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HEAT STORAGE iN
ALLOY TRANSFORMATIONS

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INTRODUCTION

The purpose of this report is to summarize the status of the congruent transformations of solid to liquid alloys as heat storage media. The past work falls into three major parts--(1) thermochemical measurements on transforming alloys, (2) development of a precise and convenient method for measuring volume changes during transformation and expansion coefficients during heat and cooling, (3) study of compatibility of container materials. Only one very modest attempt has been made to evaluate the alloys in comparison with other storage materials in a systems calculation. This aspect of the work is to be emphasized in the future at the expense of the thermochemical measurements, because numerous alloys that are potentially useful have been characterized.

Detailed papers have been prepared for public presentation on thermochemical and volume change measurements. The theory of the processes is outlined and representative measurements are given in those papers and in an earlier report (1). Only the conclusions of that work are repeated here. The thermochemical data are brought up to date. The primary emphasis in this report is on the assessment of which alloys are likely to be most useful and on what remains to be done to maximize their utility.

Heat storage materials could be useful for matching the output of a heat source to the demand on an energy converter that uses heat to produce mechanical work or electricity. The flow of heat may be regulated to a heat-consuming device such as a furnace or a building from an intensely hot source or an intermittent

source, for example from sunlight. Storage devices may simply assist in leveling the load on a power generating system so that peak load generators are omitted. Energy savings result if inefficient generation is replaced with more efficient generation or if more plentiful or renewable energy sources can be used in place of scarce, consumable resources. Material fabrication and operating costs must be kept low if storage systems are to yield net benefits. Consequently, the alloys studied by us and the salts studied by others are relatively plentiful and cheap. For just that reason the materials used for containment and structure are certain to weigh heavily in the total costs.

The choice of containment materials is not simple and straight-forward even when the basic plan of an energy conversion system is well-defined. When the details of the system are under development, as in many advanced energy conversion systems, the evaluation of alternate materials and their effect on system costs is speculative. However, the factors contributing to such a choice can be enumer-ated, and some limits can be placed on the possible solutions to the containment problem. Graphite has served well in our small scale experiments. SiC (silicon carbide), rapidly emerging as a material being developed for solar receivers (2), seems likely to meet the chemical stability and mechanical strength requirements, although fabrication of complex structures will require ingenuity.

This program has progressed from identification and charac-terization of alloys that store heat efficiently by eutectic or congruent melting transformations to the search for stable contain-ment materials in preparation for the analysis of specific concepts

for selected applications. The calorimetric and volume change work is reviewed briefly as the basis for an analysis of what remains to be done as the program evolves toward a system development stage.

As an example of one way eutectic alloys might be applied, the modification of an existing device can be mentioned. The Ommium G 'Heliodyne' solar-powered generator (3) uses aluminum melting and freezing to achieve short term stability, matching the solar input to a Stirling cycle generator with about 10 kW_e output. Some of the alloys studied in this program have greater energy storage density than aluminum and should be somewhat easier to contain. The design of solar receivers that use sodium heat pipes and eutectic salt storage (4) might be simplified and decreased in volume and mass by the substitution of alloy eutectics.

I. Alloys for the Storage of Heat

A. Choice of Elements

A first selection of elements to explore was made on the basis of cost for large amounts. The prices of metals vary periodically, often by substantial factors, but these changes have generally been cyclical, on top of the overall inflation of the reference currency. A multiple choice of storage materials in a given range of temperature provides some hedge against such changes, but the other cost factors are likely to preclude shifts after the initial design concept is chosen.

The first list of materials for study contained Al, Cu, Mg, Si and Zn. Later Ca and P were added. S also is a low cost element, but the element and the sulfides do not appear to offer much hope for high density heat storage. Fe and its alloys transform above the temperature range which has been studied. Containment of iron alloys for long periods would be very difficult.

B. Selection of Alloy Compositions for Study

If Pb, Sn, Bi and Sb are excluded on the basis of their cost, alloys as a class do not appear to be able to compete with several types of inorganic salts below about 670 K. Therefore, the temperature range from 670 up to 1000 K has been studied more intensively. The conventional fossil-fueled and nuclear fission reactors supply heat in this range. More recently an increase in interest in solar receivers as possible heat sources has brought about the search for alloys that might

ѡperate in the gap between 1000 and 1220 K. Earlier studies
in this program had shown that Mg_2Si-Si formed a eutectic with
excellent heat storage capacity at 1219 K.

