Technical Report No. 5

to

Office of Naval Research

Contract Nonr 3963-(19) NR 031-706

The Metastability of Gold-Antimony Phases Prepared by Splat Cooling

by

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November 15, 1967

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Abstract

The metastable gold-antimony phases ζ containing 15.0 at. pct Sb and π containing 76.6 pct Sb were prepared by splat cooling. The heats of formation of these phases were measured by solution calorimetry and their free energies of formation were estimated. An analysis of the free energies of the relevant phases leads to the following conclusions. (1) The phases ζ and π are unstable at all temperatures. (2) Liquid alloys containing 15.0 pct and 76.6 pct Sb, respectively, must be undercooled by at least 150° and 200°K for the phases ζ and π to form. (3) The temperature below which the π phase can form (600°K) is about 250°K lower than the temperature below which the ζ phase can form. (4) Although the free energies indicate that the π phase is more unstable than the ζ phase, the calculated degrees of undercooling required and the calculated temperature of formation of the two phases indicate that the π phase is less difficult to produce by splat cooling than the ζ phase. This is in agreement with experimental observations.

INTRODUCTION

The splat-cooling technique for the rapid quenching of liquid alloys has made possible the preparation of many new phases.[1,2] Some of these phases can be retained only at liquid nitrogen temperature,[2] whereas some others do not decompose to any detectable extent up to temperatures of about $870^{\circ}K$.[3] Problems concerning the metastability of these phases are of considerable interest.

In the system gold-antimony, two new phases, ζ and π,[4,5] have been produced by splat cooling. A stable compound $AuSb_2$ also occurs in this system.[6] This compound has the FeS_2-C2 structure and decomposes peritectically at $723^{\circ}K$. The metastable ζ phase[4] contains about 13 to 15 at. pct antimony, has the Mg-A3 structure and can be considered as a Hume-Rothery phase with a valence electron-to-atom ratio of about 1.5. The metastable π phase[5] occurs between about 72 and 84 at. pct antimony and has the simple cubic α-Po-A_h structure, which can be derived from the structure of antimony. Figs. 1a and 1b show the gold-antimony phase diagram[6] and the metastable and stable phases which may be present in splat-cooled gold-antimony alloys.

In the investigation reported here the heats of formation of the ζ and π phases were measured in a solution calorimeter and their free energies of formation were estimated. Their thermodynamic stability is analyzed and some implications of this analysis for the splat cooling technique are considered.

EXPERIMENTAL PROCEDURES

Preparation of Specimens

Alloys for use as charge materials in the splat cooling equipment were made by melting weighed amounts of 99.999 pct pure gold and antimony in evacuated and sealed Vycor tubes. The tubes were shaken vigorously and quenched into water. Small quantities of the alloys were splat cooled onto copper substrates by the blast shock tube process described previously.(2) The substrates were cooled to a temperature between 80° and 120°K in order to increase the cooling rate at the end of the cooling curve. In each run flakes of splat cooled material weighing about 20 mg were produced. Larger quantities could not be produced in a single run without reducing the cooling rate of about $10^6 - 10^8$ °K/sec.(7) Since this rate was barely adequate for the retention of the ζ phase, a serious reduction in the yield would have ensued.

The alloys were brought to room temperature after splat cooling. They were stored at 78°K to prevent decomposition which would have been appreciable at room temperature. Batches of flakes weighing 1-2 gm were accumulated. Selected flakes were broken into finer particles, which were mixed for use by X-ray analysis and calorimetry.

An alloy containing 30 at. pct antimony was used for splat cooling to produce the ζ phase. In addition to this phase, however, the splat cooled product contained $AuSb_2$ and free gold. If the starting material contained 13 to 15 at. pct antimony, appreciable concentrations of ζ in the splat cooled alloys could not be produced. An alloy containing 75 at. pct antimony was splat cooled to produce the π phase. This phase was always associated with $AuSb_2$ and free antimony.

