon to deposit preferentially on one side of the shot, e.g., because of temperature gradients or gravity, the remainder of the shot would be poorer in silicon. If the local composition of part of the shot changed to  $X_D$ , for example, melt-through could occur on the next cycle to  $T_C$  even though the liquidus temperature for the shot as a whole remained  $T_B$ .

If the highest temperature in the cycle were restricted to being just above the eutectic temperature, it would be possible to melt the eutectic core with little change in the average thickness of the silicon shell. In the HHS concept, however, the stored energy density is increased by cycling to temperatures about midway between  $T_{eut}$  and  $T_B$ , the dissolution and redeposition of a portion of the silicon shell contributing, thus, a corresponding latent heat of fusion of silicon.

Mobley and Rapp (1983) proposed, and investigated, a number of means to form integral silicon shells. These means included: (1) controlled quenching of molten spheres of aluminum-silicon alloy, having hypereutectic composition, to produce integral shells of the primary precipitate of Si; (2) aluminothermic reaction coating, in which liquid Al-Si alloy is allowed to react with solid  $SiO_2$  to form a shell of solid  $Al_2O_3$  (alumina) and silicon; (3) packed bed cementation siliconizing, in

which silicon is deposited on the surface of solid alloy shot via vapor transport from a bed of silica and a mixed chloride salt. Although the authors reported that the pack-cementation coating method seemed to show promise, no consistent results were produced that showed the formation of encapsulated spheres which did not crack or leak via exudation of alloy through the Si shell. The rationale behind the present program was that the scientific part of the HHS program with Al-Si eutectic ought to be structured as indicated in Fig. 2.

The first question is: Does an integral shell of Si, produced by whatever means on eutectic Al-Si shot, remain stable with repeated thermal cycling around the eutectic temperature (and of course below the

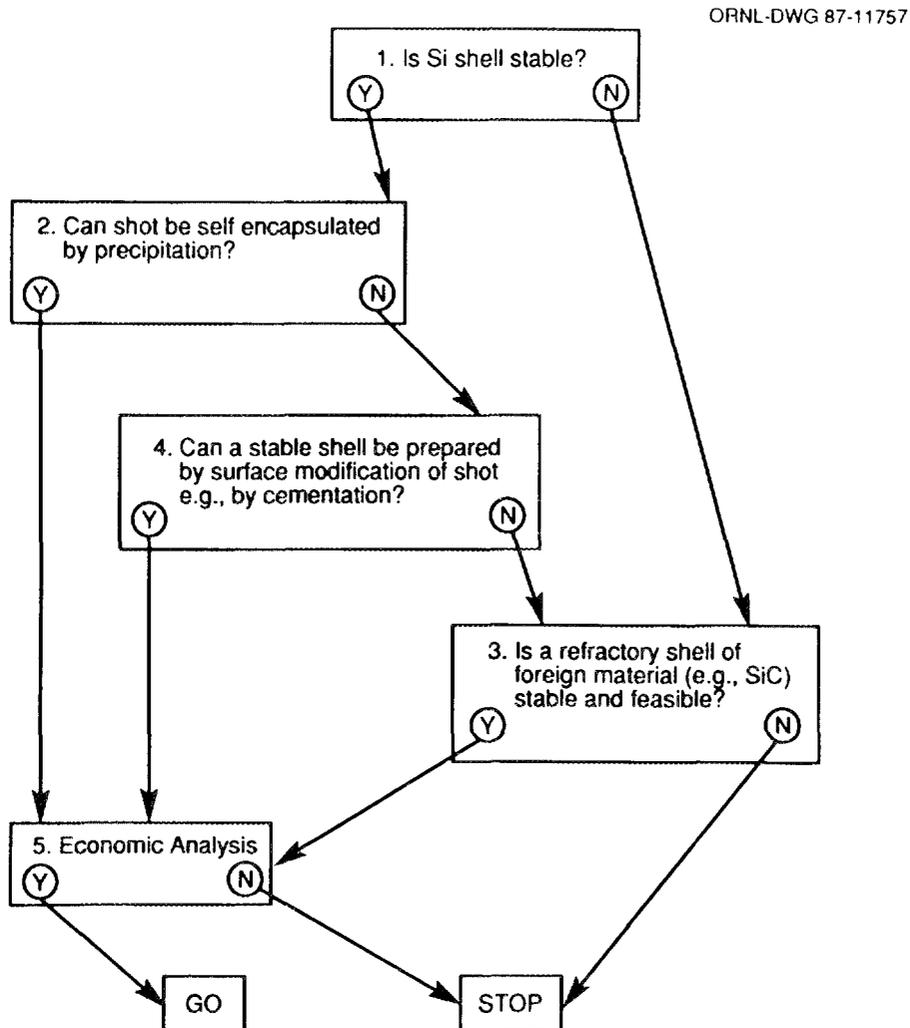


Fig. 2. Steps in HHS Study.

liquidus temperature)? For, even with an integral shell of Si around the Al-Si eutectic, and with a constant temperature, there still is a driving force for recrystallization of Al and Si, and of crystal growth, which could lead to growth of Si crystals inward and of Al crystals outward. This could lead to thinning of the shell, pinholes and leaks, or collapse of the shot. A rough first estimate of the probability of this occurring would require estimates of the diffusion coefficient. For example, Darken and Gurry (1959) consider the case of diffusion into (or out of) variously shaped objects, initially of uniform composition, whose surface is in contact with a source of different composition. The fractional saturation (i.e., the amount that has diffused into the object relative to the amount that will have entered at infinite time) is a function of  $\ell/\sqrt{Dt}$ . For a slab, or sheet, the diffusion process is 93% complete when  $Dt/\ell^2 = 1$ . Diffusion is 36% complete when  $Dt/\ell^2 = 0.1$ , i.e., for a tenfold smaller diffusion coefficient. Thus, the relaxation time for a diffusion layer is  $\tau = \ell^2/D$  where  $\ell$  is the half-thickness of the layer and  $D$  is the diffusion coefficient. For relaxation in, say, 3 h ( $\sim 10^4$  s), of a layer of thickness  $\sim 10^{-2}$  cm, the diffusion coefficient would have to be  $D \approx 10^{-4}/10^4 = 10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>. This value may appear somewhat high for solid state diffusion (in the liquid state  $D \sim 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>; for many ceramic solids,  $D \sim 10^{-12}$  cm<sup>2</sup>s<sup>-1</sup>). However, some alloys, e.g., Li-Al, Li-Si, do have diffusion coefficients as high as  $10^{-8}$  cm<sup>2</sup>s<sup>-1</sup> or higher. A diffusion coefficient of this magnitude could lead to deterioration of the shell on cycling unless there is some constraint to block it, such as a temperature gradient of appropriate direction and magnitude. Mondolfi (1975) reports relatively high diffusion coefficients in solid Al, and high diffusional mobility in the grain boundaries. Ostwald ripening and growth of silicon crystals in solid silicon-aluminum alloys has been observed at temperatures as low as 540°C (Rhines and Aballe, 1986). The diffusion coefficients in the liquid are of course higher still. There was thus the need for an experiment to test stability of a Si shell to repeated cycling before significant effort was devoted to producing an integral shell.

If a silicon-clad eutectic shows promise of stability (e.g., under simulated cycling tests of Si and eutectic), work should proceed on Si-

encapsulation. Possible routes to an integral Si shell include: vapor deposition of Si from the relatively low temperature decomposition of an organosilane, electrodeposition of Si from molten fluorosilicate bath, electrochemical siliciding (diffusion coating) in a molten salt bath (Feigelson, 1980). Cooling of the molten hypereutectic alloy, the first method proposed by Mobley and Rapp, was unsuccessful for producing an integral Si coat, and was dropped by them. This failure may result from the primary precipitation of silicon in large grains that tend to form a slush with the liquid alloy.

If a Si shell is not stable to thermal cycling in contact with Al-Si eutectic, consideration might be given to coating Al-Si spheres with a refractory coating, such as SiC. Other possibilities would include coating with colloidal oxides and then heat treating to prepare shells of aluminosilicate, aluminate, or other refractory oxides.

## 2. OBJECTIVE

As cited in the Introduction, silicon-encapsulated shot of Al-Si eutectic are an attractive possibility for direct contact, phase change, heat storage. The objective of the present work was to answer the key question: "Will an integral silicon shell remain structurally stable during repeated cycling of the shot through the eutectic temperature"? The Al-Si phase diagram indicates that, provided the upper temperature of the cycle is sufficiently lower than the liquidus temperature, the equilibrium ratio of solid silicon to liquid alloy can be high enough so that the average shell thickness could retain the alloy. However, a question of stability arises from several factors. One is the mechanical strength of the shell when subjected to the stress imposed by volume expansion of the alloy on melting. It may be possible to compensate for this by increasing the shell thickness or by the incorporation of voids. A perhaps more fundamental factor is the stability of the silicon shell to redistribution during repeated melting and crystallization, which could lead to disintegration of the shell. A number of mechanisms could provide the driving force for such redistribution. These include:

1. Even a small temperature gradient in a fixed direction across a shot provides a thermodynamic driving force for preferential deposition of Si crystals on the the cool side, leading to thinning of the shell on the hot side.
2. Dendritic growth of primary silicon crystals from supercooled liquid could lead to entrapment of alloy leading to migration of aluminum from the interior of the shot to the surface.
3. The relatively high diffusion coefficient of silicon in aluminum provides a mechanism, even isothermally in the solid state, for interdiffusion of silicon and aluminum, with gradual redistribution of silicon and aluminum.

Thus, although the equilibrium relationships show the possibility of an integral silicon shell, the equilibrium is dynamic, not static;

hence the distribution of the silicon and aluminum phases must be considered.

