

## Short Communications

The Metal Rich Region of the  
Zr-Te System

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There is but a single reference<sup>1</sup> to a metal rich phase of the Zr-Te system, *i.e.*  $Zr_3Te_3$ . During an investigation of this system, we have obtained somewhat different results, which are presented here.

Samples were prepared from 99.9 % Zr and 99.999 % Te (Koch-Light Laboratories, Ltd.) in three alternative ways according to the furnace used. Firstly, by direct reaction between the elements at 800–1200°C in a temperature regulated wire-wound resistance furnace, the heat treatment ranging from 4 h–14 days. A second series of samples were heated for ~5 min in a carbon resistance (Nernst-Tammann) furnace at ~1350–1550°C. (The temperature was measured with an optical pyrometer.) In the above methods of treatment, the samples were contained in crucibles of pure alumina which were sealed in evacuated quartz capsules. Quenching in ice-water concluded the heat treatment in these cases.

A third series of samples were prepared in an electric arc furnace by melting (in an argon atmosphere) weighed amounts of the mixed and compacted components.

X-Ray powder photographs of the samples were taken in a Guinier type camera of 80 mm diameter with monochromatized  $CuK\alpha_1$ -radiation ( $\lambda=1.54050$  Å) using KCl as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data and the indicated error limits correspond to twice the standard deviations obtained in these calculations.

Due to reactions between the sample and the quartz container, the first two series of samples were found to be contaminated with oxides and silicides of the elements concerned. In order of decreasing metal

content, the following phases were obtained:

(1) Hahn and Ness<sup>1</sup> mention that Te dissolves in Zr to an unspecified extent. We find that in samples prepared as described above Te is soluble in Zr to an amount of  $< \sim 1$  atomic %. The dimensions of the hexagonal unit cell for the maximum Te content are:  $a=3.246(1)$  Å,  $c=5.198(2)$  Å. For pure Zr the corresponding data are:  $a=3.234(1)$  Å,  $c=5.144(2)$  Å.

(2) The hitherto unknown  $Zr_5Te_4$  phase was found in samples prepared by each of the three methods employed, but in the pure form only as a result of the arc melting technique. The composition of the phase, which has no appreciable range of homogeneity, was determined by the disappearing phase principle applied to Guinier photographic data.

The diffraction data were indexed according to the tetragonal system, yielding the unit cell dimensions  $a=10.763(2)$  Å,  $c=3.840(1)$  Å. The systematic extinctions of reflections with  $h+k+l=2n+1$  showed the cell to be body-centred. All known data suggested that the phase is isostructural with  $Ti_5Te_4$ .<sup>2</sup> This was confirmed by a comparison of observed and calculated X-ray intensities.

(3) A hexagonal phase with unit cell dimensions  $a=3.763(1)$  Å,  $c=3.862(1)$  Å was observed in the composition range 45–50 atomic % Te. There is no appreciable range of homogeneity, the composition most probably being close to equiatomic. The structure is essentially of the WC type, and this phase is almost certainly identical with that reported at a composition of  $Zr_3Te_3$  by Hahn and Ness.<sup>1</sup>

Three comments are relevant in relation to the occurrence of the  $Ti_5Te_4$  type structure:

(i) The known phases with this type of structure are  $Ti_5Te_4$ ,<sup>2,3</sup>  $Zr_5Te_4$ ,<sup>4</sup>  $V_5Sb_4$ ,<sup>5</sup>  $V_5Se_4$ ,<sup>6</sup>  $V_5Sb_4(?)$ ,<sup>6</sup>  $Nb_5Se_4$ ,<sup>7</sup>  $Nb_5Te_4$ ,<sup>7</sup>  $Nb_5Sb_4$ ,<sup>8,9</sup>  $Ta_5As_4$ ,<sup>10</sup>  $Ta_5Sb_4$ ,<sup>9,11</sup>  $Mo_5As_4$ ,<sup>9,12-14</sup> and  $Ti_5W_3As_4$ .<sup>9</sup>  $V_5Te_4$  occurs as a monoclinically distorted variant.<sup>15</sup> These phases have well defined stoichiometric compositions.

(ii) Only metals from the Groups IVA-VIA of the Periodic System give rise to this structure type. The phases include a chalcogen element in combination with metals from Group IVA; a pnictogen element in the case of metals of the Group VIA; while the Group VA metals form both pnictides and chalcogenides. Using valences corresponding to the periodic group numbers appropriate to the components, the structure type occurs in the valence electron concentration range 4.88 – 5.44 per atom.

(iii) As is perhaps to be expected, the relative sizes of the component atoms appear to exert control over the appearance of phases with this structure type. Thus the larger metal atoms (*e.g.* Zr) combine with the larger non-metal atoms Te and/or Sb, while the smaller (*e.g.* V) combine with S, Se, and/or As. As a limiting case of this trend it is to be noted that Cr does not form any phase of this class.

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## Epithermal Neutron Activation Analysis of Uranium in Rocks

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Several nuclear methods are now available for the analysis of uranium in rocks (*e.g.* Ref. 1).

A method using epithermal neutrons to promote a selective activation has recently been developed which allows an accurate and rapid determination of the uranium content in such samples.<sup>2,3</sup> The present study has as its aim the simultaneous analysis of several samples since this is of importance in connection with uranium prospecting.

The irradiation was performed on the upper core surface of a swimming pool-type reactor. In this position an "excess" epithermal neutron flux is available for the activation purposes and larger cadmium covers containing several uranium samples can accordingly be introduced into the reactor without any essential change in reactivity.

The general principles of epithermal neutron activation analysis have previously been described, and only a short resumé of the technique will therefore be given here. In the activation process epithermal neutrons favour those nuclides which exhibit a large epithermal neutron cross-section, *i.e.* a high resonance integral. It is accordingly possible to enhance the activity of a specific nuclide for which analysis is desired by suppressing the activity of interfering nuclides with lower resonance integrals. Quantitatively the advantage of epithermal activation as compared with thermal activation including an epithermal contribution is expressed by the ratio:

$$F = (R_{Cd})_a / (R_{Cd})_D \quad (1)$$

$(R_{Cd})_D$  denotes the cadmium ratio of the nuclide to be determined;  $(R_{Cd})_a$  denotes the cadmium ratio of the interfering nuclide. The factor  $F$  may be described as the "advantage" factor.<sup>4</sup> The cadmium

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