For the most part, the binary phase diagrams are known for
the pairs of elements taken from the list in section 1A. Thermo-
dynamic equations for the eutectic transformation were written
and evaluated for the systems of interest to the extent that
the availability and precision of tabulated data would permit.
These equations made it clear that the desirable conditions
are:

1. the use of elements that have high entropy of
    fusion,

2. the combination of those elements as far as possible
    into ordered intermetallic compounds that have high
    heats of formation from the elements,

3. the selection of eutectic combinations that involve
    liquids in which the elements participate with nearly
    equal mole fractions (and the more elements the
    better),

4. liquid eutectics in which the elements are completely
    mixed, that is, liquids with little short range
    ordering (or tendency to associate into molecule-like
    clusters).

Condition 4 and condition 2 are somewhat incompatible, but
several intermetallic compcunds may have high enough latent
heats for congruent melting to be interesting in their own
right.

More detailed calculations have been done recently using regular solution models to see if the precision of the calculations could be improved. However, comparisons with experiment only justify the use of the qualitative rules to determine which of the eutectics, in a given system with several eutectics, is more likely to give good heat storage. In general the theory tends to overestimate storage capability, probably because the liquid solutions are not completely random. Nevertheless, deviations sometimes are negligible or even somewhat in the other direction.

Once the most promising of the known binary and ternary eutectic alloys were studied, a search was begun for other ternary or quaternary alloys in composition ranges that appeared to be favorable. Several new eutectic alloys have been discovered and measured, others are awaiting measurement, as listed in Section E and Table 1 below. In addition, several new ternary and one new quaternary intermetallic phases have been found, but the structures and transformation properties have not been determined.

C. Preparation of Alloys

Commercially pure elements or intermetallic compounds were melted in graphite under inert atmosphere with good stirring. The alloys were frozen in place, sometimes under modest pressure applied by the graphite stirrer assembly. The alloys have been investigated metallographically and by the x-ray fluorescence analyzer on the scanning electron microscope for porosity, general homogeneity of composition and fine scale of the

eutectic microstructure (to insure reliable sampling). Only calcium-containing alloys showed any tendency to react with the graphite crucibles, and that attack was not serious during the short melting time. More serious problems have been encountered with evaporation of the more volatile elements both during melting and thermal analysis. Close fitting lids on the crucibles have provided partial solution to this problem, but a method is being sought to seal the crucibles completely.

D. Heat of Transformation and Heat Capacity Measurements

For eutectic or congruent melting that takes place up to 970 K, heats of fusion can be measured to about 3% precision and heat capacities to about 10%, provided that vapor losses do not interfere with the differential scanning calorimeter (DSC). At higher temperatures the older differential thermal analyzer (DTA) gave heats of fusion to about 10%, but the heat capacities were not reliable. A newer model DTA seems to be giving acceptable heat capacities and more precise heats of fusion, although they are not as precise as the DSC measurements at lower temperatures.

The precision instruments use very small samples. To search for new eutectic alloys a qualitative DTA apparatus was built to accommodate much larger samples. These samples are large enough to yield convenient metallographic specimens and leave a residue for other tests. This larger DTA sample gives sharp differential temperature peaks, but heat flow in the relatively large samples makes it useless to attempt quantitative calibration of the system.

E. Data for High Temperature Heat Storage Materials

Table 1 summarizes heat of transformation data for many binary and ternary eutectics and a few intermetallic compounds that have been measured in this laboratory. The alloy compositions that are most likely to be useful have been underlined. Heat capacities are given for a few alloys that transform at 852 K or lower. Those compositions marked with an asterisk are newly identified ternary eutectics. The compositions, temperatures and heats of transformation have been established recently. Two newly discovered ternary alloys in the Mg-Cu-Ca and Mg-Si-Cu systems remain to be measured. Two new ternary intermetallic phases have been found in the Cu-Si-P system, one still to be measured. A quaternary intermetallic phase has been found in Al-Mg-Cu-Si, as well as a new quaternary eutectic in Al-Cu-Mg-Zn. Searches were conducted in several other ternary and quaternary systems without encountering eutectic transformations not previously considered. Several other systems that are difficult to melt and cast have given inconclusive results.