### 3. APPROACH

As part of a test of the integrity of silicon shells to be used as containers for Al-Si eutectic, experiments were designed to investigate the changes in shape of the interface between silicon and aluminum-silicon eutectic alloy on repeated melting and freezing of the alloy in contact with silicon. The experiments were intended to be independent of methods used to fabricate self-encapsulated shot, and to provide basic information on the inherent stability of such shells to migration via crystal growth and ripening under conditions of temperature cycling. The basis of the experiments was the preparation of polycrystalline shapes such as bars of silicon to be heated in contact with Al-Si eutectic, maintained at temperatures between 550 and 650°C for varying lengths of time, cooled, and then subjected to optical and metallographic examination for dimensional stability. Two sets of conditions were envisaged for the experiment. In the first set, the temperature of the samples is cycled between 550 and 650°C. In the second set, the samples would be held for differing periods of time at various constant temperatures above the eutectic temperature (577°C) before examination. The latter, isothermal, experiments provide an indication of the inherent rate of redistribution of silicon and alloy resulting from the dynamic equilibrium even in the absence of a significant temperature gradient, e.g., via Ostwald ripening. The former, temperature cycling, experiments are more complex in that some of the solid silicon must dissolve in the liquid alloy during the heating part of the cycle, and then recrystallize on the Si surface during the cooling part of the cycle. The temperature cycling conditions simulate more closely the behavior of a silicon shell during cycling of encapsulated shot, although the stresses induced by volume expansion may be smaller than in spherical shot.

For analysis, the cooled samples can be sectioned perpendicular to the plane of the interface, and examined optically and by energy dispersive X-ray fluorescence in a scanning electron microscope (SEM-EDX) (Gabriel, 1985). Electron dot maps of a section give the distribution of silicon and of aluminum, and therefore delineate the interface

between the crystallites and show whether or not degradation has occurred. Of the various methods of surface analysis available for the examination of elemental distributions, SEM/EDX provides the best combination of sensitivity and spatial resolution in the range of distances needed for examining the dimensional stability of the interface (Vallet et al., 1983).

Other means of analysis of the Si-Al/Si interface and of contacting the silicon and eutectic were considered and ruled out for the present study. Neutron activation analysis is not sufficiently localized to show the interface, and furthermore the fast neutron reaction on Si produces Al. In situ optical study of the interface, making use of the transparency of silicon to a region of the infrared spectrum, would require extensive development. Chemical vapor deposition (CVD) formation of amorphous silicon crucibles as containers for the eutectic alloy would be extremely expensive, and feasibility is not assured. Grinding of polycrystalline ingots of Si into crucible shapes with about 1 mm wall thickness was considered not feasible at the present time.

## 4. EXPERIMENTAL

4.1 Apparatus

The equipment consists of a horizontally mounted electric resistance tube furnace of the "clam shell" type, fitted with a silica tube. The silica tube is provided with an inert gas atmosphere for the experiments, and a copper block to help maintain a constant temperature in the region containing the sample. Two thermocouples were used, one for controlling the furnace temperature and the other for measuring the sample temperature. They were connected, respectively, to a proportional temperature controller and to a temperature recorder. Figure 3 illustrates schematically the furnace with samples in place.

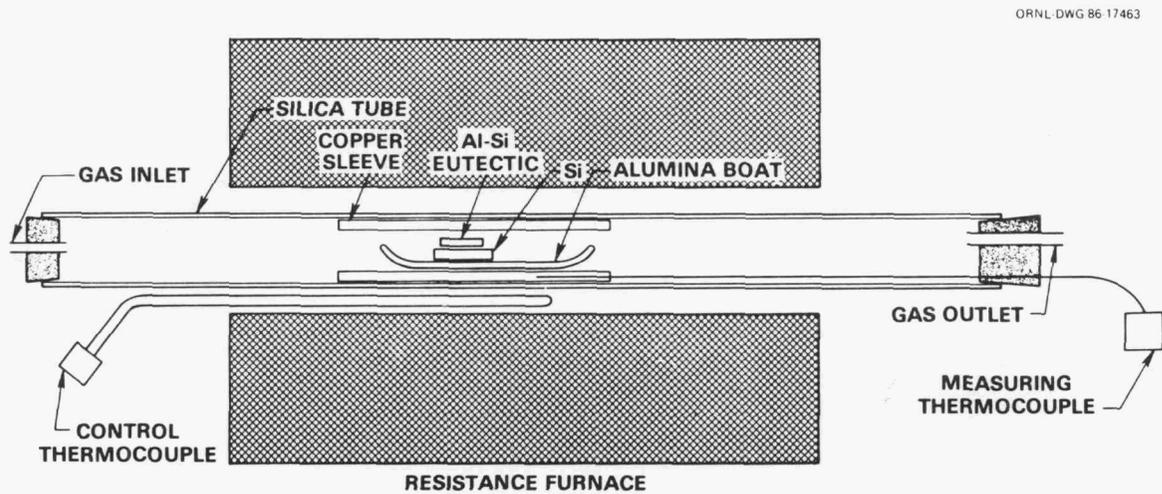


Fig. 3. Furnace Assembly for Preparation of Al-Si Eutectic/Si Couples.

4.2 Materials

The silicon and silicon-aluminum eutectic samples were contained in alumina boats which fit into the copper block in the furnace. Alumina was chosen because it is stable to reduction by silicon metal. Silica would not have been stable to reduction by aluminum under the conditions of the experiment. The inert gas supply was 96% argon — 4% hydrogen to

provide a nonoxidizing atmosphere. Pure aluminum was used for temperature calibration. Pure silicon, polycrystalline, was sawed into rectangular bars about 4 cm long and 0.6 cm wide.\* Aluminum-silicon eutectic was prepared by melting together silicon and aluminum in the eutectic proportion.<sup>†</sup> Figure 4 is a photograph of the silicon and alloy

\*Supplied by R. F. Wood and P. Fleming, Solid State Division.

<sup>†</sup>Prepared by R. Heestand, Metals and Ceramics Division.

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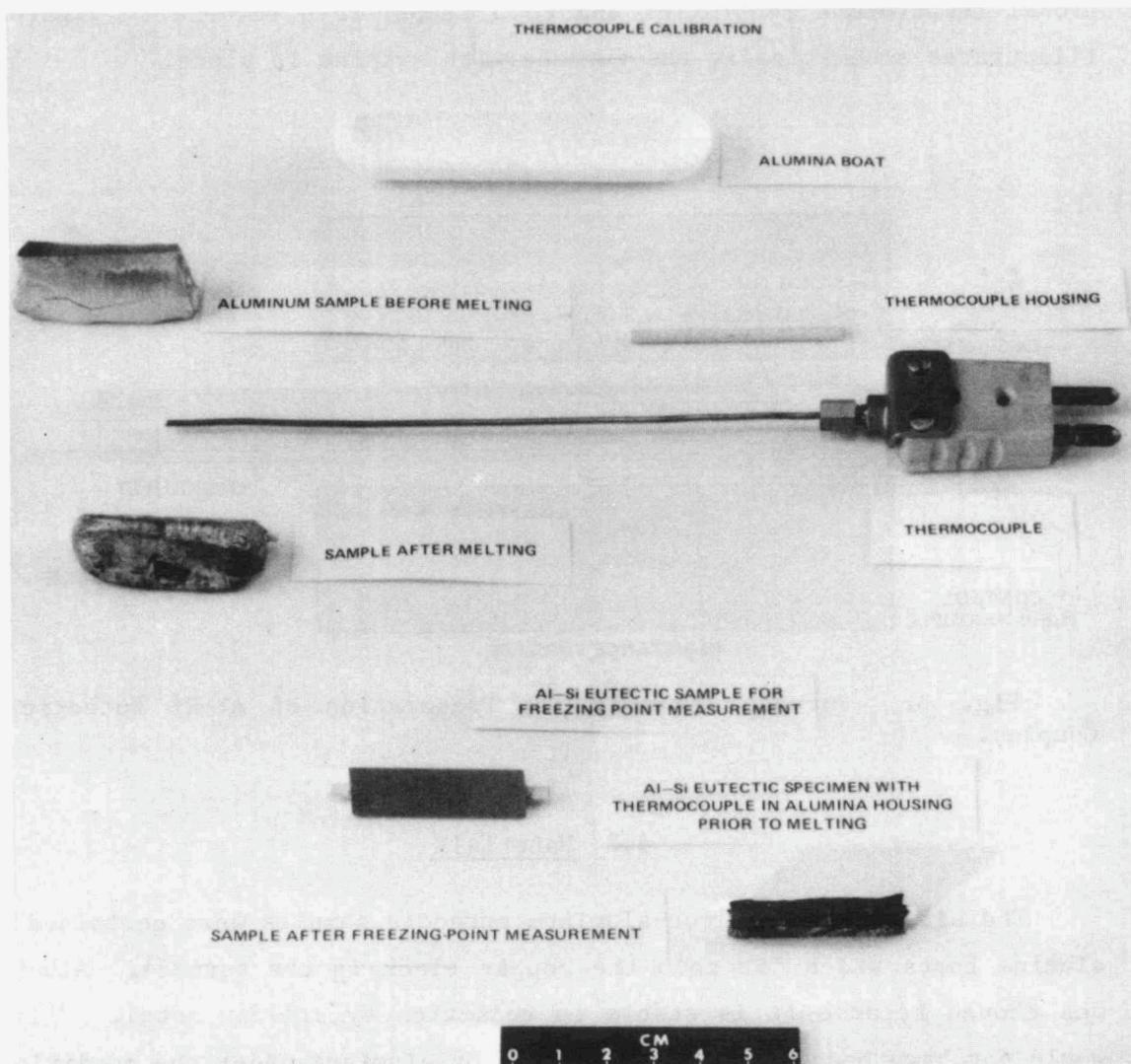


Fig. 4. Thermocouple Calibration.

samples before placing them in the alumina boat for heating in the tube furnace.

