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An X-Ray Study of the Binary Alloys of Silicon with Ag, Au, Pb, Sn, Zn, Cd, Sb and Bi

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The lattice constants of the binary alloys of silicon with silver, gold, lead, tin, zinc, cadmium, antimony and bismuth have been measured. It is shown that the lattice constants of the elements in these alloys are practically identical with those of the pure elements. This fact leads

to the interpretation that mutual solubility of the elements in these alloys occurs to only a very slight extent. It is further observed that silicon forms no compounds with any of these elements.

FOR each of the eight binary silicon alloy systems included in the present report, analogy with silicon alloys of closely related elements and, in at least one case, the earlier results of thermal and microscopic analysis would lead us to expect compound formation or appreciable ranges of solid solution or both. It was, therefore, surprising that not a single case of compound formation was observed in these alloys, and, further that in none of these systems was there a range of solid solution of sufficient magnitude to be detected by the method applied.

The method used in the present investigation was the determination of the lattice constants by means of the x-ray crystal structure analysis. The usual procedure for determining the limit of a solid solution range is to measure the lattice constants at several different compositions within the homogeneous solid solution range and then for the same phase when in equilibrium with the neighboring solid phase. By projecting this last value to the curve for the homogeneous range, the equilibrium composition can be established, frequently with a high degree of accuracy. Aside from the precision attainable in the measurement of the lattice constants, the accu-

racy of the method depends upon the difference in radii of the atoms concerned and the actual extent of the solid solution range. These two factors, however, are not entirely independent; general experience shows that if the atomic radii differ by more than about 10 percent, the solid solution range will be limited. The limit seems to be set by the amount of distortion caused by the foreign atoms which the lattice can withstand. This qualitative rule is subject to further restrictions due to influences which would cause positive deviations from Raoult's law or give rise to compound formation.

In the present cases, the usual procedure could not be applied because of the entirely insignificant changes in the lattice constants observed even when the neighboring solid phases were in equilibrium. The cameras used were of the Bohlin type as modified by Phragmén.¹ They were calibrated empirically with NaCl as the standard. Only the most deviated reflections of radiation from an iron target were used for calculating the lattice constants. The error for substances having cubic symmetry is certainly

¹ Westgren, Trans. Inst. Min. Met. Eng.; Inst. of Metals Div. 1931, p. 13.

not greater than $\pm 0.001A$; in the tetragonal and hexagonal systems, $\pm 0.001-0.002A$ for the smaller constant and possibly $\pm 0.003-0.004$ for the length of the c axis when this is more than $10A$.

As a first approximation, which is certainly sufficient for the present cases, we may assume that the change of the lattice constant is a linear function of the atomic composition and further that it may be calculated from the difference in the radii of the atoms concerned. The differences between the radius of the silicon atoms and the radii of the other atoms varies about 15 to 50 percent. Calculation shows that with the accuracy attainable in determining the lattice constants, solid solubility of one element in another in these alloys, amounting to 0.2 atom percent, should have been indicated with certainty, while for Si in Pb, Zn or Cd, as well as for Pb or Bi in Si the detectable limit is about 0.1 atom percent. As already noted, no solubility of this order was observed.

MATERIALS

Silicon of exceptional purity was supplied by the Electro Metallurgical Company through the courtesy of Dr. F. M. Becket. It had the following analysis: Si, 99.79 percent; Fe, 0.027; Al, 0.008; Ca, 0.014; C, 0.004; O₂, 0.002; N₂, 0.1; H₂, trace.

Bismuth: Merck's C.P. with total maximum impurities of approximately 0.04 percent.

Antimony and cadmium: Kahlbaum "Zur Analyse."

Gold and silver: Specially refined material from the U. S. Metals Refining Company, in each case 99.99+ pure.

Lead: Merck's C.P. with total maximum impurities amounting to 0.1 percent.

Tin: Baker's "Analyzed" with total metallic impurities of approximately 0.03 percent.

Zinc: Eimer and Amend, "Tested Purity" with total metallic impurities amounting to approximately 0.2 percent chiefly Pb and Cd.

PREPARATION OF ALLOYS

For each of the systems, alloys were made by at least two different methods. It was early realized that the miscibility of the two elements and the formation of sound and uniform ingots

might be seriously interfered with by the presence of thin oxide films, especially on the silicon. Accordingly it was attempted in each system to make at least one alloy at temperatures above the melting point of silicon, i.e., above 1420°C. This was successful except in the cases of zinc and cadmium. These elements when added to liquid silicon in a hydrogen atmosphere, boiled off completely; the alloys were, therefore, prepared by heating mixtures of the two elements just below the boiling point of zinc and cadmium respectively for several days.

In most cases, weighed amounts of the two elements were sealed off in an evacuated quartz tube, heated to the desired temperature and quenched; in the remaining cases melting was conducted in a hydrogen atmosphere. Microscopic examination of the ingots showed a relatively uniform distribution of the phases in each case. Filings of these ingots were then made and annealed in vacuo for several days or, in some cases, weeks to allow equilibrium to be reached. These final annealing temperatures are recorded in Table I. It is to be emphasized that every care was exercised, (1) to maintain the original purity of the materials, (2) to provide adequate opportunity for any reaction or solution phenomena to take place, and (3) to permit final equilibrium relations to be established.