A few binary eutectics remain to be measured: Ca-Si, Ca-Cu, Cu-P. Several reported values that seem to be too low will be checked. A few more measurements will be done at the low end of the temperature range because the heat storage capabilities of Mg-0.29Zn, the lowest melting eutectic studied, are not high. There is not much hope of extending metallic storage systems below this range without the use of much more expensive elements, notably Bi, Pb, Sn, &... Fortunately the

Table 1   Thermal Properties of Selected Metal Eutectics

Alloy (Mole Fractions)	Eutectic Temperature (°K)	Maximum Heat Storage Capacity in kJ/kg		Heat Capacity kJ/kg-°K
		Calculated	Measured*	
Mg-0.24Zn-0.05Si	608	260		
Mg-0.29Zn	616	230	210	{1.04s 1.511
Mg-0.14Zn-0.14Ca	673	405		--
Al-0.35Mg-0.06Zn	720	406	310	{1.73s
Al-0.375Mg	724	376	310	1.621
Mg-0.13Cu-0.08Zn	725	408	253	--
Al-0.17Cu-0.16Mg	779	406	360	{1.09s 1.181
Mg-0.105Ca	790	431	269	--
Al-0.175Cu	821	359	353	{1.11s 1.111
Al-0.126Si-0.051Mg	833	549	545	{1.39s 1.211
Mg$_2$Cu	841	398	243	--
Al-0.31Cu-0.07Si	844	561	423	--
Al-0.12Si	852	571	515	{1.49s 1.271
MgZn$_2$	861	259	220	--
Zn-0.4Cu-0.15Mg	978	313		
Cu-0.157P	987			
*Cu-0.25P-0.14Zn	993		368	
Cu-0.42Mg	995	235		
*Si-0.35Cu-0.28Mg	1023	892	422	
*Cu-0.17Zn-0.15Si	1038		125	
Cu-0.29Si	1076	308	196	
*Cu-0.13Si-0.17P	1093		92	
Cu-0.49Ca	1106		25	
*Si-0.45Mg-0.07Zn	1207		310	
Si-0.471Mg	19	1212	805	

*By Alan Riechman and Diana Farkas

inorganic salt eutectics should be handled most easily in that temperature range.

Although the newly discovered alloy eutectics do not surpass the storage capacities of those studied earlier, there are several promising alloys that lie in a temperature range that was open previously. The temperature gaps between promising alloys are now considerably reduced. Furthermore, the alloys with high concentrations of copper have higher densities than the other alloys, making their performance more favorable when comparison is made on the basis of volume instead of mass. Since containment is likely to be the most difficult consideration at these higher temperatures, the volumetric comparison is more significant than one based on mass.

II. Volume Changes During Transformation

It is reported that some of the salt eutectics have large volume changes, above 20%. Designing heat exchangers for efficient use is likely to be difficult for such materials. Because less is known about the volume changes when the eutectic alloys transform, it was decided to attempt to measure this property. Previous measurements have been done by determining density versus temperature for solid and for liquid independently, by different methods, and extrapolating for each to the transformation temperature to find the difference. The uncertainty in that small difference can be large proportionately. Therefore, a new technique was developed and is being refined. It uses x-ray absorption in a specimen confined within a path of

known thickness to obtain volume changes during transformation with good precision. As a bonus, the coefficients of thermal ᴄ. ᴠnsion of both solid and liquid can be obtained in the same run ᴄ ᴠeniently and satisfactorily, although not yet as precisely as they were determined in the most careful of the older stuᴅies. For example, the expansion coefficients that can be obtained from the x-ray diffraction determinations of lattice parameters and dilatometry for Al, Ag, Au and Cu (5) are more precise than those reported in this work.

A. The X-Ray Absorption Method for Volume Changes

X-rays are absorbed in proportion to the exponential of mass per unit area in the path between source and detector. The absorption coefficient is a mass weighted average of the absorption coefficient of the elements in the absorber, because state of chemical combination is without significant effect. To utilize this property to measure density changes, a well-defined beam is passed through a known length of sample as well as weakly absorbing container walls. Owing to the fine eutectic microstructure of the samples, it is assumed that the average composition of the matter in the beam path does not change during heating and transformation.

The thermal coefficients of expansion of the solid mixture and of the liquid solution can be calculated from these measurements making appropriate corrections for the thermal expansion of the container. The isothermal transformation itself is affected by the container only through referring the volume change to the density at the transformation temperature of

either the solid or the liquid. For example:

$$\frac{\Delta V_{transf}}{V_s} = \frac{\frac{1}{\rho_1} - \frac{1}{\rho_s}}{\frac{1}{\rho_s}} = \frac{\rho_s - \rho_1}{\rho_1}$$

where V is specific volume, ρ is density and subscripts s and l
refer to solid and liquid, respectively.

B. Design of Apparatus

The heat storage materials to be studied include the elements
Mg, Al, Si, P which have low atomic numbers and weakly absorb
x-rays. Ca has only a slightly higher atomic number, and Cu and
Zn are still only elements number 29 and 30, respectively. To
get substantial intensity changes in the weakly absorbing elements,
soft (long wavelength) x-rays must be used. For those elements
Cu K_α radiation was first calculated, and later demonstrated, to
be an excellent choice provided that the containers were made of
low atomic number elements with walls of small or moderate
thickness.

