An X-Ray Study of the Phases in the Silver-Zirconium System

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No structure determinations of the intermediate phases in the silver-zirconium system have been published earlier. In 1929 Sykes¹ prepared silver-zirconium alloys with a zirconium content up to about 33 at. % and reported the existence of a phase with a still higher zirconium content. He further stated that the solid solubility of zirconium in silver is very small. Raub and Engel² in 1948 published a constitutional diagram for the silver-zirconium system up to about 50 at. % zirconium. They could not detect any solid solubility of zirconium in silver by X-ray or micrographic methods and consider it to be less than 0.1 at. % at 900° C. Raub and Engel found an intermediate phase AgZr with a small homogeneity range. The powder photograph reflections indicated a tetragonal lattice with a structure probably similar to the CuAu superlattice. In an alloy with 61.6 at. % zirconium they found another intermediate phase with unknown composition.

EXPERIMENTAL

The starting materials for the preparations were zirconium, prepared by thermal dissociation of the iodide (Foote Mineral Co., Philadelphia) and silver prepared by reduction in solution according to a method given by Barth and Lunde³. The finely divided metals were carefully mixed and moulded into pastils. Specimens with a weight of about 1 g were melted in zirconia crucibles in a high-frequency vacuum induction furnace⁴ under a pressure of 10^{-4} — 10^{-3} mm mercury. Since silver as well as zirconium reduces zirconium dioxide at elevated temperatures, precautions had to be taken to reduce the contact area between the pastil and the crucible and to avoid excessive reaction temperatures. Melted samples were then heat-treated in sealed, evacuated silica tubes maintained at various temperatures up to 1100° C and quenched in cold water.

The phase analysis and structure determinations were made from powder photographs taken with CuK_α radiation in a Guinier-type camera using a curved quartz monochroma-

tor. For measurements of the high-angle reflections, additional photographs were taken with Phragmén-type focusing cameras. The intensities of the reflections were visually estimated, starting from 4:2:1 as the relative values of the intensities of $\text{CuK}\alpha$, $K\alpha_1$, and $K\beta$ lines. Relative values of $p|F|^2$ were calculated by means of the following expressions:

1. for the Guinier-type camera a formula calculated by Hägg⁵:

$$I = c \cdot \frac{1 + \cos^2 2\Theta \cdot \cos^2 2\Theta_m}{\sin^2 \Theta \cdot \cos \Theta} \cdot \frac{1}{\cos (2\Theta - \alpha)} \cdot e^{-\frac{\mu \cdot t}{2 \cos (2\Theta - \alpha)}} \cdot \left(1 - e^{-\frac{\mu_f \cdot h}{\cos (2\Theta - \alpha)}} \right) \cdot p|F|^2$$

where Θ_m = the glancing angle in the monochromator, μ_f = the linear absorption coefficient of the emulsion layer, and h = the thickness of this layer. The product $\mu_f \cdot h$ is determined experimentally.

2. for the Phragmén-type camera a formula given by Hägg and Regnström⁶.

Observed and calculated values of $p|F|^2$ are given in Tables 1 and 3.

Single crystals could not be obtained of any of the intermediate phases.

THE STRUCTURE OF THE PHASES

The α Phase. For pure silver the axial length $a = 4.080 \text{ \AA}$ ($V = 67.92 \text{ \AA}^3$) was determined. Powder photographs taken with alloys containing up to 50 at. % zirconium and quenched from different temperatures, showed α phase reflections whose lattice parameter did not vary. This agrees with the result obtained by Raub and Engel².

The β Phase. Reflections from a pure phase — the β phase — appeared in a powder photograph of an alloy containing 50 at. % zirconium which had been kept at 900°C for 10 hours. At temperatures between 900°C and 1100°C the alloy samples evidently reacted with the silica tube. The corresponding photographs showed a few weak extra lines which could not be indexed.

The photographs indicated a tetragonal cell for the β phase. The smallest dimensions (at 50 at. % zirconium) observed were $a = 3.468 \text{ \AA}$, $c = 6.603 \text{ \AA}$, $c/a = 1.904$ ($V = 79.41 \text{ \AA}^3$), and the largest dimensions $a = 3.476 \text{ \AA}$, $c = 6.629 \text{ \AA}$, $c/a = 1.907$ ($V = 80.08 \text{ \AA}^3$). If Vegard's law is assumed to be valid within this narrow homogeneity range this implies a width of the range of less than 3 at. %. The composition closely corresponds to the formula AgZr . With four atoms in the unit cell the density calculated of the composition AgZr is 8.33. The observed value was 8.20.