RESULTS AND DISCUSSION

The experimental results are summarized in Table I. All results are included except those from photographs on which the lines did not permit accurate measurement or of alloys which had separated into two distinct layers before solidification. The main result has already been mentioned, namely, that no clear-cut evidence of solid solution was found and for none of the systems examined did the films contain lines other than these corresponding to the two elements of the system.

Arrivant² found silver to dissolve in solid silicon to the extent of 10 percent.³ The maxi-

² Arrivant, *Comptes Rendus* **147**, 859 (1908). Cf. L. Loskiewicz, *Congr. Intern. Mines* (Liege 22-28 June, 1930).

³ According to J. L. Haughton (personal communication) the original thermal diagram by Arrivant has been incorrectly reproduced in *Int. Crit. Tab.* **2**, 422.

TABLE I.

| Alloying element | % Si | Final anneal Temp. °C | Lattice Constants | |
|------------------|---------|-----------------------|---------------------------------|---------|
| | | | Alloying element | Silicon |
| | Pure Si | — | — | 5.4170 |
| Ag | Pure Ag | — | 4.0765 | — |
| | 5.0 | 825 | 4.0769 | 5.4174 |
| | 40.0 | 635 | 4.0765 | 5.4176 |
| | 40.0 | 635 | 4.0768 | 5.4186* |
| | 40.0 | 635 | 4.0771 | 5.4173 |
| | 40.0 | 825 | 4.0769 | 5.4181* |
| | 50.0 | 770 | 4.0764 | 5.4167 |
| | 70.0 | 635 | 4.0773 | 5.4175 |
| | 80.0 | 825 | † | 5.4176 |
| | 85.0 | 750 | 4.0761* | 5.4174 |
| Pb | Pure Pb | — | 4.9385 | — |
| | 50.0 | 130° | 4.9375 | 5.4156 |
| | 50.0 | 150° | 4.9382 | 5.4160 |
| Au | Pure Au | — | 4.0693 | — |
| | 50.0 | 240° | 4.0682 | 5.4176 |
| Sn | Pure Sn | — | <i>a</i> 5.8167 <i>c</i> 3.1728 | — |
| | 12.0 | 595° | 5.8156* | 3.1744* |
| | 50.0 | 150° | 5.8178 | 3.1728 |
| | 80.0 | 595° | 5.8151* | 3.1748* |
| Zn | Pure Zn | — | 2.6581 | 4.9341 |
| | 50.0 | 275° | 2.6578 | 4.9353 |
| Cd | Pure Cd | — | 2.9713 | 5.6046 |
| | 50.0 | 257° | 2.9709 | 5.6058 |
| Sb ¹ | Pure Sb | — | 4.295 | 11.247 |
| | 40.0 | 595° | 4.296* | 11.247* |
| | 50.0 | 580° | 4.297 | 11.243 |
| | 80.0 | 595° | 4.296 | 11.250 |
| Bi ¹ | Pure Bi | — | 4.535 | 11.836 |
| | 50.0 | 240° | 4.534 | 11.830 |

* Value uncertain due to poor lines.

† Lines present but too poor to measure.

¹ Reported in terms of hexagonal axes instead of usual rhombohedral axes.

mum solubility from the results of Table I would be of the order of 0.2 percent by weight.

For the antimony alloys, R. S. Williams⁴ found a solid solution of antimony in silicon up to 1 percent by weight and of silicon in antimony up to 0.3 percent. He also found that bismuth dissolved up to 0.8 percent of silicon. The present results indicate that the solubility of antimony in silicon is under 0.5 percent by weight. Rough calculation shows that the presence of 0.3 percent Si in antimony or 0.8 percent in bismuth would change the lattice constants

⁴ R. S. Williams, Zeits. f. anorg. Chemie 55, 1 (1907).

of these two elements by approximately 0.25 percent and 1.5 percent respectively and it is evident from Table I that no such change has occurred. A probable reason for the difference between the older results and the present is the greater purity of the silicon used in this investigation. The silicon used by Williams, for example, contained 0.95 percent Fe and 0.4 percent Al.

The failure to find any solubility in the Au-Si system agrees with the work of Di Capua,⁵ Tamaru's⁶ similarly negative results in Pb-Si and Sn-Si are also confirmed.

Note added in proof: In view of the facts (1) that the preparation of silicon of a high degree of purity has been developed only during the last few years and (2) that many of the binary alloy systems of metallic elements with silicon have not yet been systematically investigated, it is of some interest to inquire what metallic elements may be expected to form compounds or extensive solid solution with silicon. In this connection it is interesting to note that silicon has been observed to form compounds with all of the first twenty elements of the periodic system except its immediate neighbors Al and P, the rare gases, and the two alkali metals Na and K. In the case of Al a small range of solid solution of silicon in aluminum is observed at high temperatures. The alloys of the alkali and alkaline earth metals with silicon, excepting Li and Ca, appear not to have been studied. Of the metallic elements remaining in the periodic system, compound formation or extensive solid solution may be expected only in the alloys with transition elements, i.e., elements having incomplete inner electron shells (atomic numbers 21–28, 39–46, 57–78). The only thoroughly established exception to this statement known to the writers is copper and it has been observed by other workers that this element in alloys sometimes exhibits the behavior of a transition element. The basis for these generalizations was found chiefly in the results of x-ray structure analysis.

⁵ Di Capua; Atti della reale accademia nazionale dei Lincei 291, 111 (1920). Cf. L. Loskiewicz, reference 2, who finds that Si dissolves to a limited extent in Au.

⁶ S. Tamaru, Zeits. f. anorg. Chemie 61, 40 (1909).