Initial calculations suggested that graphite, boron nitride,
silicon carbide, magnesium oxide and aluminum oxide can be use-
ful materials from which to make absorption cells. For reasons
of chemical compatibility with the heat storage alloys, availa-
bility and ease of fabrication, graphite was chosen to be the
material for the first system. It has the added advantage of
a very low coefficient of thermal expansion. An alloy specimen
fitted into a graphite chamber at room temperature will continue
to fill that chamber completely as the temperature increases.

The alloy must be sufficiently ductile to relieve pressure on the chamber by plastic flow. A graphite cell backed with stainless steel plates has been strong enough to contain the aluminum-based eutectics investigated to date. It seems likely that silicon carbide would serve as well or better when less ductile alloys are to be studied, although fabrication of the silicon carbide cells will be more difficult.

The cell was heated in a chamber that could be evacuated. The chamber was mounted on the camera track of a Philips x-ray generator. Transmission of heat through the chamber base, through firebrick and other insulation, limited the temperature range to about 1070 K.

The x-ray output from the standard generator and silver-targeted x-ray tube was so intense that the beam, after passing through a graphite monochromator, the furnace chamber ports (Be) and the sample cell and sample, still required attenuation before entering the Ge(Li) counter. Over the long measurement period some instability of the x-ray output was encountered as a consequence of obstructing particles in the cooling water supply to the x-ray tube. Substitution of a Cd^{109} source of Ag K_α x-ray appears to be successful in overcoming most of the instrumental problems. There seems to be sufficient intensity that a standard NaI(Tl) scintillation counter can be used to feed a pulse height analyzer with only a single energy window. There is a small amount of high energy radiation from the radioactive Cd which should be excluded from the counting. With this radiation source the furnace chamber can sit on an

additional refractory base, instead of the camera track. Higher temperatures should be reached with only minor additional modifications.

The results in section D below are measurements made with the old system. The new system is not expected to give an increase in precision of measurement, only in convenience, reliability and temperature range of operation. Future measurements will be on different metals, alloys and possibly salts.

C. Preparation of Alloys

The metals and alloys used in this investigation must be uniform in composition, have a microstructure that is fine and randomly oriented on the scale of the x-ray beam width (about 3mm), and be devoid of porosity. Therefore, the melt must be thoroughly stirred and frozen moderately rapidly under sufficient pressure to prevent pores from forming. Satisfaction of these conditions is verified by optical microscopy and scanning electron microscopy with x-ray fluorescence analysis. The alloys are shaped to fit precisely into a cavity in the absorption cell so that the path lengt' is defined. The space above the cavity is open to receive expanding alloy as the cell is heated.

Now that the absorption cell and x-ray sources have been tested, sample preparation is the limiting step for this measurement. Avoidance of porosity is difficult, especially in those samples that contain volatile elements such as Zn and Mg. It is likely that crucibles of more sophisticated design

than those used heretofore will be necessary to melt, homogenize
and freeze some of the alloys that remain to be measured.

D. Results and Conclusions

Table 2 summarizes the thermal coefficients of expansion
for Al and its eutectics with 17.5 at. pct. Cu and with 12 at.
pct. Si and the volume changes when the solids melt. Those
previous measurements that have been published are in good agree-
ment with these new results. The older thermal expansion
coefficients appear to have been measured carefully by dilatometry
for solids and pycnometry or equivalent methods for liquids.
They should be considered more reliable than these new values
until some low temperature irregularities are identified and
eliminated. However, the isothermal volume changes that occur
during melting should be given most precisely by this new method.

The expansion of Al during melting, a volume increase of
7.2 pct., is somewhat higher than that for most close-packed
metals. Measurements on commercially pure aluminum and on very
high purity aluminum show no differences that can be attributed
to trace impurities. The presence of intermetallic phases of
more open crystal structure in the eutectic mixtures probably
is responsible for the lower volume change found in those cases.
These volume changes, 4.8 and 5.1 pct. for the silicon and
copper alloys, respectively, and 7.2 pct. for Al, are much
smaller than those for chloride salt eutectics, which are
reported to exceed 20 pct. in some instances.

