HEAT STORAGE IN ALLOY TRANSFORMATIONS*

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SUMMARY

Heats of transformation of eutectic alloys have been measured for many binary and ternary systems by differential scanning calorimetry and thermal analysis. Only the relatively cheap and plentiful elements Mg, Al, Si, P, Ca, Cu, Zn were considered. A new method for measuring volume change during transformation has been developed using x-ray absorption in a confined sample. Thermal expansion coefficients of both solid and liquid states of aluminum and of its eutectics with copper and with silicon also were determined. Preliminary evaluation of containment materials lead to the selection of silicon carbide as the initial material for study. Possible applications of alloy PCMs for heat storage in conventional and solar central power stations, small solar receivers and industrial furnace operations will be examined.

RESEARCH PROGRAM

The initial purpose of this work was to identify alloys that transform by the eutectic mechanism or by congruent melting and that have sufficiently large heats of transformation to be considered for heat storage applications. Where good precision of calorimetric measurement could be achieved, heat capacities of the solid and liquid states were also desired. Because the volume change during transformation was considered to be important for the design of a reliable and efficient storage system, a new method based on x-ray absorption was devised, to be tested and refined for the study of this property. It was recognized that the cost of containment is likely to determine the feasibility of using heat storage systems in various applications, so the emphasis in the program is shifting toward this problem. Although it would suffice to find container materials to hold specific alloys in their appropriate temperature ranges, silicon carbide is to be investigated as a material that might serve for all alloys studied over the whole temperature range.

As alloy characteristics are defined by measurement it becomes possible to develop realistic models for system applications. Modeling should permit cost comparisons of alloy storage with molten salt storage for the same overall system operating parameters. Also some estimates of the feasibility of using heat storage on an absolute basis should be possible for some applications that offer no technical difficulties. Work of this sort is being initiated and the emphasis on it will increase.

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RESULTS TO DATE

The quantitative measurements are summarized in Tables 1 (heat of transformation and heat capacity) and 2 (volume change during melting and coefficients of thermal expansion). For alloys that transform below 970K the thermal measurements have been made by differential scanning calorimetry (DSC) with an estimated precision of 3 pct. for heats of transformation and 10 pct. for heat capacities. Alloys that transform at higher temperature have been measured by differential thermal analysis (DTA) with an estimated precision of about 5 pct. for heats of transformation. Work is in progress to attempt to improve the heat capacity measurements in the high temperature range.

The alloys with underlined compositions are the best in their respective temperature ranges. Between 779 and 852K the alloys do not appear to have competition from other materials when comparisons are made on either a mass, or especially a volume, basis. The Si-Mg eutectic at 1219K is likely to be most advantageous for any applications in that temperature range. Below 608K metallic storage does not appear to be feasible without the use of more expensive metals such as Pb, Sn, Bi and Sb. Inorganic salt eutectics are much more likely to be used in this range.

The volume change measurements show that the aluminum eutectics expand about 5 pct. on melting, in contrast with some salts which expand more than 20 pct. The 7 pct. expansion of pure aluminum is likely to be close to the maximum among the alloys being considered for heat storage applications.

The volume change measurements reported were done by absorption of x-rays from a conventional generator for an x-ray diffraction apparatus. The characteristic K_α radiation from a copper or molybdenum tube was selected using absorption filters and an energy dispersive counting system with discriminator or by using a graphite crystal monochromator at the source with the same detector system. A new system offering greater stability and simplicity with some sacrifice in intensity has been assembled in which AgK_α radiation from radioactive Cd 109 is the x-ray source. With this simpler system it is anticipated that higher furnace temperatures can be achieved because the furnace does not have to fit on a diffractometer track.