#### 4.3 Freezing Point and Composition

Thermal analysis was carried out on samples of pure Al and of the Al/Si eutectic in order to check the consistency of temperature and composition measurements. Advantage was taken of the high surface tension of the liquid metals to provide good thermal contact between a thermocouple and the molten metal. Samples of the Al/Si eutectic and of Al were drilled longitudinally to accommodate a thin alumina tube into which a thermocouple could be inserted. The alumina tube also passed through holes drilled through the ends of the alumina boat. The surface tension of the liquid metal prevents it from spreading throughout its container and leaking out of the holes. Figure 4 shows the components used in the thermocouple calibrations including aluminum and eutectic samples before and after melting. The configuration is similar to that used in the actual experiments. A single thermal arrest was observed as expected for a eutectic, with no evidence of a slope change which would indicate an off-eutectic composition. The freezing point measurements with pure Al and with eutectic served to calibrate the thermocouple and to establish the uncertainty of the temperature measurements.

Results are shown in the following table:

	<u>Freezing Points/°C</u>			
	<u>Al</u>	<u>δT</u>	<u>Al-Si Eutectic</u>	<u>δT</u>
Literature Value	660.4		577	
Measured	664.0	+3.6	575	-2
	660.5	+0.1		

#### 4.4 Preparation of Al-Si Eutectic/Si Couples

Figure 5 is a photograph of silicon and of eutectic samples prior to heating and after melting and refreezing of the eutectic. Also shown are sawed sections of couples which had undergone seven one-hour cycles

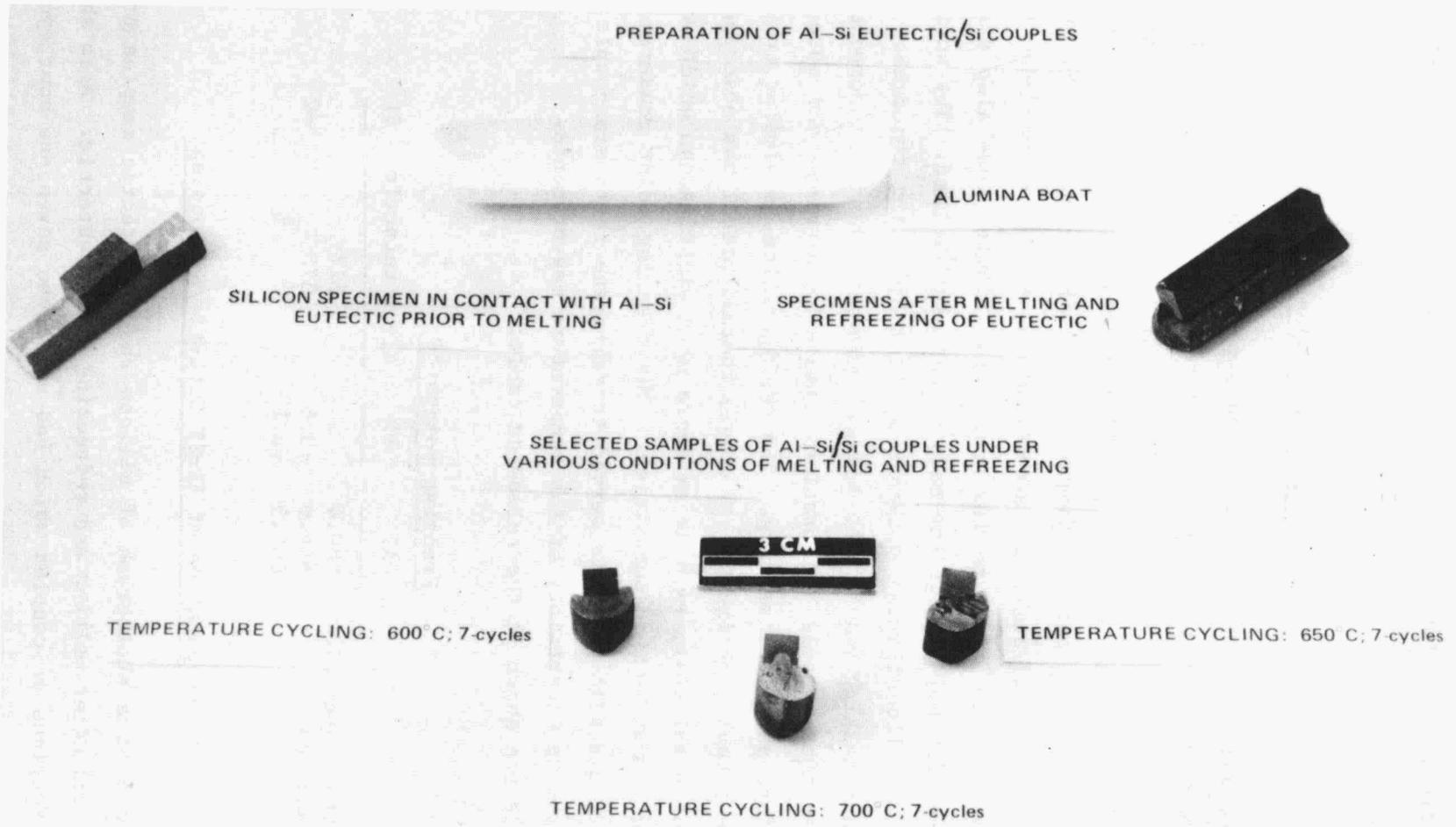


Fig. 5. Silicon and Alloy Samples Prior to Loading in Alumina Boat and Furnace, and Sections of Couples Heated to 600°C, 650°C and 700°C.

between a lower temperature of 550°C (just below the eutectic temperature) and an upper temperature of 600°C, 650°C and 700°C. Although electron microscopy was needed to investigate details of the interface structure, many of the features are observed in the optical photographs of the sections. The interface in the section heated to 600°C shows little evidence of gross degradation. The sample heated to 700°C shows a large intrusion of eutectic into the silicon. The sample heated to 650°C shows some roughness at the interface, but electron microscopy is needed to determine the extent. In the sample shown in Fig. 5, the silicon (which does not melt and therefore retains its sharp corners where not in contact with the alloy) had been placed above the eutectic sample in the alumina boat, so that it floated on the molten alloy, since silicon is less dense than the Si-Al eutectic. The molten alloy did not spread through the alumina boat because of its high surface tension and nonwetting of the alumina. Most subsequent couples were prepared with the alloy sample resting on the silicon sample. No significant difference was observed between results obtained with the two configurations.

#### 4.5 Examination of Interfaces

##### 4.5.1 Photomicrography

Figure 6 is a photomicrograph of sections of three samples heated to 650°C, without cycling, for periods of time between 72 and 240 h. These show the penetration of the eutectic alloy (upper) through the initially planar surface of the silicon bar (lower). This photograph shows many of the features observed. These features include: gross penetration or intrusions of the eutectic into the silicon; roughness of the interface region and cracking of the silicon, presumably due to the stress resulting from the volume change on melting and crystallization of the alloy. Even though the configuration of a slug of alloy in contact with a (initially) planar silicon surface does not subject the sample to the same stresses it would be subjected to when confined in a closed shell, the wetting of the silicon by the liquid alloy during

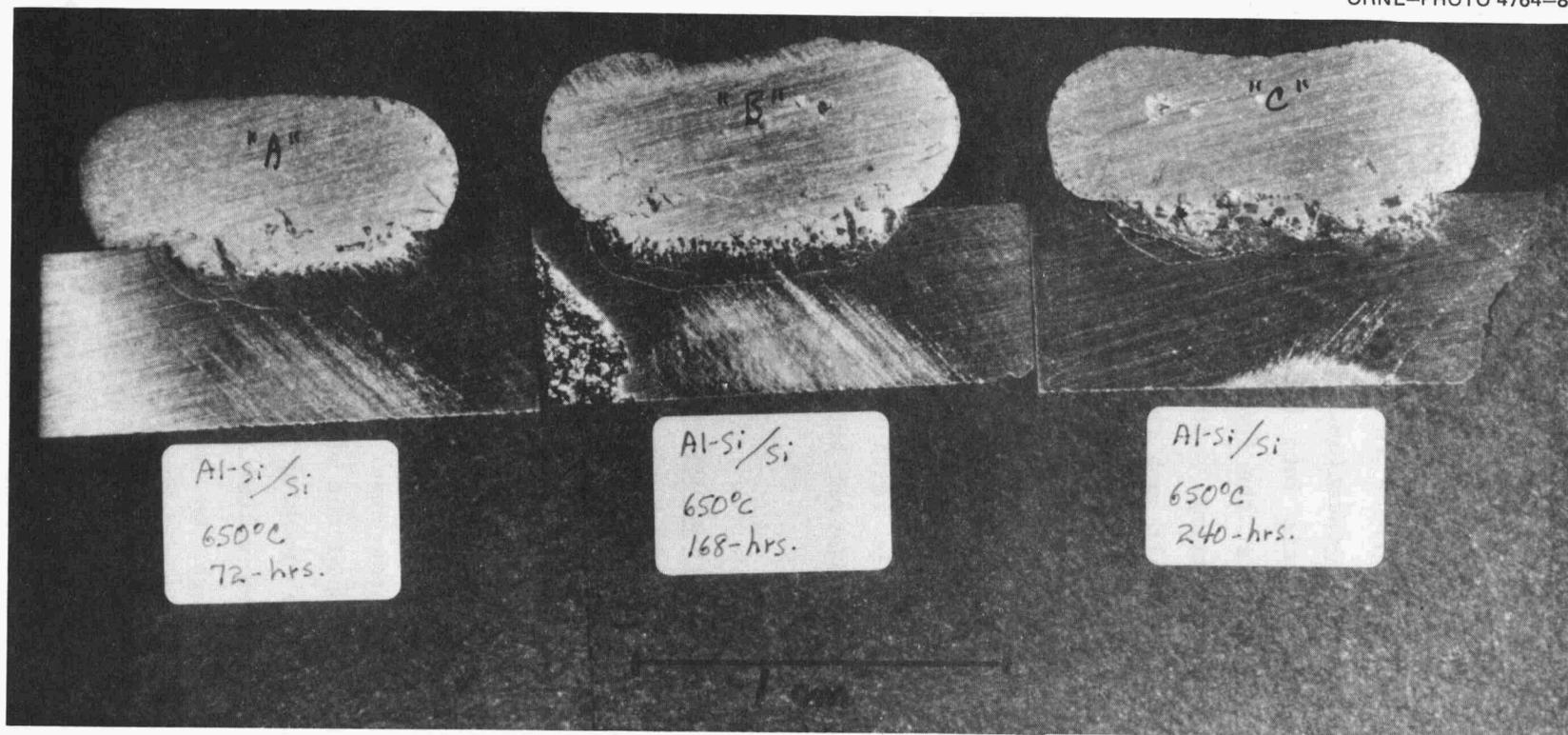


Fig. 6. Photomicrographs of Sections of Couples Heated to 650°C for 72, 168 and 240 h.

crystallization causes stresses sufficient to crack the silicon. Typically, the crack does not occur at the interface but at a distance about 0.5 to 1 mm from the interface.