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X-Ray Diffraction

The fractions of the phases present in the mixtures produced by splat cooling were determined by quantitative X-ray analysis. An original mixture of phases α, β, γ ... and the same mixture to which a known amount of β has been added may be assumed. If the diffracted intensities of the two mixtures are measured under the same experimental conditions, the following equation holds:

$$w_\beta = \frac{A}{\xi - 1}$$

where w_β = weight fraction of β in the original mixture

A = (weight of β added to the original mixture)/(weight of the original mixture)

ξ = $[I'_{\alpha(h_1k_1\ell_1)}/I'_{\beta(h_2k_2\ell_2)}]/[I''_{\alpha(h_1k_1\ell_1)}/I''_{\beta(h_2k_2\ell_2)}]$

$I_{\alpha(hk\ell)}$ = integrated intensity of a peak due to the $hk\ell$ reflection of the α phase.

The original mixture is indicated by ' and the mixture to which β has been added by ''.

In alloys containing the ζ phase, the amounts of $AuSb_2$ were determined by the X-ray technique and the amounts of the free gold were calculated from a gold balance. The antimony content of ζ was assumed to be 15 at. pct.[4] In alloys containing the π phase, the amounts of free antimony and $AuSb_2$ present were determined by X-ray diffraction and the amount of π was found by difference.

Calorimetry

The heat effects on addition from 273°K of samples of a splat cooled alloy and corresponding mechanical mixtures of gold and antimony to a liquid tin-rich bath at 623°K were measured. The difference between these heat effects adjusted for changes in the composition of the bath is the heat of formation ΔH_{sp} of the splat cooled alloy at 273°K. The samples were wrapped in tin foil. Tin was also used for calibration; a value of 4.08 kcal/g-atom was adopted for $(H_{623^o} - H_{273^o})_{Sn}$.[8] The calorimeter and the experimental procedure have been described elsewhere.[9]

The heat of formation of a splat cooled alloy is given by:

$$\Delta H_{sp} = \sum_i X_i \Delta H_i$$

where ΔH_i is the heat of formation of the i phase and X_i is the fraction of i in the splat cooled alloy. From the values of X_i obtained from the X-ray analysis and the heat of formation of $AuSb_2$ of -1.04 kcal/g-atom,[10] the heats of formation of the ζ and π phases were calculated.

RESULTS AND DISCUSSION

Data pertaining to the X-ray and calorimetric experiments are listed in Table 1. The heats of formation of the phases present in splat cooled gold-antimony alloys are listed in Table 2. The positive values of the heat of formation of the ζ and π phases are consistent with their metastable nature. A large part of the spread in these heats of formation is due to the uncertainty of the amounts of the phases present in the samples.

The resulting error is estimated as $\pm$ 0.11 kcal/g-atom. The root-mean square random error of the calorimetric measurements is $\pm$ 0.04 kcal/g-atom. The approximate total error is estimated as $\pm$ 0.15 kcal/g-atom.

The results are confirmed by four additional experiments in which the amounts of the metastable phases present in the splat cooled alloys were determined in a different manner. The atom fractions of these phases were found by comparing the integrated intensities of the X-ray diffraction pattern of the sample under investigation with those of a splat cooled alloy, the composition of which had been determined by the X-ray method described above. The heats of formation of the ζ and π phases measured in these experiments were within 0.15 kcal/g-atom of the values listed in Table 2.

The Metastability of the ζ and π Phases

The relative stabilities of the ζ and π phases can be analyzed in terms of their free energies compared with those of the competing phases. The free energies of formation were calculated by assuming that the ζ and π phases obey the Kopp-Neumann rule and have a disordered structure.[4,5] Since only limited thermodynamic data are available for the compound $AuSb_2$,[8] its free energy of formation was estimated from the heats of formation at 273^oK[10] and 723^oK[8] by assuming the difference in the heat capacities of the compound and the component elements to be a linear function of temperature. The resulting equation for the free energy is