Table 2

a. Density Changes During Melting for Al and Two Al-Eutectic Alloys

| T°C | Density in kg/m^3 | | $\Delta V/V_s$[‡] | |
	Measured[§]	Tabulated[*]	Measured[§]	Tabulated[*]
Pure Al				
20(s)	2690	2699(6)		0.0769(8)
660(s)	2558	2555(5)	0.072	0.0759(9)
660(1)	2377	2368-2410(6)		
760(1)	2343	2338(6)		0.069 (7)
Al - 17.5 a/o Cu				
20(s)	3506	3570		
548(s)	3424	3400	0.051	0.050 (7)
548(1)	3258	3290 }(7)		
748(1)	3186	3200		
Al - 12 a/o Si				
20(s)	2626	2639(7)		
579(s)	2553		0.048	0.040 (7)
579(1)	2445			
779(1)	2382			

b. Linear (Solid) and Volumetric (Liquid) Expansion Coefficients

| Linear Expansion Coeff. | | Volumetric Expansion Coeff. | |
Measured[§]	Tabulated[*]	Measured[§]	Tabulated[*]
Pure Al			
2.77×10^{-5}	2.95×10^{-5}(10) 2.50×10^{-5}(6)	0.9×10^{-4}	1.1×10^{-4}(6)
range: 20-660°C		range: 660-760°C	
Al - 12 a/o Si			
1.7×10^{-5}	none	1.3×10^{-5}	none
range: 20-579°C		range: 579-679°C	
Al - 17.5 a/o Cu			
1.5×10^{-5}	none	1.1×10^{-4}	none
range: 20-548°C		range: 548-748°C	

* Numbers in parentheses are references
‡ At the transformation temperature
§ By Andrew Harrison and Silvia Balart

III. Containment of Materials for Heat Storage and Exchange

Long-term containment of liquids between 700 and 1300 K is a problem worthy of careful consideration. The working substance and the container either must not react or they must react to form a slow growing solid product that is protective to the container. Experiences with coolant systems that use liquid metal or salt coolants and metal containment have shown that low level contaminants , such as oxygen dissolved in the coolant,often have a large effect on dissolution rates (1). In the case of molten salts, dissolved water often plays a similar accelerating role. These experiences have been obtained mainly in heat transfer loops where large temperature differences are present. Eutectic storage should be operated close to the transformation temperature so that differential solubilities leading to a dissolution-transport-deposition cycle should not contribute on the storage side of the system. But some other fluid must be employed as a heat transfer agent, subject to the kinds of difficulties mentioned above.

For the time being only compatibility of the heat storage material with its container is considered. Phase change storage by a eutectic involves a liquid-solid volume change which can lead to periodic loss in contact between the storage medium and the container wall over part of its area and, at other times, the development of stress in the container walls owing to local expansion in the storage medium. Problems of this sort probably can be solved by careful design of the heat exchanger, so they are not to be considered at this stage, although it is hoped

that alloys with small volume change on transformation will
simplify these problems.

In any case the advantages of relatively inexpensive alloys
will be lost if containment cannot be achieved with materials
that are intrinsically cheap and easy to fabricate to meet system
requirements. A further restriction is imposed by the fact that
one of the main advantages of alloys with respect to salts is
the much better heat conductivity of the former. The use of
poorly conducting heat exchanger tubes would dissipate this
advantage.

The elements used in this study oxidize readily when oxygen
is available. They should scavenge any oxygen that enters the
containment system and keep the effective oxygen pressure very
low. Although small composition changes in the heat storage
medium are not likely to have much direct effect on the storage
operation, the oxides that form might accumulate at heat transfer
surfaces and interfere with heat conduction. For that reason
the containment system should be constructed in a manner that
prevents access of oxygen, including tight closure and the use
of an inert gas cover under positive pressure if necessary.

Any satisfactory material for use in this temperature range
must retain a fairly high level of strength, preferably with
some ductility so that large wall thicknesses are not required.
If the material is also resistant to attack by traces of oxygen,
water vapor and other common contaminants that might enter the
system, the initial assembly and later maintenance would be
facilitated. For the heat storage alloys that performed best
in our calorimetric measurements, three types of materials are

being considered. The obvious advantages and disadvantages are listed here.

1. Graphite

All of the alloys in this program have been handled in graphite with no apparent problems, except for those alloys that contain Ca. Ca reacts with graphite to form CaC_2 which yields acetylene when it comes in contact with water. The smell of acetylene is detected when a system is opened after a Ca-containing alloy has been melted in graphite. Most of the alloys do not contain Ca.