The absence of the $hk0$ reflections, for which $h + k = 2n + 1$, is characteristic for the space-groups $C_{4h}^3 - P 4/n$ and $D_{4h}^7 - P 4/nmm$. The phase is

Table 1. Observed and calculated $p |F|^2$ values for the a phase.

$h k l$	$p F ^2$		$h k l$	$p F ^2$	
	Observed	Calculated		Observed	Calculated
001	17	16	215	0	4.7
002	0	0.1	116	0	0.1
101	0	0.6	224	17	13
110	150	169	313	0	1.3
102	250	298	321	0	0.0
111	6	6.6	304	0	0.0
003	0	2.5	007	0	1.0
112	0	0.1	206	0	0.1
103	17	20	322	30	27
200	85	70	314	30	22
201	0	3.1	107	0	4.9
004	30	24	225	0	3.0
113	0	4.9	216	17	15
202	0	0.1	323	0	2.8
211	0	0.1	117	0	3.5
104	0	0.2	305	0	1.8
212	150	124	400	6	6.8
114	50	46	401	0	0.3
203	0	2.3	315	6	6.5
005	0	2.7	402	0	0.0
213	0	8.5	411	0	0.0
105	0	4.1	324	0	0.1
220	10	16	207	0	4.1
221	0	0.8	008	0	1.2
204	17	22	226	0	0.1
115	0	5.7	330	6	9.1
222	0	0.0	412	30	36
301	0	0.0	331	0	0.5
214	0	0.1	403	0	0.9
006	0	0.0	217	10	15
310	17	21	108	0	0.2
302	17	19	306	10	13
311	0	1.0	332	0	0.0
223	0	0.7	413	0	6.7
205	0	4.0	118	0	9.4
106	0	9.4	325	0	9.5
312	0	0.0	316	0	0.4
303	0	1.8	420	30	37

Table 2. Interatomic Distances in the β Phase. (50 at. % Zirconium.)

Atom	Surrounding Atoms	Interatomic Distance, Å
Ag in 2 (<i>a</i>)	4 Ag	2.812
	4 Zr	2.952
	1 Zr	3.037
Zr in 2 (<i>a</i>)	4 Zr	3.107
	4 Ag	2.952
	1 Ag	3.037

isomorphous with γ -CuTi⁶ and thus has a *B* 11 structure. The four atoms can be placed in only two two-fold positions 2 (*c*) : $0 \frac{1}{2} z : \frac{1}{2} 0 z$ in the space-group $P_{4h}^7 - P 4/nmm$. The best intensity agreement and the best distribution in space were obtained for the values $z_{\text{Ag}} = 0.105$ and $z_{\text{Zr}} = 0.645$. Calculated and observed $p |F|^2$ values are recorded in Table 1, and the values of interatomic distances may be found in Table 2.

It may be well to point out that attempts were made to prepare Ag—Zr—O alloys in order to ascertain the possible existence of metallic oxides of low oxygen content, analogous to the Cu—Ti—O system where the oxide Cu₃Ti₃O^{7,8} has been found. The starting materials were silver, zirconium and zirconium dioxide. At the melting point of silver a rather strong evolution of oxygen began to take place. Powder photographs proved this reduction process to be almost complete. The resulting X-ray pattern from the melt corresponded to the phases in the binary metal system. Only very weak extra lines were visible.

The γ Phase. Reflections from this phase appeared faintly in photographs taken with a specimen containing 60 at. % zirconium. But at the same time α -zirconium reflections appeared. Maximum intensity of the γ phase reflections was obtained with zirconium contents between 70 and 80 at. %. In spite of prolonged heat-treatments it was not possible to reach equilibrium or to obtain this phase pure. Photographs of an alloy with 85 at. % zirconium still contained very weak β phase lines.

The composition of the γ phase evidently corresponds closely to the ideal formula AgZr₃ and as a matter of fact the structure has been found to be isomorphous with the structure of CuTi₃ and CuZr₃⁷, which may be considered as a tetragonal deformed AuCu₃ (*L* 12) type. The smallest and largest dimensions observed were : $a = 4.566$ Å, $c = 3.986$ Å, $c/a = 0.873$ ($V = 83.10$ Å³)

Table 3. Observed and Calculated $p |F|^2$ Values for the γ phase.