$$\Delta G = - 1.09 - 6.47 \times 10^{-7} T^2 \qquad \text{kcal/g-atom}$$

The free energies of formation at 298^oK of the stable and metastable phases in the gold-antimony system are plotted in Fig. 1c. The difference of the free energy of formation of a metastable phase and that of the mixture of stable phases at the same overall composition may be considered as a measure of the metastability of that phase. This difference is 0.68 kcal/g-atom for the ζ phase and 1.51 kcal/g-atom for the π phase (Fig. 1c). The π phase, therefore, may be considered to be relatively more unstable than the ζ phase. It should also be recognized that even if the compound $AuSb_2$ did not exist or were itself unstable, the ζ and π phases would be unstable with respect to gold and antimony.

The analysis of the instability of the ζ and π phases as a function of temperature involves the free energies of formation of the liquid alloys from the liquid elements. These free energies relative to liquid gold and liquid antimony $\Delta G_{(\ell)}$ of the alloy containing 15 at. pct antimony were calculated from the heat of formation of the liquid alloy containing 30 at. pct antimony[11] on the basis of the regular solution model.[12] The free energies of the alloy containing 76.6 at. pct antimony were estimated from the antimony-rich end of the phase diagram.[13]

$$\Delta G_{(\ell)} = -0.29 - 0.84 \times 10^{-3}T \quad \text{kcal/g-atom}; \quad x_{Sb} = 0.15$$

$$\Delta G_{(\ell)} = -0.20 - 2.0 \times 10^{-3}T \quad \text{kcal/g-atom}; \quad x_{Sb} = 0.766$$

The free energies of formation of the supercooled liquid alloys relative to solid gold and solid antimony were calculated by combining these equations with the heats of fusion and entropies of fusion of gold and antimony.[8] The free energies of formation relative to the solid components of the liquid alloys, the metastable phases and the equilibrium mixture of stable phases are plotted in Fig. 2. This plot shows that the ζ and π phases are unstable at all temperatures.

Formation of Metastable Phases by Splat Cooling

The free energies shown in Fig. 2 support two further conclusions. Alloys containing 15 at. pct and 76.6 at. pct antimony must be supercooled by at least 150° and $200^{\circ}K$, respectively, for the metastable phases ζ and π to form. Secondly, the temperature below which the π phase can form is about $250^{\circ}K$ lower than the temperature below which the ζ phase can form.

Since the ζ phase is expected to form by solidification from the undercooled liquid at a temperature about $250^{\circ}K$ higher than the corresponding temperature for the π phase, the preparation of ζ by splat cooling may be expected to be more difficult because of the greater difficulty of undercooling at the higher temperature. Furthermore, since the ζ phase can form at a temperature which is higher than the temperature at which the π phase can form, it may also be more difficult to prevent the decomposition of ζ during splat cooling. These considerations are consistent with the experimental observation that it is easier to produce the π phase by splat cooling a 75 at. pct antimony alloy than the ζ phase by splat cooling an alloy containing 15 pct antimony.

At room temperature several months are required for the complete decomposition of the ζ phase,[(4)] while the decomposition of π is complete in 6 to 14 days.[(5)] This difference in decomposition rates must result from factors other than the relative stabilities of the two phases, e.g., the rates of nucleation and growth of the equilibrium phases.

As shown by Fig. 1b, the ζ phase can be produced together with $AuSb_2$ by splat cooling alloys containing more than 15 at. pct antimony. With increasing antimony content, the free energy of the liquid and the liquidus temperature decrease. Since relatively small changes in the free energies of formation of the mixtures (ζ + $AuSb_2$) and (Au + $AuSb_2$) occur with increasing antimony content of the splat cooled material, both the undercooling required to produce the ζ phase and the temperature of formation of this phase are also reduced. It should be easier to produce the ζ phase by splat cooling starting material with an antimony content greater than 15 at. pct. This is borne out by this investigation, in which the ζ phase was produced by splat cooling an alloy containing 30 at. pct antimony.