#### 4.5.2 Electron microscopy

Figures 7 and 8 show electron micrographs, at different magnifications, of two couples heated to 700°C, one for three hours (Fig. 7), and

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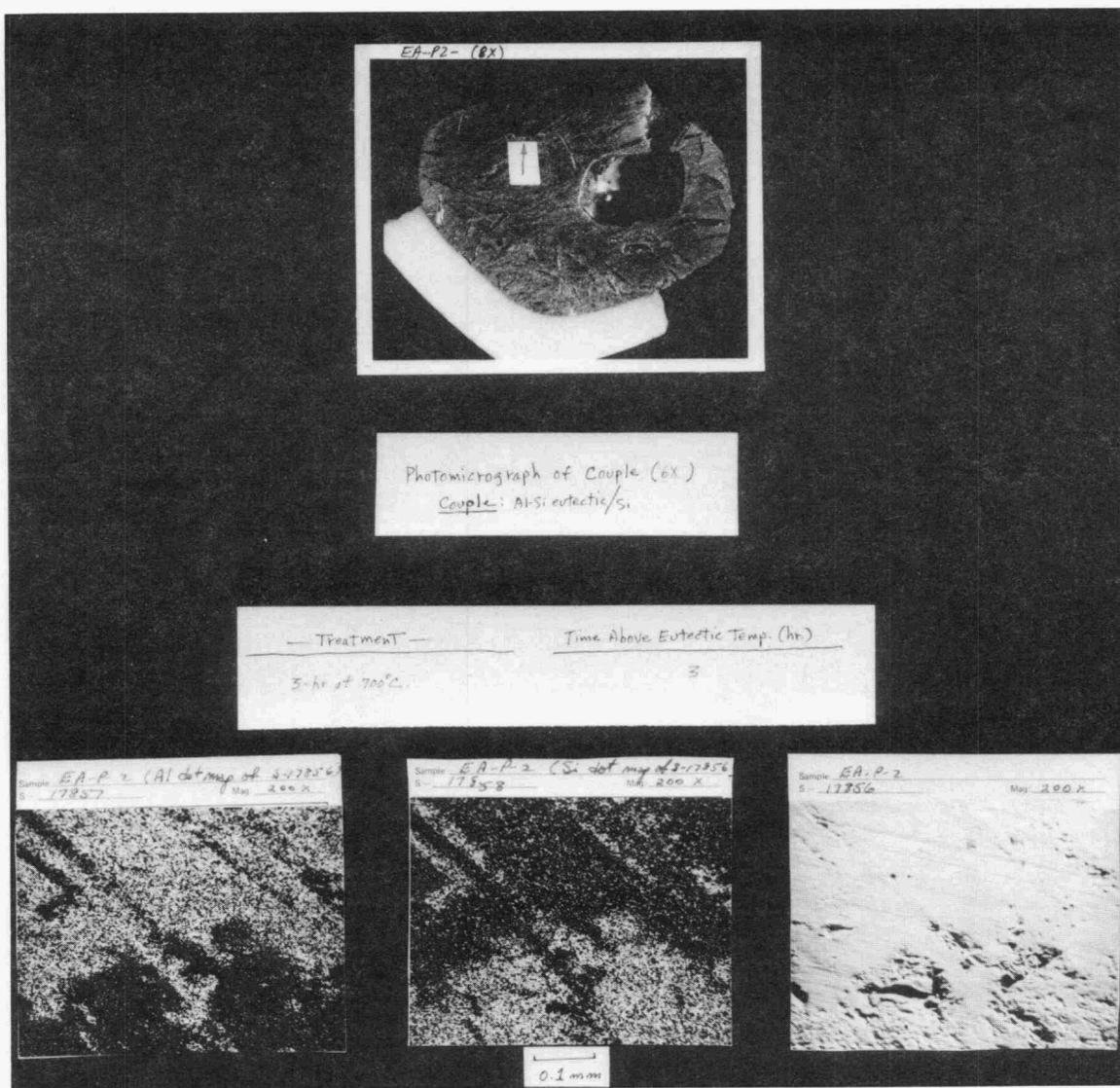


Fig. 7. Photomicrograph and Electron Micrographs of Sections of Couple Heated to 700°C for 3 h.

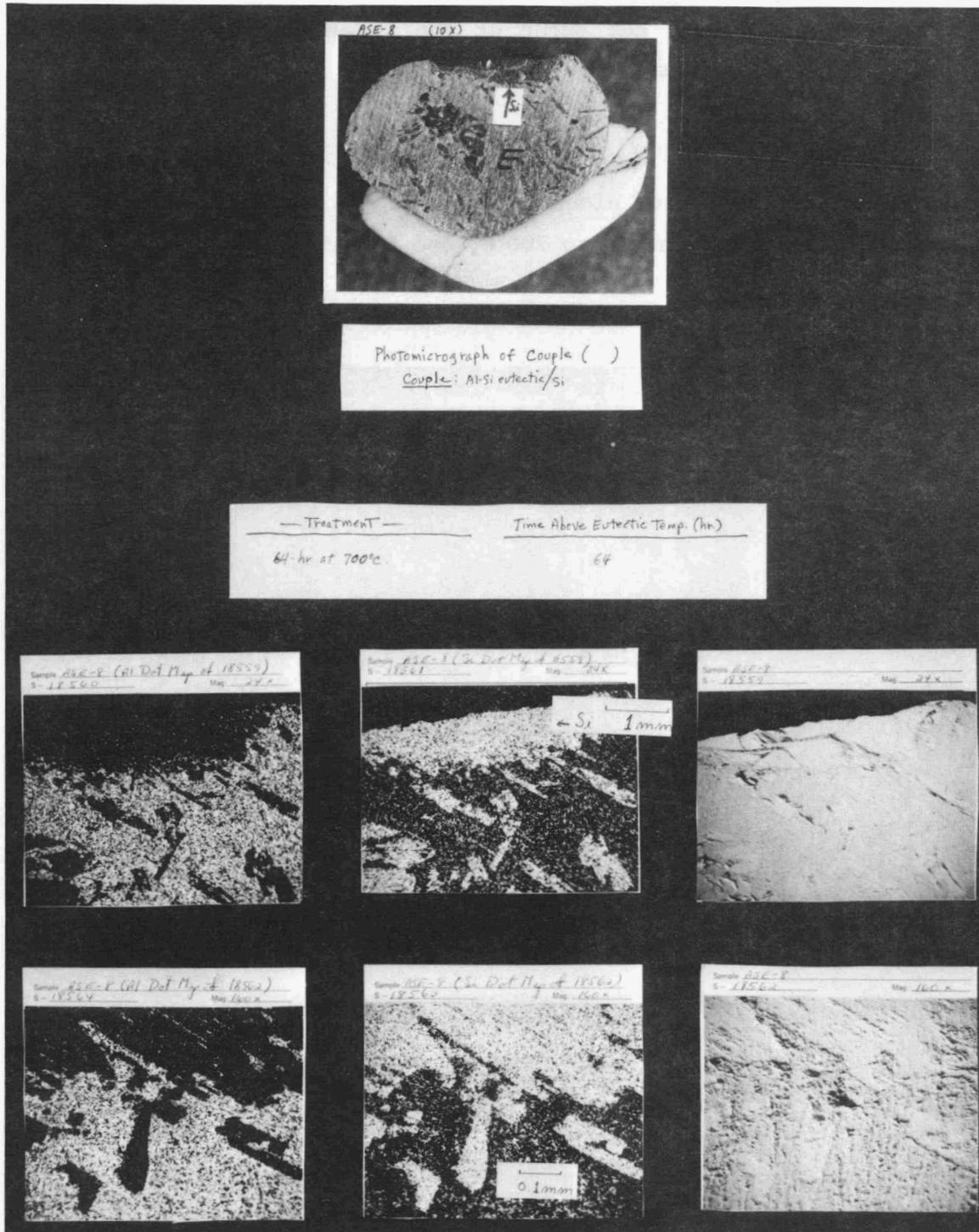


Fig. 8. Photomicrograph and Electron Micrographs of Couple Heated to 700°C for 64 h.

the other for 64 h (Fig. 8). Photomicrographs of sections through the couples are centered above the electron micrographs. Three kinds of electron micrographs are shown: electron backscattering images, on the right; silicon  $K_{\alpha}$  dot maps, in the center; and aluminum  $K_{\alpha}$  dot maps, on the left. The electron backscattering images show the texture of the surface but do not permit unequivocal distinction between the aluminum and silicon phases. The silicon and aluminum X-ray dot maps show regions of high density of silicon and of aluminum respectively. Thus the silicon region should show a high density of white dots on the Si map and a very low density on the Al dot map. Conversely, the eutectic, containing mostly aluminum, should show much higher density of white dots in the Al dot map than in the Si dot map. The interface thickness for the section in Fig. 8 is several tenths of a millimeter, indicating the likely degradation of a silicon shell of thickness less than 1 mm at temperatures of 700°C.