WORK IN PROGRESS

A few additional alloys are to be melted in search of new ternary or quaternary eutectics or congruently melted intermetallic phases. Newly discovered ternary eutectic alloys in the Mg-Cu-Ca and Mg-Si-Cu systems and a new ternary intermetallic phase in Cu-Si-P will have their heats of transformation determined by calorimetry. The only additional calorimetric measurements that are planned are checks on values that do not appear to be consistent with expectations or in which errors may have arisen owing to vapor losses of one of the components

The volume measurements will be extended to cover the most promising eutectic systems. It is anticipated that the casting of pore-free samples is the most difficult and critical step in the procedure. Several other metals and possibly some eutectic salts will be measured for comparison.

SiC test plates are being prepared for determining chemical compatibility with the eutectic alloys. Wetting angles, weight loss and the structures of phases that grow at the interface will be considered in assessing the suitability of this material. Some conventional high temperature alloys also will be tested for comparison. Later the preparation of alloys with coated surfaces will be attempted if the need remains.

APPLICATIONS APPRAISAL

Heat storage might offer economic advantages for applications at several size levels. Only those applications whose storage might be done between 670 and 1220K will be considered. The following types of systems applications will be surveyed: 1. Storage to level the heat generating rate of fossil- or nuclear-fueled central power stations. 2. Short term storage to regulate the temperature of solar receiver surfaces and long term storage to match solar input to output demand. 3. Storage with temperature regulation by the transformation in industrial furnaces. 4. High temperature storage of heat for home comfort control.

The purpose of 1 is to improve heat generating efficiency of central power stations. However, the need for load-following electrical generating capacity would not be eliminated. The system load might be leveled if enough distributed heat storage of type 3 could be installed. Solar receivers, large or small, must absorb heat at high flux density during periods of high insolation. They require short term storage to smooth the fluctuations in solar radiation intensity and long term storage to supply energy at night and during periods of dense cloud cover. Industrial furnaces often are operated isothermally, a condition supplied naturally by eutectic storage. The problem in this application is a simple, reliable detector to signal when the alloy is nearly completely melted or nearly completely frozen. Economy might be achieved in this application if energy is taken during off-peak periods for use during peak-load periods when labor is likely to be cheaper. The benefit from alloy storage for home comfort conditioning must come from the large reduction in storage volume when compared with storage in hot rocks or water.

One or more specific cases will be chosen for engineering evaluation of the potentialities of alloy storage. It appears that the industrial furnace storage and control and solar receiver storage may be the most favorable cases at this stage of development of the alloy storage technology. However, only a few preliminary calculations have been done.

CONCLUSIONS

Eutectic alloy systems with good volumetric heat storage density have been demonstrated for the temperature range 670 to 1220K. The volume changes during transformation appear to be near 5 pct. The alloys that do not contain Ca appear to be compatible with graphite as a container material. SiC should be less reactive, stronger and a better heat conductor. Containment in coated alloys also may be practical.

Heat storage in alloy transformations should be technically feasible for a wide range of applications. Studies are being started to determine which are likely to be the most favorable applications economically for the present state of understanding.

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 1.621
Al-0.375Mg	724	376	310	
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_2Cu	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	1219	1212	805	

*By Alan Riechman and Diana Farkas

Table 2. Density Changes During Melting for Al and Two Al-Eutectic Alloys. Linear (Solid) and Volumetric (Liquid) Expansion Coefficients.*

Material	Temp. °C	Density kg/m^3	$\frac{\Delta V}{V_s}$	Linear Expansion Coeff. (Solid), K^{-1}	Volume Expansion Coeff. (Liquid), K^{-1}
Al	20(s) 660(s) 660(l) 760(l)	2690 2558 2377 2343	0.072	2.77×10^{-5} (20 to 660°C)	9×10^{-5} (660 to 760°C)
Al-17 at. pct. Cu	20(s) 548(s) 548(l) 748(l)	3506 3424 3258 3186	0.051	1.5×10^{-5} (20 to 548°C)	1.1×10^{-4} (548 to 748°C)
Al-12 at. pct. Cu	20(s) 579(s) 579(l) 779(l)	2626 2553 2445 2382	0.048	1.7×10^{-5} (20 to 579°C)	1.3×10^{-5} (579 to 679°C)

*Measured by Andrew Harrison and Silvia Balart