If the preceding considerations are applied to the splat cooling technique generally as a means for producing metastable phases, it is apparent that a large undercooling temperature interval ΔT must be attained by inhibiting the formation of the equilibrium phase. Undercoolings of 150° and $200^{\circ}K$ calculated for the gold-rich ζ phase and the antimony-rich π phase, respectively, are large and can be compared with the maximum degrees of attainable undercooling of $230^{\circ}K$ for gold and $135^{\circ}K$ for antimony.[14] Since droplet size in undercooling is also important,[14] improvements in splat cooling equipment should be capable of producing droplets of smaller size than the diameter of 1 to 10 microns currently attained[7] and should provide microscopically smooth cooling surfaces to minimize heterogeneous nucleation.

The ζ phase containing 13 to 15 at. pct antimony has been prepared by splat cooling in equipment which employs a powder charge to generate the atomizing shock wave.[4] The inability to produce ζ from a charge of this composition with the blast shock tube process used in this investigation suggests that higher cooling rates can be attained by the use of a powder charge. The latter method, however, is less suitable for producing by repetition the sample quantities required for calorimetry.

CONCLUSIONS

The metastable ζ and π phases in the system gold-antimony were prepared by splat cooling. Their heats of formation, measured by liquid metal solution calorimetry, are positive. The free energies of formation of the metastable and relevant stable phases were estimated.

The following conclusions can be drawn:

(1) The ζ and π phases are unstable over their entire composition ranges at all temperatures.

(2) The free energy of formation of the ζ phase is positive and approximately half that of the π phase, indicating that π is relatively more unstable than ζ.

(3) By contrast, the ζ phase is more difficult to produce by splat cooling than the π phase, presumably because of kinetic factors.

(4) The production of the metastable phases ζ and π by splat cooling requires the attainment of undercooling temperatures, which are estimated to be of the order of 150° and 200°K, respectively.

ACKNOWLEDGMENTS

The authors thank Miss U. Wolff and Mr. L. I. Sudenfield for technical assistance. Financial support by the Office of Naval Research under Contract Nonr 3963-(19), NR 031-706 is acknowledged.

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Table I

Experimental Data for the Splat Cooled Gold-Antimony Alloys

Overall Composition of Alloys, at. pct Sb	Phases in Splat-cooled Alloys, at. pct					Metastable Phase	
	Free Au	ζ	$AuSb_2$	π	Free Sb	Composition, at. pct Sb	Heat of Formation, kcal/g-atom
30	1.6	68.9	29.5	-	-	15.0	+0.74
30	2.1	68.3	29.6	-	-	15.0	+0.61
75	-	-	35.0	59.0	6.0	77.4	+0.98
75	-	-	18.6	77.7	3.7	75.8	+1.08

Table II

Composition and Heat of Formation of the Phases Zeta, $AuSb_2$ and Pi

Phase	Composition, at. pct Sb	Heat of Formation, kcal/g-atom
ζ	15.0	+0.67 $\pm$ 0.15
$AuSb_2$	66.6	-1.04 $\pm$ 0.03*
π	76.6	+1.03 $\pm$ 0.15