Figure 9 shows a section of a silicon-silicon aluminum eutectic couple that had been cycled between 500°C and 700°C. Although the couple was at temperatures above the eutectic temperature for only fourteen hours, the photomicrograph, in the upper part of the figure, shows a massive intrusion of the eutectic upward into the silicon bar. The intrusion is nearly globular, with a diameter of about 2 mm. The electron micrographs in the lower part of the figure show that the roughness of the interface is of the order of tenths of a millimeter. The dark area near the center of the electron backscattering micrograph (right hand photographs) is a void, since it appears dark both in the Al dot maps (left photographs) and in the Si dot maps (center photographs).

The resolution in the SEM/EDX scans is probably of the order of 50 micrometers (0.05 mm). This is a useful resolution for studies of diffusion since it is fine enough to show the composition variations typical of diffusion but coarse enough to avoid spurious effects due to surface impurities, or smudging by the action of the saw blade. The dot maps show clearly the regions of silicon and of eutectic in the sections. The "fingers" of Si and of eutectic have an interpenetration depth which is estimated of the order of 0.2 to 0.3 mm, much larger than the 0.1 mm thick silicon shell initially proposed. This probably rules

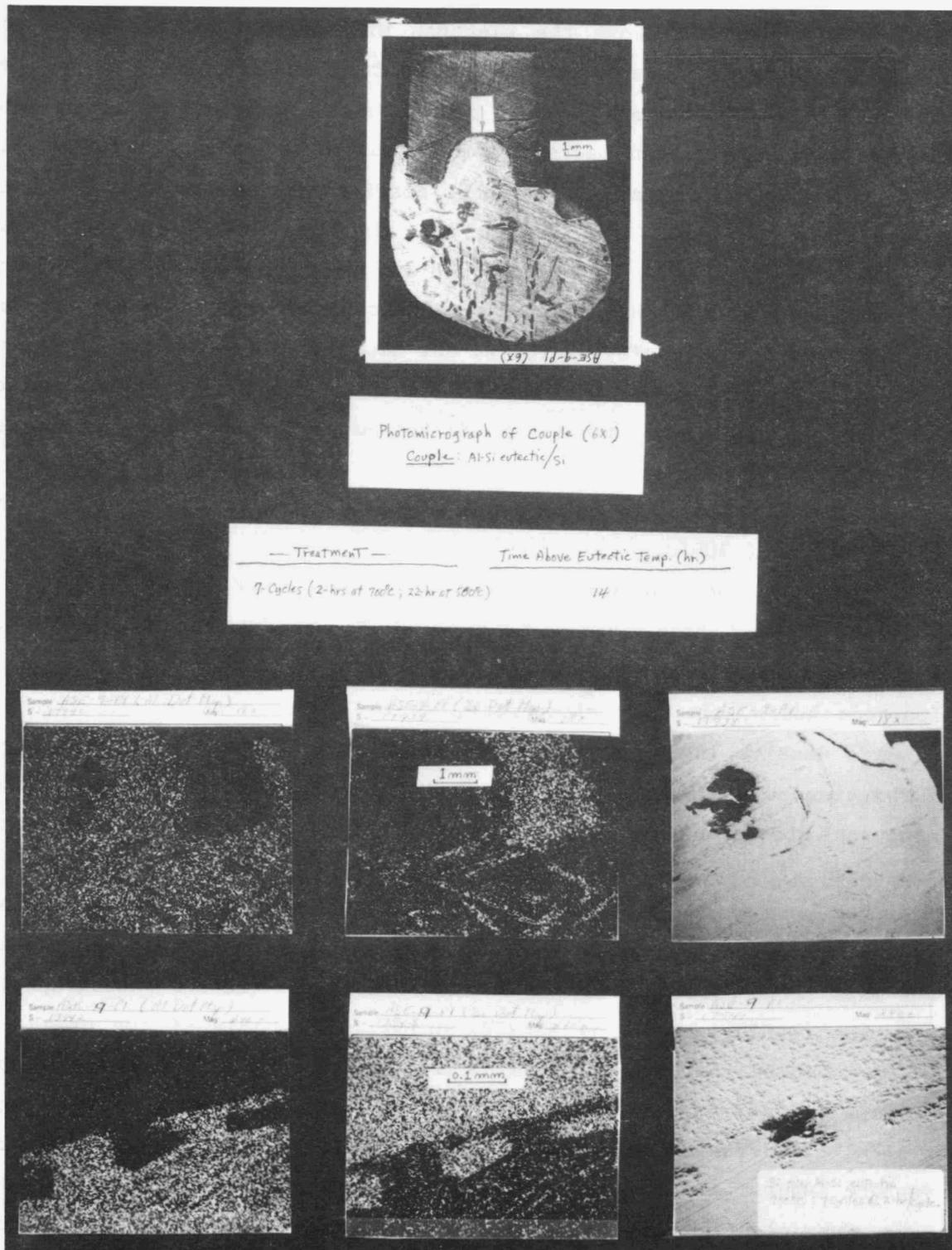


Fig. 9. Photomicrograph and Electron Micrographs of Couples Cycled Between 550°C and 700°C.

out the use of Si encapsulated shot for applications in which temperature excursions up to 700°C could occur.

At 600°C, on the other hand, there is little interpenetration or roughening of the interface. Figure 10 shows micrographs of sections of a couple which had first been held at 600°C for 16 h before cooling and sectioning, and then cycled twenty times between 550°C (just below the

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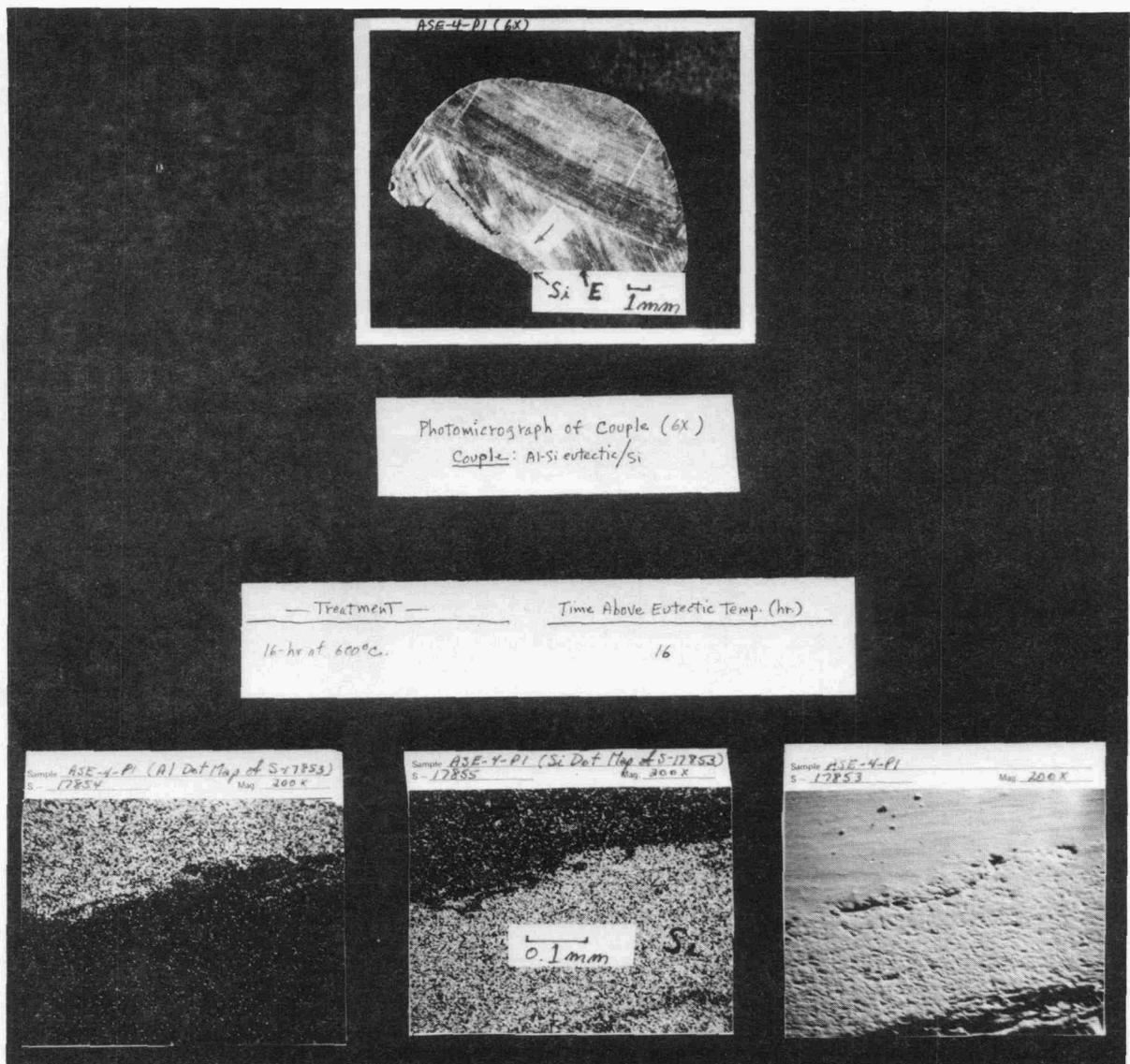


Fig. 10. Photomicrograph (Top) and Electron Micrograph of Couple Heated for 16 h at 600°C and Then Cycled 20 Times.

