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ABSTRACT

Heats of formation of gold-zinc alloys of compositions Au_3Zn and AuZn were measured at several temperatures by liquid tin solution calorimetry. The data for Au_3Zn show that much smaller heat and entropy effects are associated with the $\alpha_2 \rightarrow \alpha_1$ transformation than for the $\alpha_1 \rightarrow \alpha$ transformation. This result is consistent with reported X-ray diffraction studies which indicate that the α_1 and α_2 phases have ordered structures which only slightly differ, whereas the α phase is disordered. The heat of formation of AuZn(β') does not change significantly between 322° and 800°K, confirming that the β' alloy remains highly ordered to high temperatures.

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Not many measurements have been made of the energies of order-disorder transformations in alloy phases. In many cases these energies may be conveniently determined by measuring heats of formation as a function of temperature. Many alloy phases approximately obey Kopp's law of additivity of heat capacities; as a consequence their heats of formation do not change with temperature. In ordered alloys, however, a decrease in degree of order with increasing temperature will contribute an endothermic component to the heat of formation. Thus, for ordered phases where other anomalous contributions to heat capacity in the alloy or its pure components are absent, a measured change in the heat of formation may be attributed to the energy of disordering.

A portion of the Au-Zn phase diagram[1,2] is shown in Fig. 1. The composition AuZn(β') has a well-ordered superlattice structure of the CsCl type at room temperature. The alloy is considered to remain ordered to its melting point;[1] although from X-ray diffraction data and emf measurements of zinc activities, Terpilowski[3] concluded that considerable disordering began at ~673°K.

The Au_3Zn composition is a disordered fcc solid solution (α) at high temperatures. Between 693° and 543°K, the alloy orders to form the α_1-phase, having a structure based on the $L1_2(AuCu_3)$ type, but with a regular distribution of ordering faults in the c-direction, making it tetragonal. Below 543°K, the alloy orders further by means of slight atomic shifts, without diffusion, yielding a complex long-period orthorhombic superlattice structure, α_2.[4-7]

Heats of formation of $Au_3Zn(\alpha_2)$ and $AuZn(\beta')$ were measured at 363°K by Biltz et al.[8] by aqueous solution calorimetry. Heat capacities of several alloys between 14.9 and 38.4 at. pct zinc in the range from 373° to 723°K were measured by Iwasaki et al.[6] Stoichiometric Au_3Zn, however, was not included in the alloys measured, the nearest composition being 26.1 at. pct zinc. Also, the heating rate used for the measurements, 2 deg/min, may not have permitted equilibrium to be reached in the neighborhood of the transformations. Heat contents of solid and liquid AuZn were measured between 488° and 1138°K by Kubaschewski.[9]

It was decided to determine the ordering energies of Au_3Zn and to check on the possible disordering of AuZn by measuring the heats of formation of these alloys at several temperatures. The present paper reports measurements by liquid tin solution calorimetry of the heats of formation of the three phases of Au_3Zn at temperatures within their regions of stability, and of AuZn at a low (322°K) and a high (800°K) temperature.

EXPERIMENTAL

Alloy Preparation and X-ray Examination. Ten gram ingots of Au_3Zn and AuZn were prepared by melting weighed amounts of gold (99.95 pct Au) and zinc (99.99 pct Zn) together in sealed evacuated Vycor tubes at 1060°K, followed by rapid quenching. The resulting ingots were homogenized at 900°K for 10 days. The Au_3Zn alloy lost no weight in preparation; the loss from the AuZn alloy was enough to introduce an uncertainty of only 0.1 at. pct in its composition.

Filings for X-ray examination were taken from various parts of each ingot and strain annealed at 723°K for 20 min in vacuo. The Au_3Zn filings were quenched rapidly to retain the disordered phase. Diffraction patterns were determined with an X-ray diffractometer using copper $K\alpha$ radiation.