Graphite has moderate room temperature strength, but its strength is retained at high temperatures, whereas most other materials tend to soften. Although it is not ductile in the conventional sense, it is resistant to brittle fracture. It cannot be fabricated by conventional welding techniques (12), but is readily shaped by machining so that it can be stacked in many geometrical patterns. Also it can be coated on many substrates by chemical vapor deposition (pyrolytic graphite). Broad experience exists in the nuclear power industry with graphite as a moderator. It is particularly well adapted to heat transfer with an inert gas such as helium as the transfer medium.

2. Silicon Carbide

SiC has been used mainly as an abrasive cutting material because it has hardness approaching that of diamond. Its high strength is retained to very high temperatures, but it is brittle at low temperatures. The material also has been used

for decades as high temperature resistance elements ('Globars') that can be used in air up to about 1400°C for long periods. Frequent heating and cooling does not damage the rods seriously, but prolonged heating in air at somewhat lower temperatures is not recommended because the oxide that forms there is not as protective as it is at higher temperatures.

SiC has been investigated as a high temperature semiconductor, because the band gap in the electronic energy level spectrum is wider than in Si. Its other application in electronics is as a resistor with negative temperature coefficient to limit the initial current when a television set is switched on.

SiC is fabricated by hot pressing. Two different, but closely related, crystal modifications are produced commercially which transform at high temperatures. Lower temperature poly-types have long-range stacking sequences of alternating cubic and hexagonal packing reflecting the thermal history of the material. These changes occur well above the range of concern in this heat storage program and should have no significant consequences.

SiC cannot be fabricated by conventional welding, and it is shaped by grinding only u ing diamond as the abrasive. However, large heat exchange tubes in hairpin form have been fabricated and tested in solar receiver prototypes (2), so this material must be included in the eligible list for high temperature storage. SiC may be the main receiver surface through which heat enters the system after the sun's direct rays are diffused by a fibrous alumina mat. Chemical vapor deposition of SiC has been achieved by the pyrolysis of methyl trichlorsilane. The properties of this pyrolytic coating on graphite-coated nuclear fuel particles have

been investigated (13). Both oxidation resistance and mechanical durability appear to be satisfactory for the heat storage application.

SiC has a high heat of formation. It is unlikely to be attacked below 1000°C by any of the ingredients in the heat storage list, including Ca. For the reasons cited, this material is being studied as the most promising candidate for containing the eutectic alloys, in spite of the difficulty in shaping samples. Its brittleness will limit design options, but its great strength should help prevent failures.

3. Surface-Coated Iron Alloys

Iron is the cheapest and most plentiful metal, possessed of excellent ductility, capable of being strengthened in various ways for use to moderately high temperatures. Unfortunately, it dissolves in or reacts with nearly all of the elements in this heat storage program to at least some extent. Iron-base alloys can be fabricated by welding. This technology for their production and fabrication is widely available.

In order to overcome the tendency of iron to react with the heat storage alloys and oxygen, heavy alloyed iron can be treated on its surfaces in the hope that a surface layer can be formed that is slow-growing and protective in contact with the eutectic liquids. One of the procedures under consideration is the development of a SiC coating on a Si-rich steel by reactive chemical deposition from the gas phase analogous to the procedure used to coat nuclear fuel particles (13). Although this path is still open, it appears less likely to succeed quickly than the use of bulk SiC, which will be pursued first.

IV. System Considerations for the Use of Alloy Eutectic Storage

Alloy eutectic storage is likely to be used only above 670V. The high thermal conductivities of alloys relative to those for salts favor application for high heat flux densities and to short term and intermediate term storage. Also the compatibility of alloys with graphite, and presumably with silicon carbide, should make them readily adaptable tc graphite-moderated nuclear reactors and to solar receivers that use silicon carbide surfaces to withstand the high temperatures generated by focussing solar reflectors. The isothermal nature of the eutectic transformation and the high energy storage density suggest industrial furnace control applications. Sketches are given here to illustrate two simple examples.

A small-scale solar receiver to be mounted at the focus of a parabolic dish is shown in Fig. 1a. Sodium heat pipes serve to remove heat rapidly from the irradiated receiver surface and transfer it to a salt storage system. With a large condenser area per unit volume of salt the low thermal conductivity of the salt can be matched to the high heat flux at the receiver surface. An alternative system which appears to be much simpler uses alloy eutectic storage to cool the receiver surface directly, as shown in Fig. 1b. Both systems heat the working fluid for the generator through heat exchanger tubes passing through the storage chamber. Fig. 1a resembles the system being developed by the Jet Propulsion Laboratory, California Institute of Technology. Fig. 1b is similar to the scheme in use by a commercial Omnium-G 10KWe solar receiver—generator system (3). With a small shift in operating temperature

of the latter system, the Al-0.12Si-0.051Mg alloys developed in
this program can increase the energy storage density and extend
the operating period. Material changes would also be incorporated
to increase the life of the container. A second PCM transforming
at a lower temperature could be used in a preheater-precooler
chamber if the working fluid is to be used at a lower temperature
than the transformation temperature of the primary storage medium.