$h k l$	$p F ^2$		$h k l$	$p F ^2$	
	Observed	Calculated		Observed	Calculated
100	1	0.5	320	0	0.0
001	0	0.2	222	10	13
110	1	0.3	113	10	12
101	1	0.4	302	0	0.0
111	150	131	321	0	0.1
200	50	51	312	0	0.1
210	0	0.2	203	0	0.0
002	17	18	400	6	4.4
201	0	0.2	213	0	0.0
102	0	0.1	410	0	0.0
211	1	0.3	401	0	0.0
112	0	0.1	331	6	6.8
220	17	22	420	6	6.8
300	0	0.1	004	0	1.7
202	50	42	402	6	6.6
221	0	0.1	313	10	12
310	0	0.1	204	6	5.1
212	0	0.1	422	10	10
301	0	0.1	511	10	9.9
311	50	42	224	6	5.4
003	0	0.0	333	6	5.5
103	0	0.0	440	0	3.6

and $a = 4.582$ Å, $c = 3.989$ Å, $c/a = 0.871$ ($V = 83.75$ Å³), indicating a homogeneity range of approximately 3 at. %.

The space-group of the γ phase is $D_{4h}^{17} - P 4/mmm$ with 1 Ag in $1(a) : 0 0 0$ and 3 Zr in $1(c) : \frac{1}{2} \frac{1}{2} 0$ and $2(e) : 0 \frac{1}{2} \frac{1}{2} ; \frac{1}{2} 0 \frac{1}{2}$. The observed and calculated $p |F|^2$ values for this structure are compared in Table 3. The interatomic distances of closest approach (8 coordination) are 3.030 Å and 3.038 Å, respectively at the lower and upper phase boundaries.

As the γ phase disappeared in photographs of specimens quenched from 800°C and higher temperatures this phase evidently only exists below this temperature. It was not possible to determine the exact decomposition temperature.

A survey of alloys of the composition $\text{Me}(1) \text{Me}(2)_3$ with $\text{Me}(1) = \text{Cu}$, Ag or Au and $\text{Me}(2) = \text{Ti}$ or Zr shows an interesting correlation between the

Table 4. Alloys $Me(1) Me(2)_3$ with $Me(1) = Cu, Ag$ or Au and $Me(2) = Ti$ or Zr .

Alloy		c/a	$r_{Me(1)}/r_{Me(2)}$
$CuTi_3$ ⁷	Tetragonally deformed $AuCu_3$ type	0.86	0.88
$AgTi_3$ ¹⁰	No homogeneous phase	—	0.99
$AuTi_3$ ¹⁰	$AuCu_3$ type	1	0.99
$CuZr_3$ ⁷	$CuTi_3$ type	0.82	0.82
$AgZr_3$	$CuTi_3$ type	0.87	0.92
$AuZr_3$ ⁹	No evidence of any phase of $CuTi_3$ type	—	0.92

axial ratio c/a and the radius ratio $r_{Me(1)}/r_{Me(2)}$ as is evident from Table 4. No phase $AuZr_3$ isomorphous with $CuTi_3$ exists although the radius ratio in this case is the same as in $AgZr_3$.

Zirconium-rich Alloys. In powder photographs from specimens with compositions between 75 and 100 at. % zirconium, no reflections indicating any new intermediate phase were visible.

For pure zirconium (α -Zr) the axial lengths were found to be $a = 3.227$ Å, $c = 5.142$ Å, $c/a = 1.593$ ($V = 46.09$ Å³). If the α -zirconium lattice is assumed to dissolved silver atoms in a solution of the substitution type, the cell volume may be expected to decrease. No such decrease was, however, noticed.

SUMMARY

The silver-zirconium system has been investigated by X-ray methods. Two intermediate phases have been found: β and γ with the ideal compositions $AgZr$ and $AgZr_3$. The ranges are narrow.

The structure of the β phase is of the $B11$ type (isomorphous with γ -CuTi) and that of the γ phase may be considered as a deformed $L12$ ($AuCu_3$) type (isomorphous with $CuTi_3$ and $CuZr_3$).

No solid solubility of zirconium in silver or of silver in α -zirconium could be detected.

The author wishes to express his gratitude to Professor G. Hägg for his encouraging interest in this investigation.

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Received February 7, 1952.