Diffraction patterns for both samples were very sharp with well resolved back reflection peaks, indicating the homogeneity of the alloys. The pattern for the quenched Au_3Zn sample showed it to have the fcc structure of the α-phase alloy; no superlattice lines were present. The lattice constant found, 4.046Å, was in fair agreement with that determined by Raub et al.[10], 4.039Å, but was considerably higher than the value reported by Owen and Roberts,[11] 4.028Å. The AuZn sample pattern corresponded to that for a CsCl superlattice structure with a lattice constant of 3.148Å.

In order to develop the α_2 phase, the Au_3Zn ingot and filings were heated in vacuo at 600°K for 2.5 hours followed by slow furnace cooling. The diffraction pattern showed excellent agreement with reported data[4,7] for the ordered orthorhombic structure.

Calorimetry. Heats of solution of gold, zinc, and the alloys in liquid tin were measured using the calorimetric apparatus and methods described previously.[12] Specimens weighing about 0.75 g were prepared by enclosing cuttings of the alloys or pure metals in gold foil capsules. The pure metals and the $Au_3Zn(\alpha_2)$ alloy specimens were dropped from an initial temperature, T_i, of about 330°K into the tin solvent bath at approximately 600°K, T_f. In order to develop the α_1 and α phases, specimens of Au_3Zn were held at temperatures of approximately 594° and 798°K, respectively, for periods

up to 21 hours, then dropped from these temperatures into the bath. Specimens of AuZn(β') were held at ~322° and ~800°K prior to adding them to the bath. The average solution time for each of the alloys was about 10 min.

The heat capacity of the tin bath was measured at regular intervals by dropping specimens of pure tin and using tabulated heat content data.[13] The tin bath was changed when the solute concentration reached 1.5 at. pct.; within this range, concentration effects were found to be negligible within the experimental scatter. The runs were made in an argon atmosphere in order to reduce the rate of zinc evaporation from the tin bath, which proved to be inappreciable under these conditions.

RESULTS

The measured heat effects are given in Table I. From the data for the pure metals and tabulated heat content data,[13] heats of solution of the solid elements for $T_i = T_f = 600°K$ were calculated, yielding average values of -5441(±16) cal/g-atom for gold and 3938(±14) cal/g-atom for zinc. The data for gold were corrected for the small differences between the actual solution temperatures and 600°K using the value of $\Delta\bar{C}p_{Au(x_{Sn}=1)} = 4.2$ cal/deg g-atom.[13] No such correction was required for zinc, since $\Delta\bar{C}p_{Zn(x_{Sn}=1)} = 0$.[13]

Heats of formation of the alloy phases at their initial specimen temperatures, T_i, were obtained by subtracting the heats of solution of the alloys from those of corresponding amounts of the pure metals between the same initial and final temperatures. The latter values were calculated

from the average heats of solution of gold and zinc at 600°K, tabulated heat content data,[13] and the value of $\Delta\bar{C}p_{Au}$ referred to previously. Values above the melting point of zinc, 692.7°K, have been referred to superheated solid zinc assuming a constant value for the heat of fusion, 1765 cal/g-atom.[13] Resulting heats of formation are given in Table II. Values given in parentheses are the mean deviations of the measured values. Absolute uncertainties of the average values are estimated to be of the order of ±50 cal/g-atom.

DISCUSSION

The value reported by Biltz et al.[8] for the heat of formation of both the α_2 and β' phases, -5500 cal/g-atom, differs considerably from those found here. Since their data were obtained by aqueous bromine-bromide solution calorimetry, they are not likely to be highly accurate.

Differences between the heats of formation of the three modifications of Au_3Zn yield the heats of transformation given in Table III. Although the transitions occur over ranges of temperature, as shown by the Cp data of Iwasaki et al.[6], entropies of transformation have been approximated by referring these heats to the respective critical temperatures. The resulting values, which are lower limits of the actual entropies of transformation, are also listed in Table III.

