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TITLE: STRUCTURAL EXAMINATION OF IRIDIUM-BASED SINGLE-CRYSTAL PREPARATIONS

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STRUCTURAL EXAMINATION OF IRIIDIUM-BASED SINGLE-CRYSTAL PREPARATIONS

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INTRODUCTION

A high-temperature crystal growth experiment produced discrete single-crystal products of AlIr and IrSi. The preparation and examination of these phases is described within. This project is part of a materials compatibility study relating to radioisotopic heat sources. These heat sources are comprised of a PuO₂ fuel pellet encapsulated in an Ir alloy containment shell. Th is introduced as an additive within the Ir to maintain ductility.¹ Si and P are picked up inadvertently in the fuel processing. The compatibility of the heat sources with Al is of interest because of potential interactions with the Al alloy hardware associated with the heat source environment.

MATERIALS PREPARATION

Single crystal products were obtained utilizing a technique in which the reactants were dissolved in a molten metal flux. A similar technique is described by Meisner² in a previously reported work. The starting materials were Th metal with a minimum purity of 99.9%, red amorphous P with a minimum purity of 99.7%, hydrogen-reduced Cu powder with a purity of 99.36%, and Ir metal with a minimum purity of 99.9%.

The Th, Ir, P, and Cu were combined in a molar ratio of 1:1:1:15 with additional P added to achieve an 8.4 wt. percent with the Cu. The additional P extended the liquid range of the flux by achieving the eutectic³ composition within the Cu-P system. This provided a larger range of temperature for crystal growth. The materials were mixed thoroughly and then pressed into a pellet @ 5000 PSI. The pellet was then placed into an Al₂O₃ tube with the end packed with quartz wool and then sealed under vacuum. The sample was allowed to equilibrate at a maximum temperature of 1150°C for 24 hours. The furnace was then cooled at a rate of 1°C/h until the sample was down to 660°C. When the heating cycle was completed, the tube was opened and the Cu-rich matrix appeared as a dark friable material which was dissolved in nitric acid. Microscopic examination of the remaining material revealed discrete metallic crystals with two distinct habits. One was cubic in appearance and the other was a rectangular prism with faceted faces on each end.

PRODUCT ANALYSIS

X-ray precession photographs of cube-shaped crystals indicate that they are indeed cubic. The space group is $Pm\bar{3}m$. The refined lattice constant obtained from a Gandolfi film is $2.9867(1) \text{ \AA}$. The lattice constant and space group suggest a metallic CsCl structure type. This structure has an Ir atom at the corner of the cubic unit cell and an Al atom in the center of the cube at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Based on the crystallographic data obtained, this crystal was identified as AlIr. Previously published information⁴ on this compound confirms our identification. Elemental Al was made available in situ by the reduction of the Al_2O_3 crucible by Th. This is evident because of the relative stability of ThO_2 in respect to Al_2O_3 at the elevated temperatures of the experiment. The Gandolfi film clearly reveals weak lines of a second material which is identified as ThO_2 . Figure 1 is a SEM photograph (250 X magnification) of an AlIr crystal viewed approximately along the cube body diagonal. The surface contamination is ThO_2 .

A comparison between the observed and calculated intensities for the Gandolfi powder pattern of an AlIr crystal is given in Table 1. The observed intensities were obtained from visual estimates of the Gandolfi film. The calculated intensities for AlIr include the effects of absorption for a crystal approximately 0.1 mm in size.

X-ray precession photographs of the prismatic-shaped crystals revealed orthorhombic symmetry. Characteristic extinctions indicated space group $Pnma$. Refined lattice constants obtained from a Gandolfi film are $a = 5.4996(7)$, $b = 3.3052(9)$, and $c = 6.1857(13) \text{ \AA}$. The lattice constant ratios and space group suggest the IrSi structure as reported in the literature.⁴ X-ray fluorescence techniques applied to the single crystal revealed only the presence of Ir. Si cannot be detected by this method as fluorescence techniques are generally valid for elements heavier than Ca in the periodic table. The important point is that no heavy elements other than Ir were found. Elemental Si was made available in situ by the dissolution of the quartz wool into the metal flux and the subsequent reduction of the quartz by the Th metal. Figure 2 is a SEM photograph (350 X magnification) of a crystal of IrSi viewed approximately along the unit cell diagonal. It is of interest to note that the crystal faces are clean and well defined in contrast to Fig. 1 where the surface contamination was identified as ThO_2 .

The IrSi crystal has the B31 (MnP) structure type with the Ir atoms in the position set (4c) with $x = 0.005$ and $z = 0.20$. The Si atoms are also in the position set (4c) with $x = 0.19$ and $z = 0.57$. A comparison between observed and calculated intensities for the Gandolfi pattern of the material is given in Table 2. The observed intensities were visually estimated from the Gandolfi film. The calculated intensities are for position sets fully occupied. Corrections for absorption were not deemed appropriate for the small range of d spacings listed.