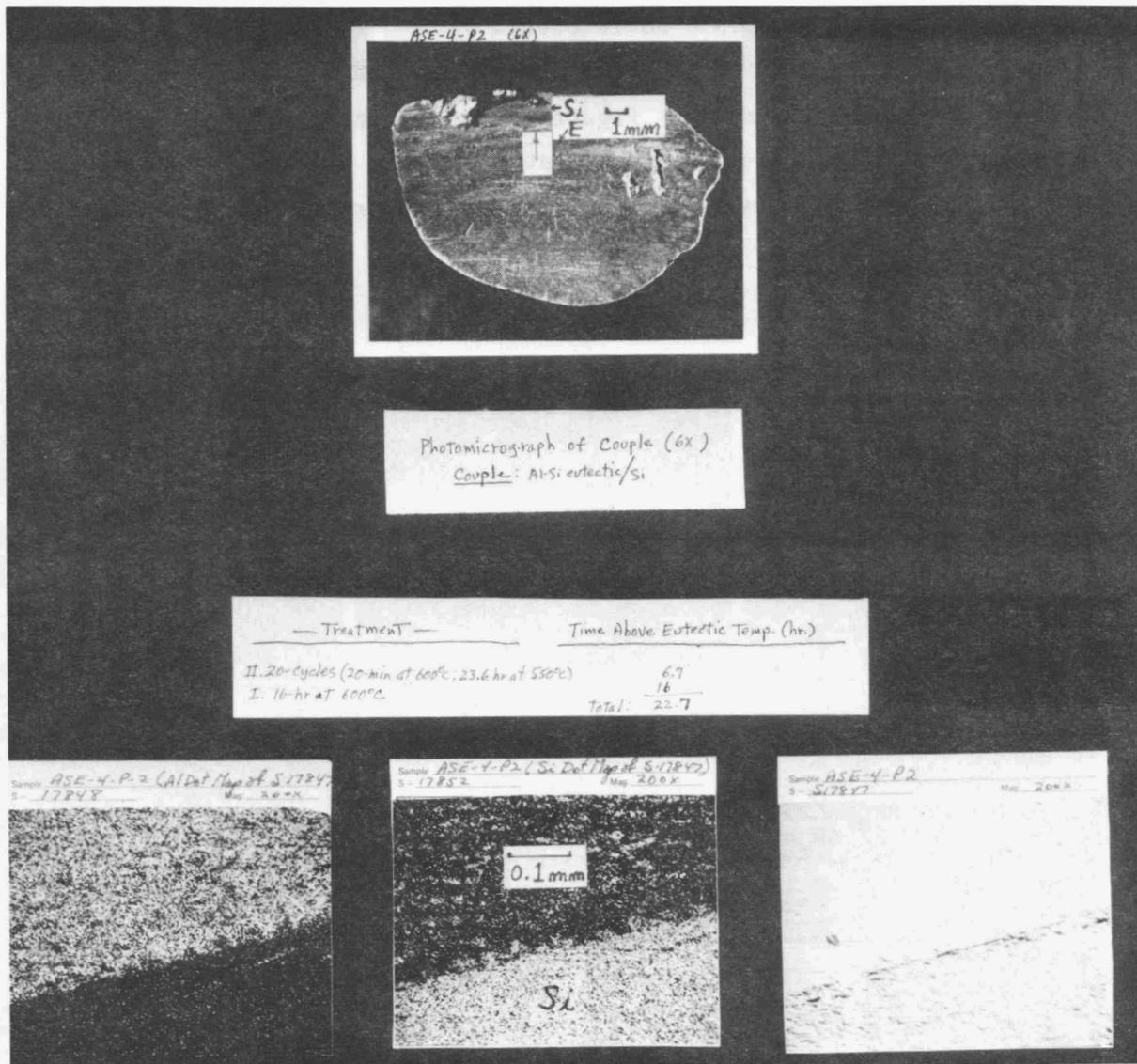


Fig. 10 (continued)

eutectic temperature) and 600°C, giving a cumulative time of 23 h above the eutectic temperature. In both cases the interface thickness is clearly smaller than 0.1 mm, and there appears to be no significant increase in roughness with cycling when the upper temperature is 600°C.

Figure 11 is a section of a couple held at 600°C for 240 h. There has been lenticular penetration of the eutectic into the silicon bar, probably resulting from temperature gradients, surface tension, and the

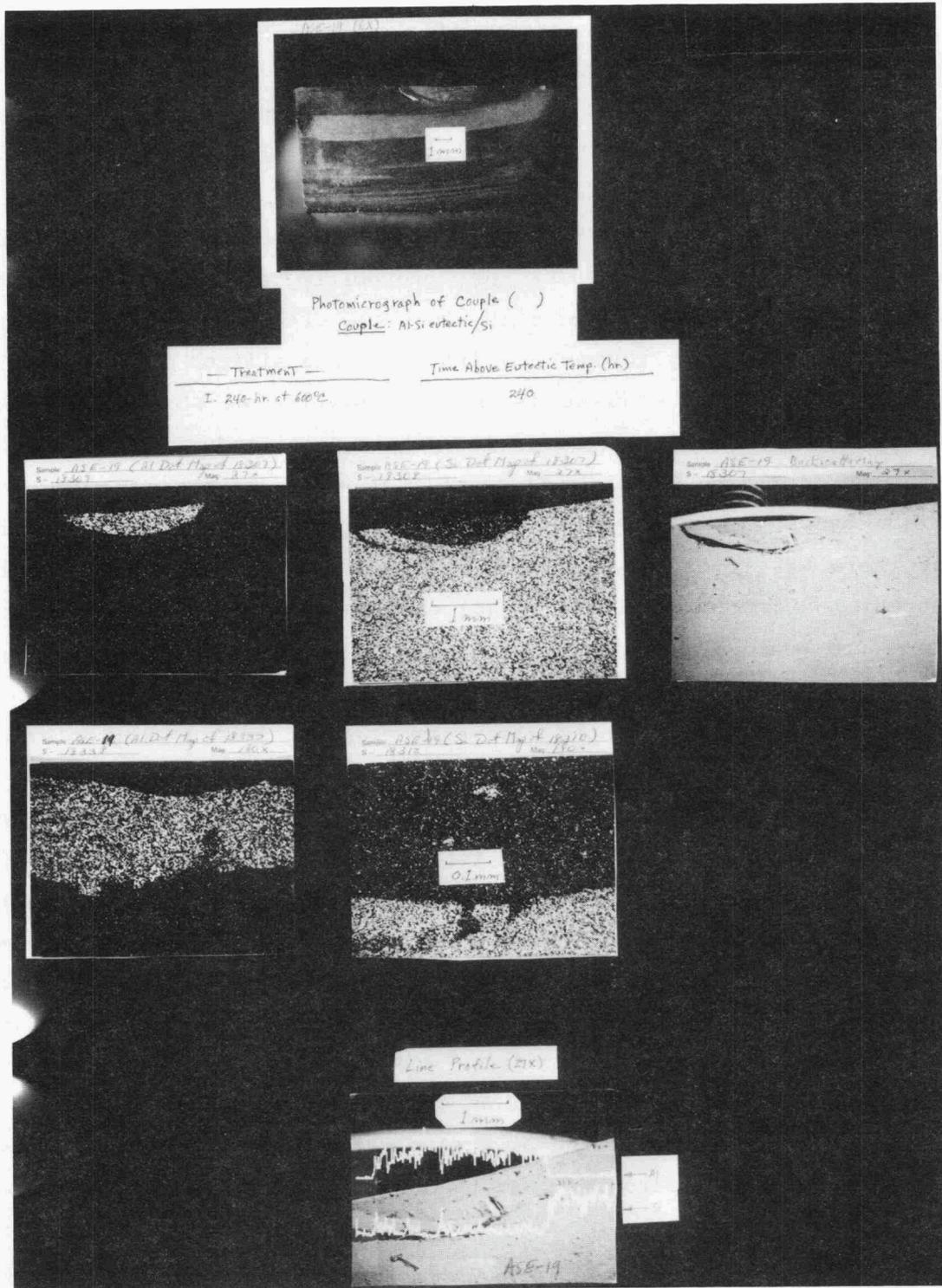


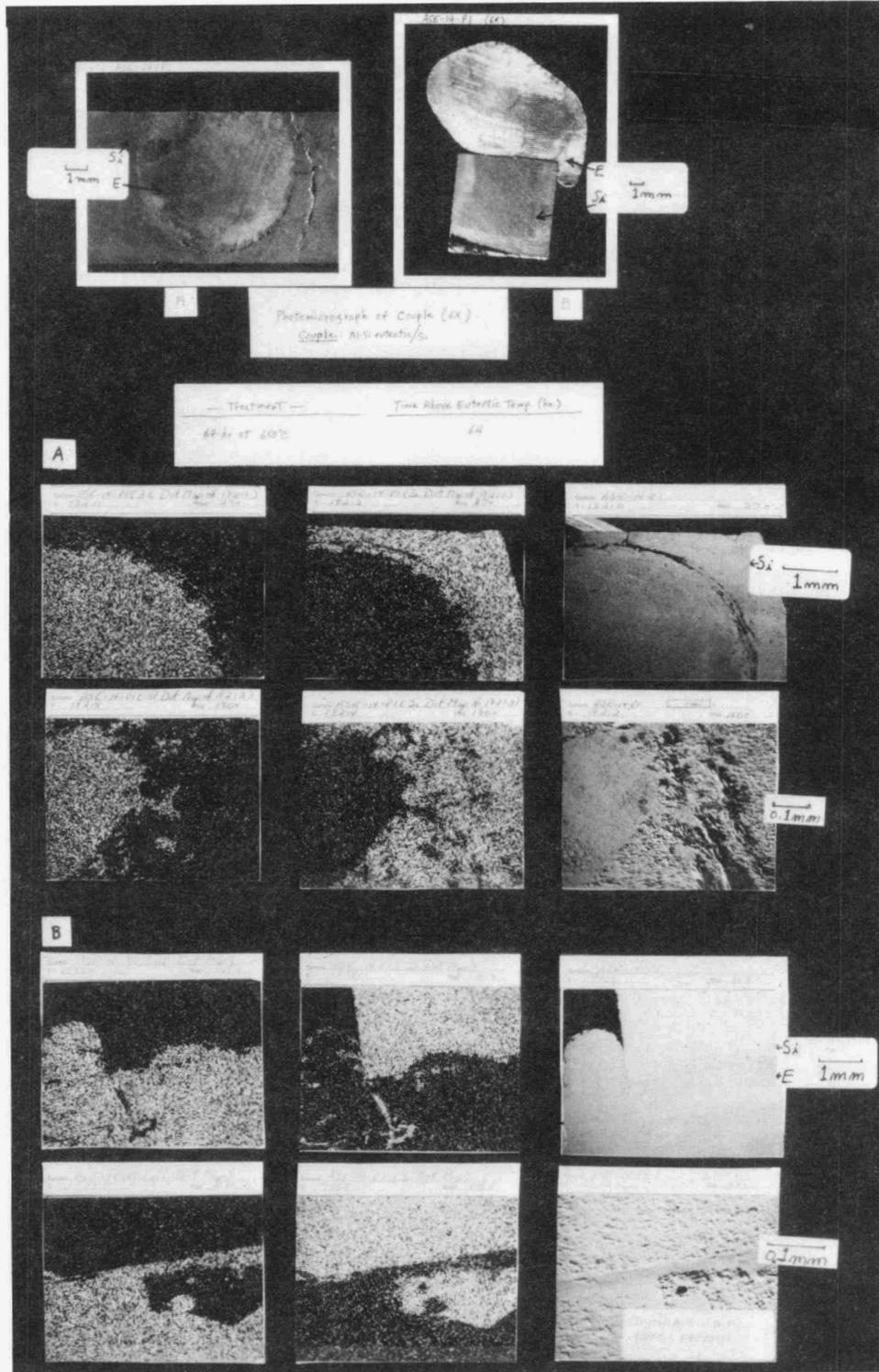
Fig. 11. Photomicrograph (Top) and Electron Micrographs of Couple Heated at 600°C for 240 h.