Figure 2 illustrates a furnace that might be used for
homogenizing aluminum alloys prior to age hardening or austenitizing
steels in preparation for quench hardening. The operating temper-
ature, hence the storage material, would differ for these cases,
but the operating principle is the same. Energy could be supplied
from an external source during off-peak hours by electrical resis-
tance heating or by burning gas. Conversion of eutectic solid to
liquid stores heat but does not increase temperature. Input is
cut off when the PCM is nearly melted. The temperature is main-
tained by reverse transformation during peak load periods on the
central energy supply system without demand on that external
source. A simple device needs to be developed, probably based
on electrical resistivity or volume change as the indicator
property, to signal the approaching end of the melting and
freezing cycles. Alternatively temperature rise or fall after
complete melting or freezing might be used. The only other
procedure for regulating on and off periods would seem to be
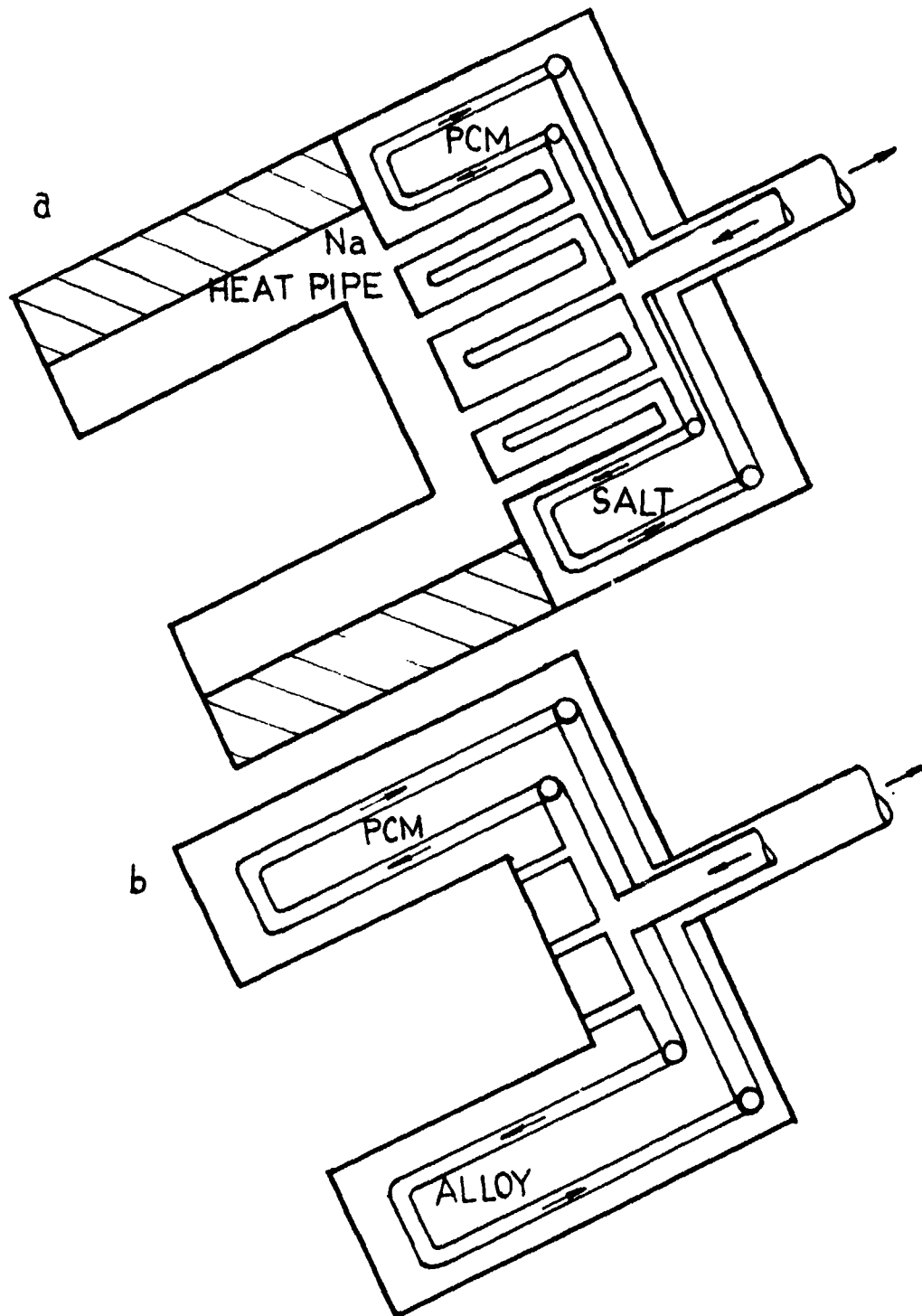continuous energy monitoring.