The small values of ΔH and ΔS associated with the $\alpha_2 \rightarrow \alpha_1$ transformation are consistent with the conclusions of the X-ray diffraction studies,[4-7] which indicate only a slight difference in the ordered structures of the two phases. Much larger values result from the disordering of the α_1 phase, as would be

expected. For the overall disordering process, $\Delta H_{\alpha_2 \rightarrow \alpha} \approx 632$ cal/g-atom and $\Delta S_{\alpha_2 \rightarrow \alpha} \approx 0.95$ cal/deg g-atom, which compare favorably with the corresponding values reported by Iwasaki et al.[6] for a 26.1 at. pct zinc alloy, 700 cal/g-atom and 1.01 cal/deg g-atom, respectively. Those investigators did not report a separate value for the $\alpha_2 \rightarrow \alpha_1$ transformation, but their $\bar{C}p$ curve for the 26.1 at. pct alloy yields an approximate value of $\Delta H_{\alpha_2 \rightarrow \alpha_1} = 150$ cal/g-atom, which, when subtracted from their total value of 700 cal/g-atom, yields $\Delta H_{\alpha_1 \rightarrow \alpha} = 550$ cal/g-atom. According to Iwasaki et al.[6], the latter transformation is partially one of first order, with a latent heat effect of 145 cal/g-atom.

The approximate total disordering entropy of Au_3Zn calculated from the present data, 0.95 cal/deg g-atom, is only slightly less than the ideal configurational value, 1.12 cal/deg g-atom. The lower value found could well result from short-range order in the α phase, the existence of which is indicated by the anomalously high Cp values reported by Iwasaki et al.[6] for the 26.1 at. pct Zn alloy just above the $\alpha_1 \rightarrow \alpha$ transformation temperature. Of course, non-configurational factors may also contribute to the difference.

Within the experimental uncertainties, the present results show that the heat of formation of the β' phase does not change significantly between 322° and 800°K, in disagreement with the heat content data of Kubaschewski[9] for AuZn, which yield $(\Delta H_{800} - \Delta H_{298}) = 110$ cal/g-atom. The present results indicate the alloy to remain fully ordered to 800°K. This is consistent with earlier evidence that AuZn retains an ordered structure to its melting point[1] and contradicts the conclusion of Terpilowski[3] that considerable disordering begins at ~673°K.

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Table I. Measured Heats of Solution in Liquid Tin

Solute	T_i, °K	T_f, °K	$\Delta H_{sol'n}$ cal/g-atom
Au	329.0	598.5	-3758
	330.5	602.1	-3720
	333.5	602.1	-3780
Zn	330.9	602.0	5677
	333.2	602.0	5691
$Au_3Zn(\alpha_2)$	336.9	613.2	2767
	330.4	601.6	2712
	330.1	599.7	2655
$Au_3Zn(\alpha_1)$	594.4	607.2	1020
	592.9	599.9	933
$Au_3Zn(\alpha)$	796.8	607.6	- 982
	797.4	607.6	- 915
	799.2	600.4	- 892
	798.6	600.4	- 959
$AuZn(\beta')$	322.6	597.8	7156
	322.4	597.8	7127
$AuZn(\beta')$	798.4	597.7	4026
	801.4	597.7	4040

Table II. Heats of Formation of Alloys

$$(1 - x)Au_{(s)} + xZn_{(s)} = Au_{1-x}Zn_{x(s)}$$

Phase	T, °K	$\Delta H_{formation}$, cal/g-atom	
		Measured Values	Average
$Au_3Zn(\alpha_2)$	332	-4078, -4095, -4054	-4076(±14)
$Au_3Zn(\alpha_1)$	594	-4011, -3983	-3997(±14)
$Au_3Zn(\alpha)$	798	-3356, -3427, -3531, -3460	-3444(±52)
$AuZn(\beta')$	322	-6165, -6135	-6150(±14)
$AuZn(\beta')$	800	-6158, -6193	-6176(±18)

Table III. Approximate Heats and Entropies of Transformation of Au_3Zn

Transformation	T_c, °K	ΔH cal/g-atom	ΔS cal/deg g-atom
$\alpha_2 \rightarrow \alpha_1$	543	79	0.15
$\alpha_1 \rightarrow \alpha$	693	553	0.80