differing densities of silicon and of the eutectic. Cracking of the silicon is observed, at a distance of about 0.1 mm from the interface, but very little roughening of the interface is observed.

The initially proposed temperature for HHS application of silicon-aluminum alloys had been 650°C. The remaining figures show sections of typical couples which have been heated to 650°C.

Figure 12 shows two sections (a and b) through a couple which had been heated for 64 h at 650°C. The photomicrograph at the upper left shows a spherical intrusion of alloy into the silicon bar. This section was cut longitudinally through the intrusion and silicon substrate. The photomicrograph at the right is of a transverse section of the same couple in a region which appeared to contain no silicon intrusion and in which there appears to be a separation of the eutectic slug from the silicon bar. The electron micrographs in Fig. 12b, however, indicate that there was contact between the two during the heating. The back-scattering micrographs (lower right) suggest an area of penetration of alloy into the silicon which is confirmed by the Al (left) and Si (center) dot maps, which show a lenticular region of alloy in the silicon bar. The micrographs also show cracking both at the interface and in the silicon bar. The "roughness" of the interface is of the order of 0.1 to 0.15 mm. This thickness of the interface between the eutectic slug and the silicon bar (of about 5 mm thickness) may differ from what would be observed with a one centimeter sphere of eutectic coated with a one mm thickness of silicon. A thin shell might accommodate the stresses better than the more massive silicon bar. However, the thermal mass of the thinner silicon shell would be smaller, giving rise to larger temperature gradients and possibly a greater degree of interface roughening and penetration.

Figure 13 shows a section of a couple which had been held for 64 h at 650°C. The photomicrograph, at the top of this figure, shows a part of a spherical intrusion of eutectic into the silicon. The electron micrographs at two magnifications, Al dot maps on the left, Si dot maps in the middle and electron backscattering on the right, show the roughness of the interface between the intrusion and the silicon to be about



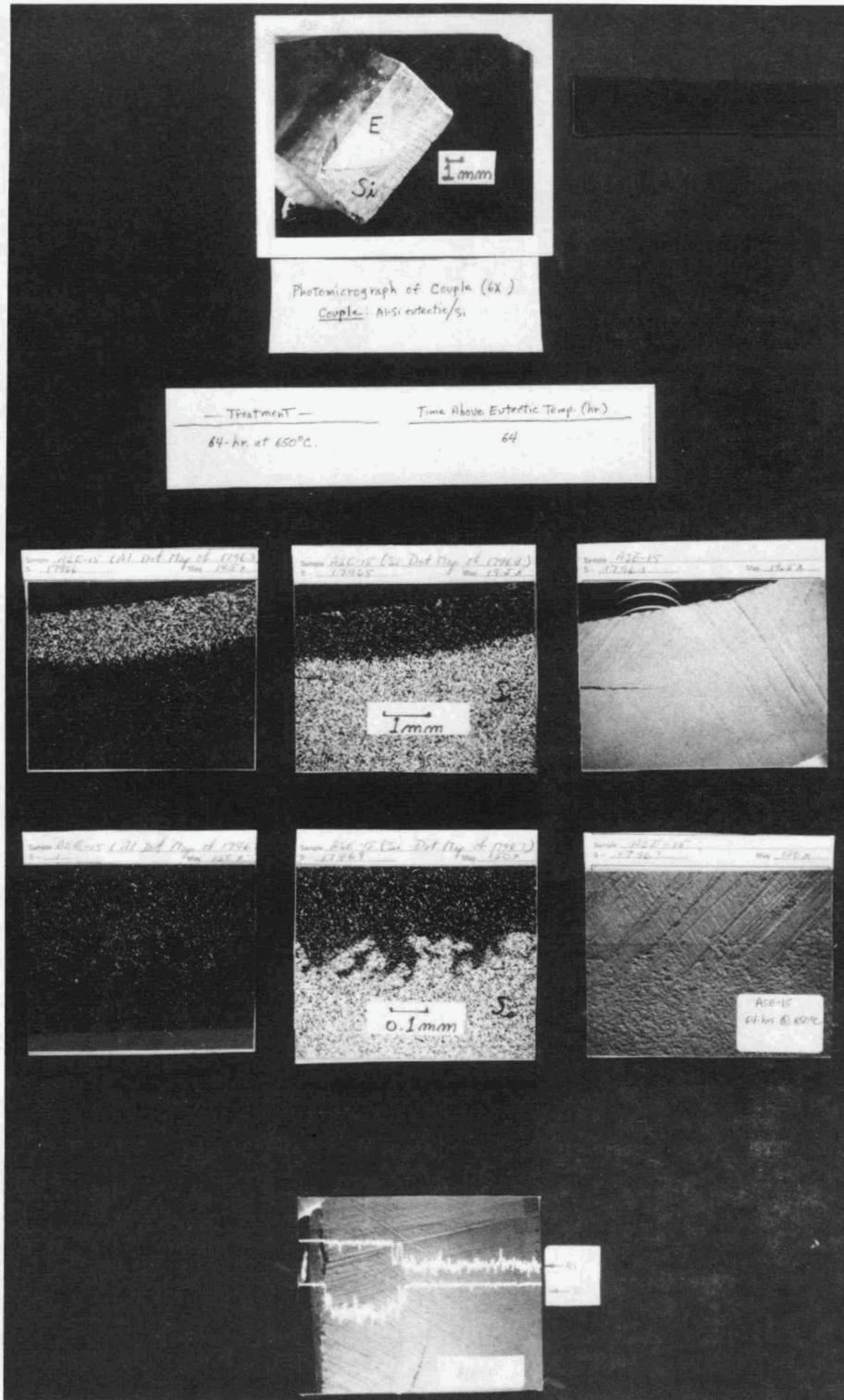


Fig. 13. Photomicrograph and Electron Micrographs of of Couple Heated for 64 h at 650°C; Section Through Spherical Intrusion.

0.13 mm. The electron backscattering photograph, at lower magnification, shows the crack in the silicon bar along a line running from 0.2 to 0.5 mm from the interface.

Figure 14 shows the same couple after cycling seven times between 500 and 650°C after having been held at 650°C for 64 h. Although the eutectic had penetrated the silicon in at least one region (as seen in Fig. 13) the portion of the couple from which the section shown in Fig. 14 is taken shows little contact between the silicon and the eutectic. The two separated during sawing of the sample. This behavior appears to result from the high surface tension of the molten alloy, which prevents the edges of the ellipsoidal liquid slug from contacting the silicon bar. A thin residual oxide skin also may impede contact. It is not evident whether the silicon regions near the surface of the alloy, shown in the Si and Al dot maps, are penetration of Si into the alloy or merely growth of large crystals of Si in the eutectic mixture during solidification. Such large Si crystallites were on occasion seen even in alloy samples which had been melted and solidified in the absence of the Si bar.

Figure 15 shows electron micrographs of the couple which had been held at 650°C for 240 h, a photomicrograph of which was shown in Fig. 6. Although no large intrusions were observed, the micrographs indicated significant interpenetration, although not markedly greater than for shorter contact times.