* From Ref. 10

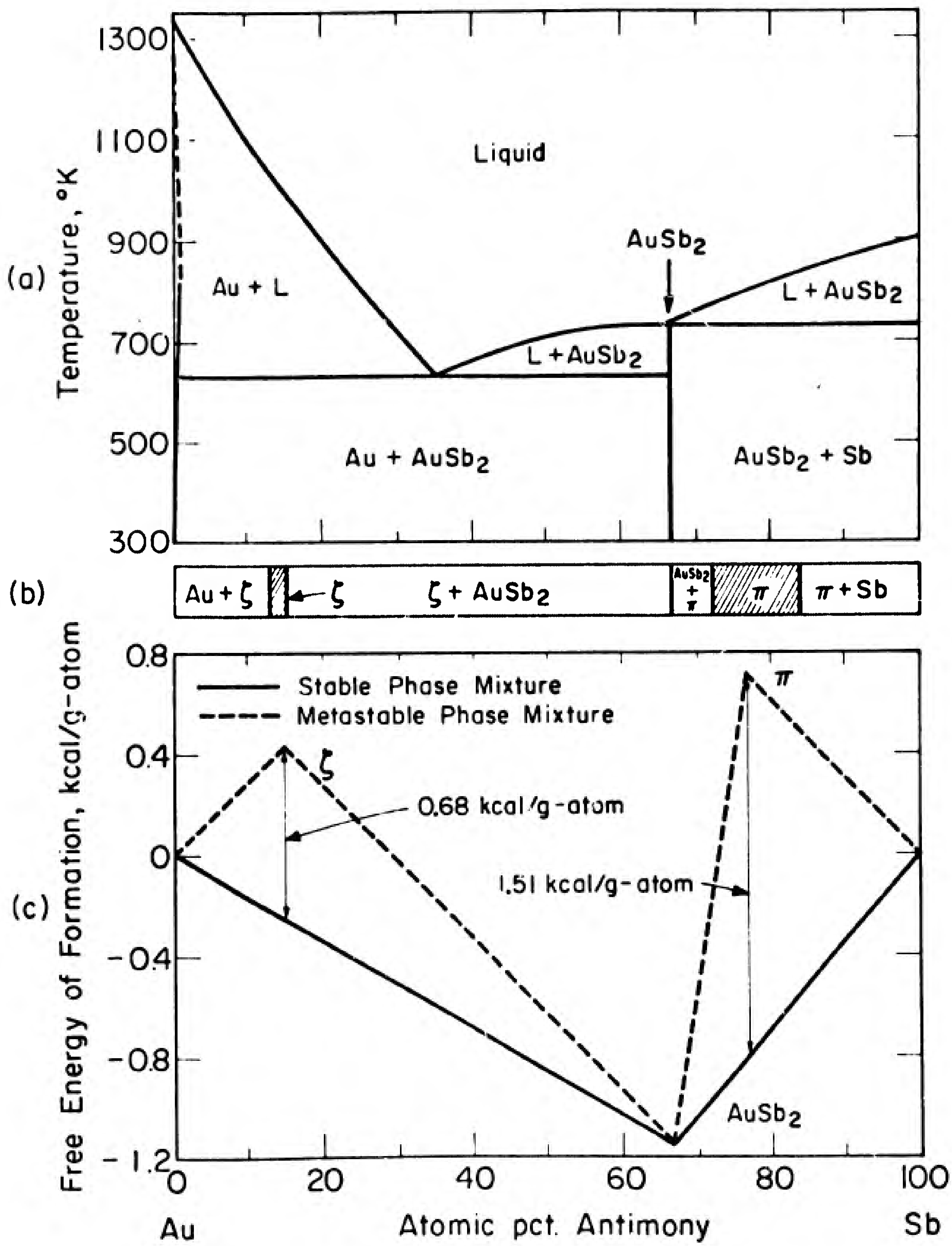

FIG. 1 (a) Stable Phases in the System Au-Sb.
(b) Metastable and Stable Phases Present at 298°K in the Splat Cooled Au-Sb Alloys.
(c) Free Energies of Formation at 298°K of Stable Phase Mixtures and Metastable Phase Mixtures in the System Au-Sb.