Figure 1a.   Solar receiver surface cooled by sodium heat pipe
             transmitting heat to salt storage (JPL concept).
       1b.   Direct cooling of receiver surface by storage alloy
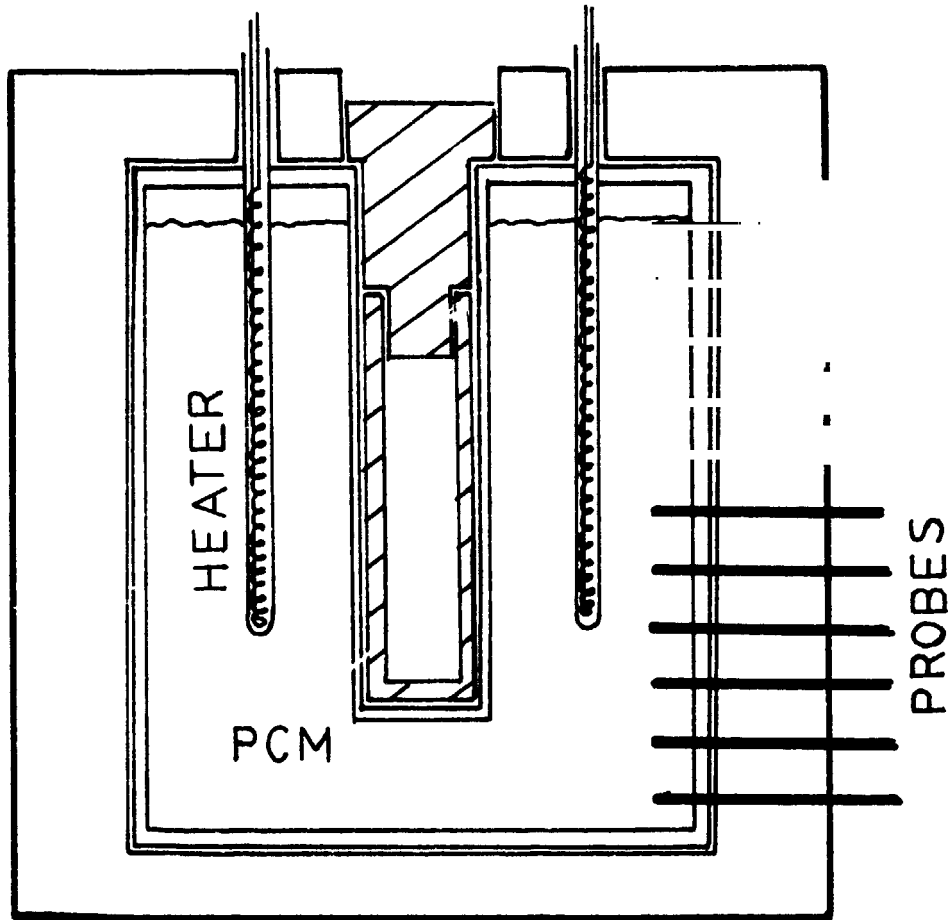   (Omnium-C Delaware concept).

Figure 2.   Small industrial furnace with PCM heat storage and
            temperature regulation.

References

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2. A 0.25 MW_t solar receiver that incorporates a gas-cooled SiC honeycomb has been tested by Sanders Associates, Inc., Nashua, N. H., (A. R. Poirier). A 1 MW_t bench model solar receiver has been designed at MIT/Lincoln Laboratory, Lexington, Mass. (P. O. Jarvinen), that includes a hemi-spherical SiC dome for direct irradiation. A Black and Veatch (P. O. Box 8405, Kansas City, Mo., E. McBride) design uses SiC heat exchanger tubes as secondary receivers after sunlight is diffused by an Al_2O_3 fibrous mat.

3. Ommium G, 1815 1/2 North Orangethorpe Park, Anaheim, California.

4. Dynatherm Corporation, Cockeysville, Md. (W. Bienert) has designed a heat pipe to interpose between the high thermal flux of a solar receiver surface and a heat transfer gas. Storage was not a part of that concept.

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