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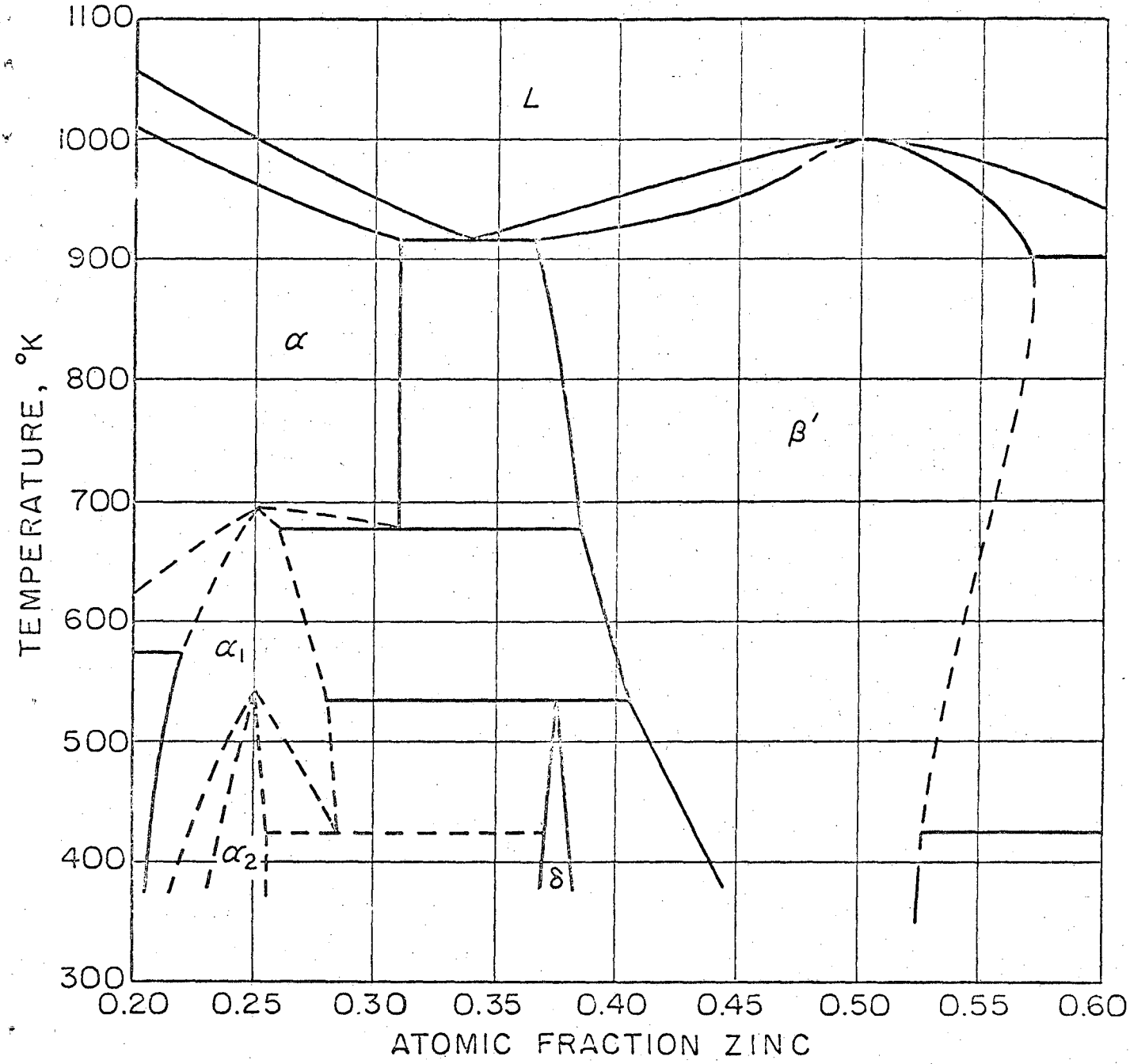

FIG. 1 PORTION OF GOLD-ZINC PHASE DIAGRAM.