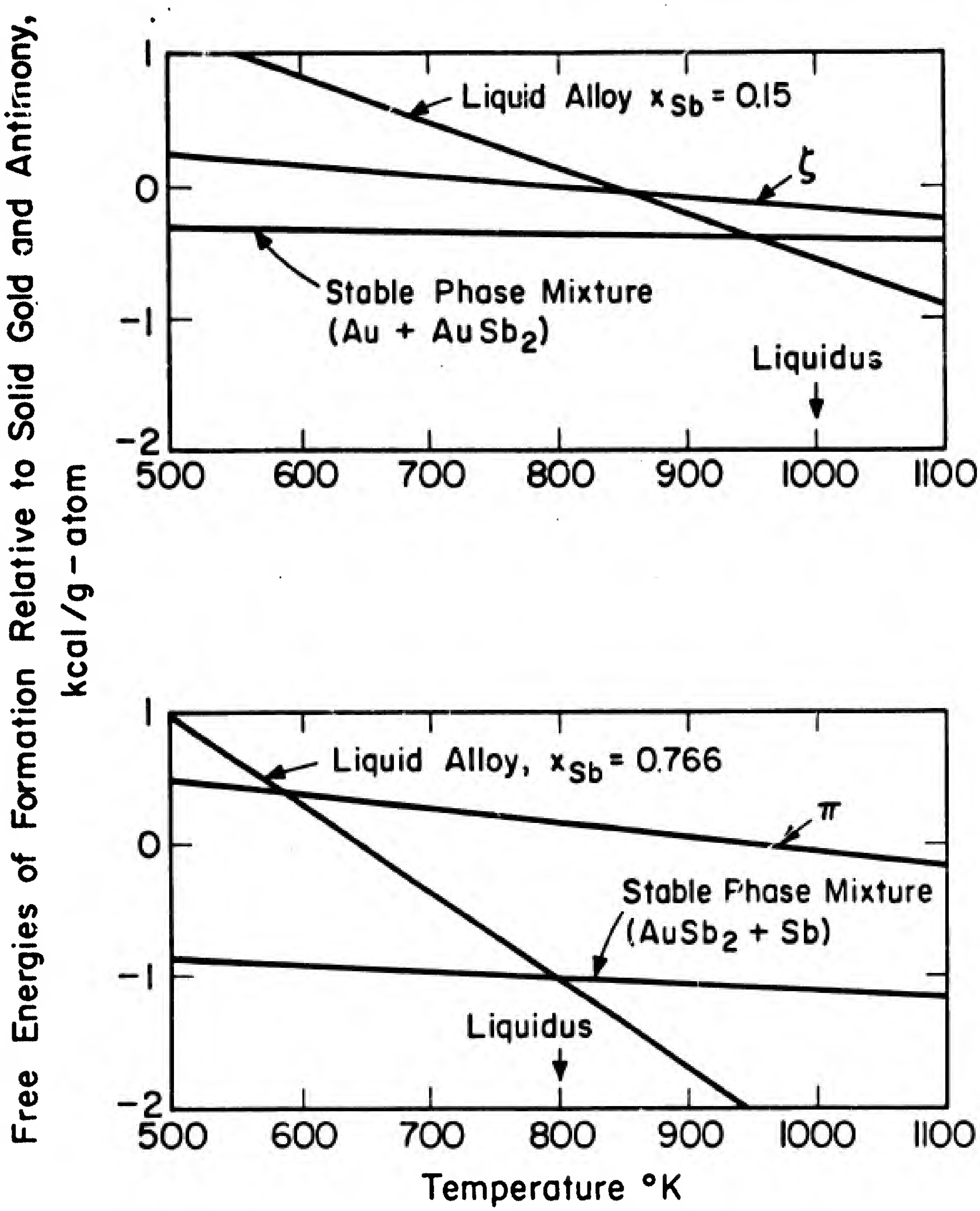

FIG. 2 Free Energies of Formation Relative to Solid Gold and Antimony of the Phases Zeta and Pi, the Liquid Gold-Antimony Alloys with x_{Sb} = 0.15 and 0.766 and the Corresponding Stable Phase Mixtures.

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1. ORIGINATING ACTIVITY (Corporate author) Department of Metallurgy Massachusetts Institute of Technology	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP Not applicable

3. REPORT TITLE

THE METASTABILITY OF GOLD-ANTIMONY PHASES PREPARED BY SPLAT COOLING

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Technical Report No. 5

5. AUTHOR(S) (Last name, first name, initial)

Jena, A. K., Giessen, B. C., Bever, M. B., and Grant, N. J.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 15, 1967	14	14

8a. CONTRACT OR GRANT NO. Nonr 3963-(19) b. PROJECT NO. NR 031 706 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 5 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

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