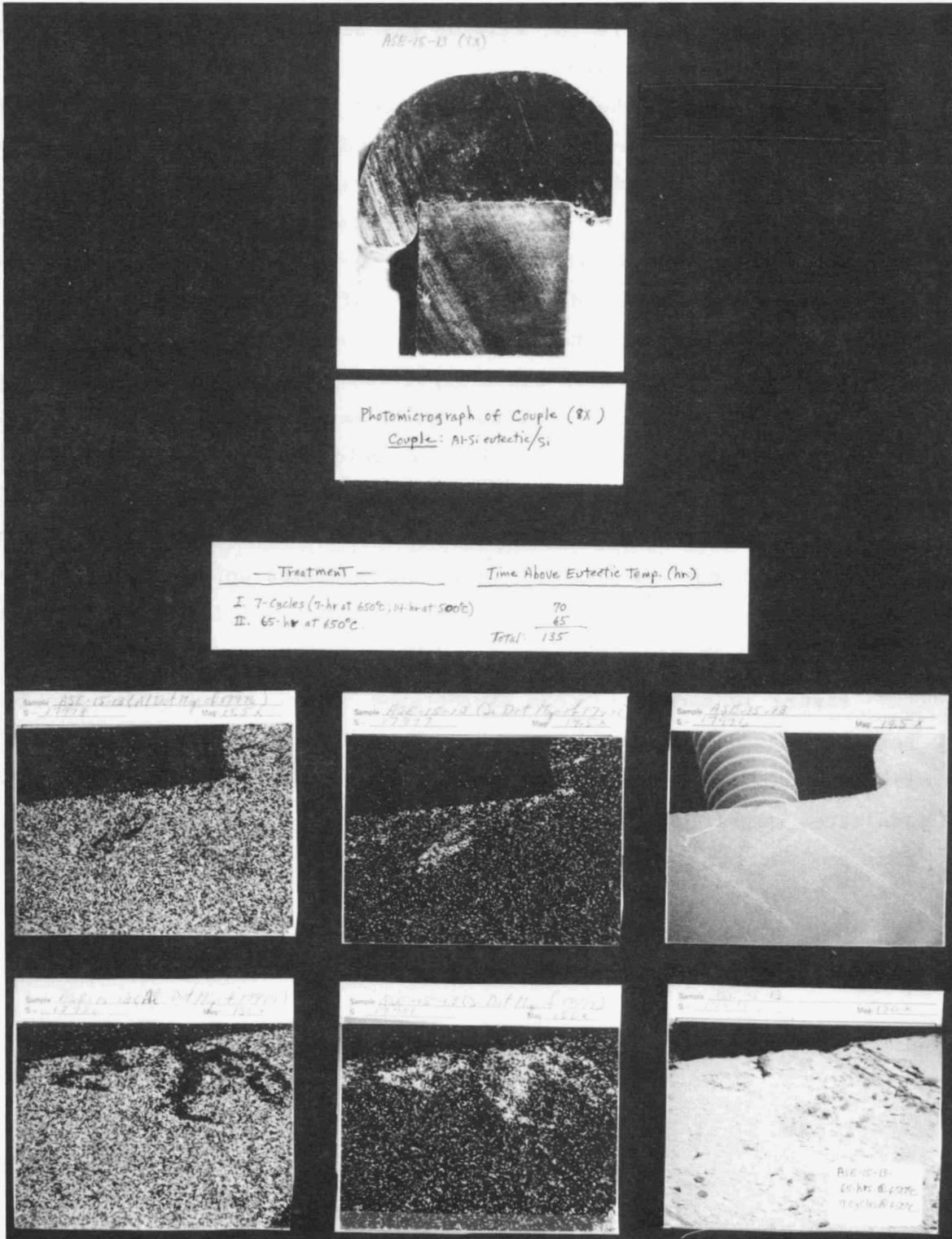


Fig. 14. Photomicrograph and Electron Micrographs of Couple Held at 650°C for 64 h and Cycled 7 Times Between 500°C and 650°C.

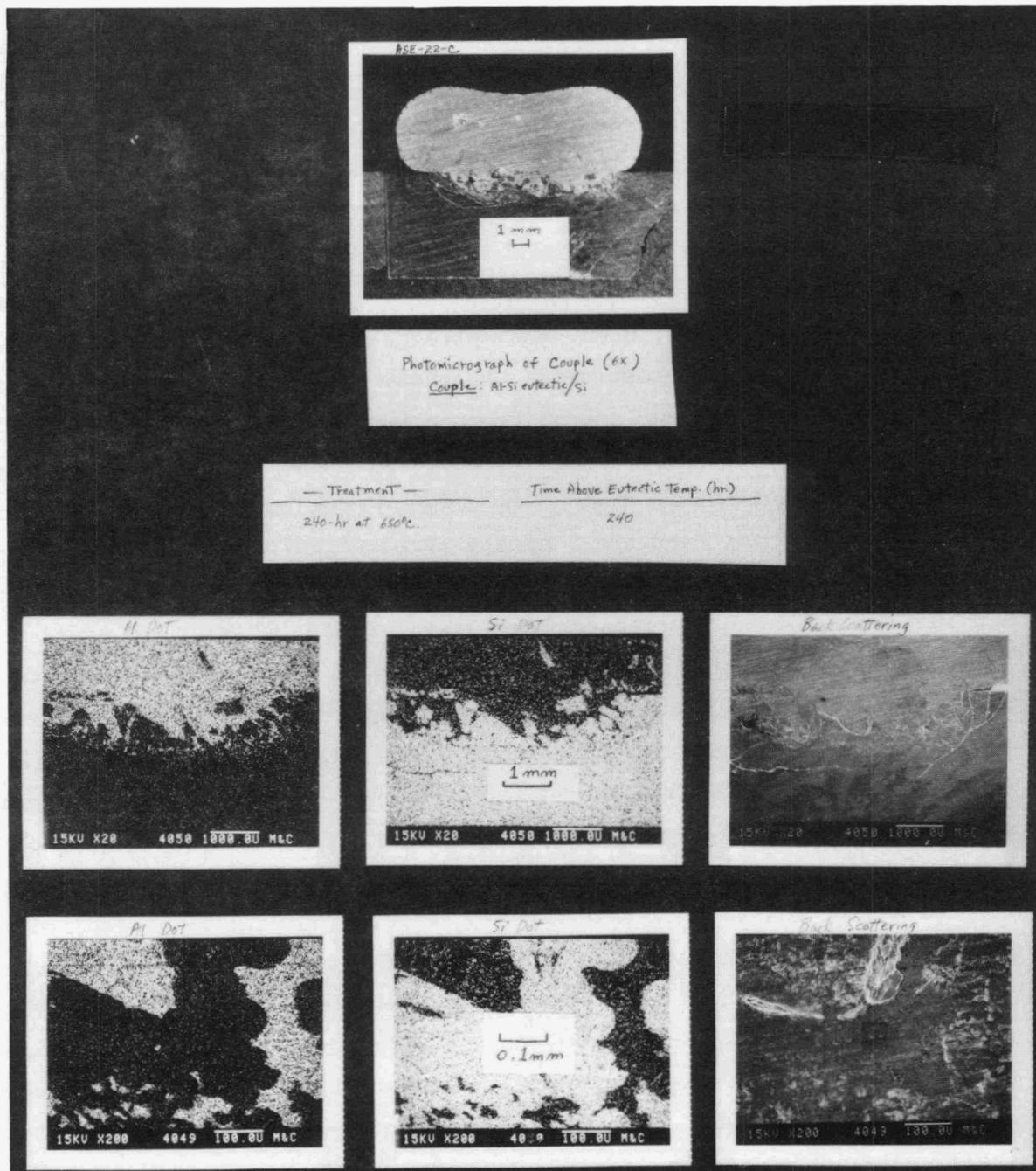


Fig. 15. Photomicrograph and Electron Micrographs of Couple Heated for 240 h at 650°C.

## 5. CONCLUSIONS

Based on the experiments to date, the following behavior has been observed. Initially flat surfaces of contact between Si and Al-Si eutectic show development of a lenticular shape after heating for several hours at temperatures above the eutectic temperature (577°C). The penetration is very slight for temperatures up to 600°C; in some cases, possibly because of oxide films, there is no evidence of wetting. At 650°C and above interpenetration generally occurs. At 700°C and above, the interpenetration occurs to such a large extent that experiments at these temperatures were discontinued, and subsequent experiments were done at 650°C. The lenticular penetration observed, e.g., in Fig. 6, indicates that there must have been lateral transport of silicon, possibly driven by surface tension forces, to accommodate the slug of eutectic. Once penetration has occurred, it does not seem to continue through the silicon bar via a "China Syndrome," as the penetration (Fig. 6) is substantially the same for samples heated for 72, 168, or 240 h.

If this indeed represented the steady state behavior of encapsulated eutectic it would suggest possible stability of the encapsulated shot under these conditions. However, two modifications of the penetration are observed. One is the formation of interpenetrating "fingers" of Si and Al-Si, the "roughening" of the interface. This appears in most cases, at 650°C, to be of the order of 0.15–0.25 mm. Since the roughness does not appear to progress markedly with increased heating time or with cycling, this result would suggest that shells of the order of 1 mm thickness could be stable to cycling up to 650°C. However, the initially proposed shell thickness was about 0.1 mm, which would clearly not be stable. A thicker shell would reduce thermal energy storage density. Even if this were tolerable, the fact that stress cracks occur at distances less than 1 mm from the interface suggest that a thick shell would not be stable.

The second modification of the lenticular penetration is the intrusion of nearly spherical globules of eutectic, of the order of 2–3 mm in diam, into the silicon. There is no evidence that this intrusion occurs because of a preexisting void of that size in the silicon.

Attempts were made to determine whether such intrusions occurred preferentially at scratches or slots inscribed on an Si bar prior to heating, but intrusion did not occur preferentially at those sites. Such intrusions, which occurred with about ten percent of the samples heated to 650°C, could eliminate the possibility of stable self-encapsulated shot, and the mechanism of formation of these intrusions would have to be established.

In summary, application of self-encapsulated Al-Si shot probably is not feasible for temperatures of 700°C and above. It may be feasible for temperatures up to 650°C if the mechanism of globular intrusion can be determined and controlled, and if temperature excursions to 700°C can be avoided. Application at temperatures up to 600°C probably is feasible if the somewhat reduced storage capacity is acceptable and if temperature excursions can be avoided. For applications to temperatures not far from the eutectic, there would be little advantage to self-encapsulation over encapsulation by an inert material, as the latent heat available would be primarily that of the eutectic core with little contribution from a partially dissolving and reprecipitating shell. The choice would have to be based on density and chemical stability of the candidate shell materials.

## 6. NEEDED FUTURE WORK

The present results indicate that silicon encapsulated aluminum-silicon eutectic shot would not be stable to cycling at temperatures of 650°C and above. A more extensive investigation of the stability of the interface at 600°C would be warranted if the thermal storage capacity is still considered attractive and if the applications are ones in which excursions to higher temperatures can be avoided. The mechanism of formation of the globular intrusions should be investigated since, if they occurred at 600°C, they would invalidate the usefulness of self-encapsulated shot. It should be emphasized that the present work does not eliminate the possibility that under carefully controlled conditions (e.g., of temperature gradients, and of heating and cooling rates) self-encapsulation might be feasible, and such conditions would need to be investigated if a reliable storage system were to be developed.

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