Although the lattice constants obtained in the current work are slightly different than the previously reported values⁴ we maintain that the material is IrSi. Other known compounds of Ir (aluminides, silicides, and phosphides) do not have the proper combination of axial ratios and space group to match our observed data.

ACKNOWLEDGMENT

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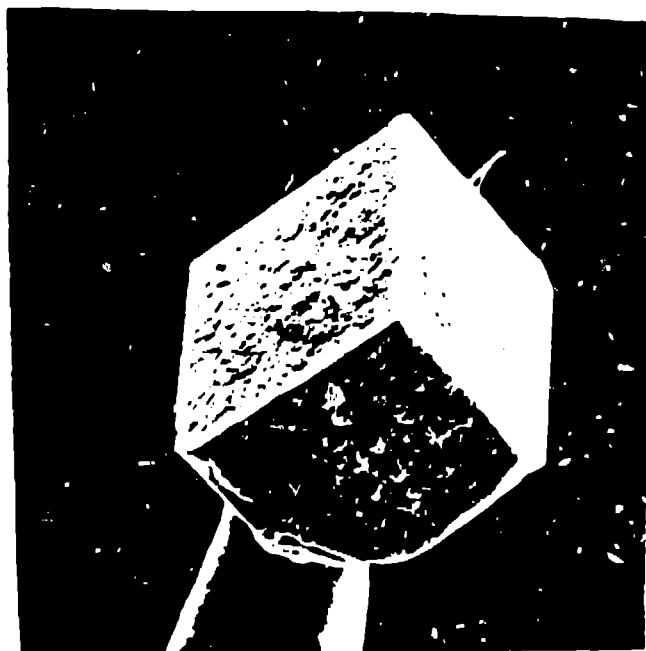


Figure 1. SEM photo of a crystal of AlIr viewed approximately along the cube diagonal. Surface contamination is ThO₂. See text for further details. 250 X.

Table 1. Comparison of observed and calculated intensities for AlIr. See text for details.

$d_{obs}, \text{\AA}$	$d_{calc}, \text{\AA}$	I_{obs}	I_{calc}	hkl
2.976	2.987	10	11	100
2.107	2.111	20	22	110
1.723	1.724	5	6	111
1.492	1.493	5	6	200
1.334	1.336	15	12	210
1.218	1.219	20	17	211
1.056	1.056	5	8	220
0.995	0.996	10	12	300,221
0.944	0.945	15	17	310
0.900	0.901	10	12	311
0.862	0.862	10	8	222
0.828	0.828	30	20	320
0.798	0.798	100	100	321

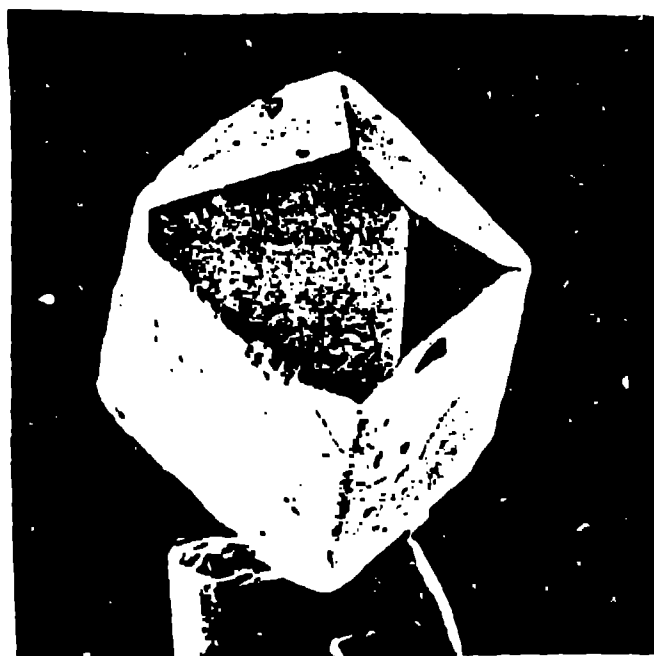


Figure 2. SEM photo of a crystal of IrSi viewed approximately along the orthorhombic unit cell diagonal. In contrast to Fig. 1 the surfaces are clean. See text for further details. 350 X.

Table 2. Comparison of observed and calculated intensities for IrSi. Only the low angle lines and intensities greater than 2% are listed. Intensities for d spacings smaller than 1.5 Å are in general quite weak.

d_{obs} , Å	d_{calc} , Å	I_{obs}	I_{calc}	hkl
4.12	4.11	15	19	101
3.09	3.09	40	38	002
2.906	2.915	100	100	011
2.742	2.756	40	43	020
2.575	2.576	5	3	111
2.087	2.089	30	40	112
2.053	2.055	30	37	202
1.997	2.000	100	88	211
1.931	1.931	30	27	103
1.760	1.758		{ 5 }	301
1.749	1.749	30		{ 16 }
1.650	1.653	15	15	020
1.530	1.533	--	3	121