

On the System Titanium-Zirconium

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The Ti-Zr system was reinvestigated using both metallographic and X-ray diffraction techniques. It was found that titanium and zirconium are soluble in all proportions in both the α and β phases. The minimum in the α/β transformation was found at 50 at. pct and 535°C.

THE Ti-Zr system has previously been the subject of several investigations.¹⁻⁶ A study by Hayes *et al.*⁵ using magnesium-reduced titanium and zirconium melted in graphite crucibles indicated that the system was a continuous series of solid solutions in both α and β phases with a minimum at approximately 545°C and 65 pct* Zr. These conclusions were substantiated

*All percentages are weight percent except where otherwise noted.

by the work of Duwez⁴ as well as by the limited data of Craighead *et al.*,³ Fast,² and deBoer.¹ However, a more recent investigation of the titanium-rich region by Ence and Margolin⁶ indicated that the solubility of zirconium in α titanium at 500°C is approximately 22 pct with the $\alpha + \beta$ field extending to approximately 47 pct Zr. Therefore in order to resolve this discrepancy the following investigation was initiated.

EXPERIMENTAL PROCEDURES

The alloys used in this investigation were prepared as 20- to 30-g buttons by nonconsumable electrode melting in a helium atmosphere. The starting materials were Bureau of Mines titanium BHN 71 and Foot Mineral iodide crystal bar zirconium. The titanium was premelted before the alloys were prepared to avoid excessive weight losses in the final melting. The compositions of the alloys prepared were as follows: Ti-12.0, 22.2, 29.0, 39.6, 50.0, 58.0, 72.4, 83.5, and 90.8 pct Zr.

Prior to heat treatment the alloys were cold-worked 10 to 20 pct, stopping at the first signs of cracking. Specimens for heat treatment were wrapped in molybdenum sheet and annealed in argon-filled quartz capsules for the following times and temperatures: 750°C—40 days, 675°C—61 days, 600°C—109 days, 575°C—112 days, 550°C—112 days, 525°C—127 days, and 450°C—153 days. Quenching was accomplished by breaking the capsules in an iced-brine solution.

The standard techniques used for polishing the specimens involved belt grinding, grinding on emery paper, polishing electrolytically, and etching with Remington "A" etch⁷ or "R" etch.⁸

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Debye-Scherrer X-ray powder photograms were obtained for a number of samples using a 114.6-mm camera and $\text{CuK}\alpha$ radiation. Exposure times were from 19 to 23 hr. The powder samples were obtained by filing to 270 mesh size. After filing the samples were wrapped in molybdenum foil capsuled in quartz and reannealed at the temperature of original heat treatments; following the heat treatment the samples were quenched into iced brine without breaking the capsules.

RESULTS AND CONCLUSIONS

On the basis of the microstructural examinations of the heat-treated samples and of the X-ray diffraction data, the Ti-Zr system shown in Fig. 1 was constructed. The data indicate that α and β titanium form a complete series of solid solutions with α and β zirconium. The minimum was found to occur at 65 pct (50 at. pct) Zr and 535°C, in excellent agreement with the earlier investigations,¹⁻⁵ see Fig. 2. Typical microstructures are shown in Figs. 3 to 7. Figs. 3, 4, and 5 show the 22.2, 39.6, and 50.0 pct Zr alloys after heat treatment at 675°C for 61 days with the 22.2 pct Zr showing equiaxed α and the 39.6 pct Zr alloy $\alpha + \beta$ transformed β , while the 50 pct Zr alloy shows only transformed β . Figs. 6 and 7 show the 29.0 and 39.6 pct Zr alloys after heat treatment for 109 days at 600°C. The 29 pct Zr alloy has an equiaxed α structure while the 39.6 pct alloy has a partially recrystallized $\alpha + \beta$ structure.

X-ray diffraction data obtained from the 50 pct Zr alloys after heat treatment at 525° and 450°C as well as from the as-cold-rolled material showed only those lines which could be indexed as α titanium, $c = 4.859\text{\AA}$, $a = 3.051\text{\AA}$, $c/a = 1.593\text{\AA}$, which was in good agreement with the previously published values.^{2,4,5,9} Chemical analysis* of the 50 pct Zr alloy

*Chemical analyses were performed by Academy Testing Laboratories, N.Y., N.Y.

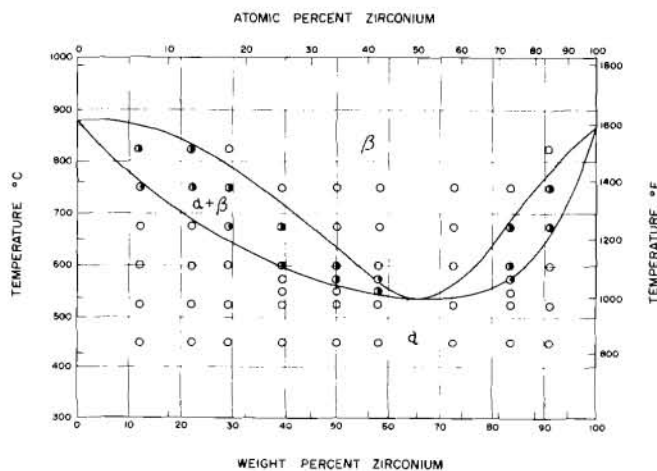


Fig. 1—The Ti-Zr phase diagram.

after heat treatment at 525°C indicates a carbon content of 0.03 pct and a nitrogen content of 0.026 pct, indicating that no appreciable contamination had taken place during the rather lengthy heat treatments.

The discrepancies between this work as well as that of previous investigators¹⁻⁵ with that of Ence and Margolin⁶ can be explained by the fact that the specimens used by Ence and Margolin were heated to 900°C after rolling and before heat treatment at lower temperatures. This dehydrogenation treatment produces large β grains which transform upon cooling to a transformed β structure. The β anneal removed the effects of the working treatment, and recrystallization upon subsequent heat treatment was not completed in the annealing times used. Therefore, structures which appeared to be two-phase upon metallographic examination were produced. The detection of a small amount of β by X-ray diffraction in the 49 pct Zr alloy must have been interpreted by Ence and Margolin⁶

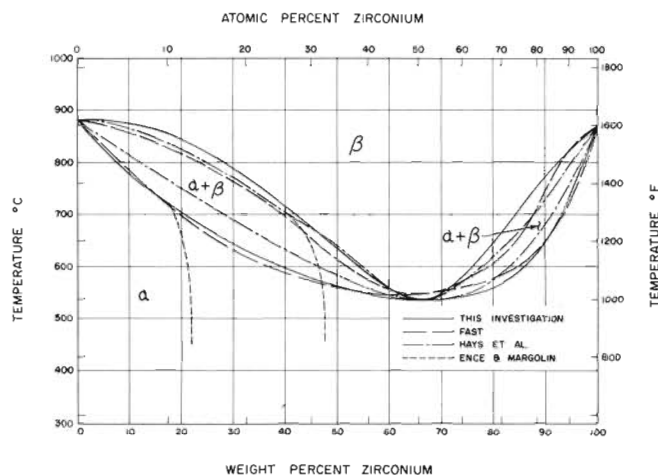


Fig. 2—Comparison of phase boundaries in the Ti-Zr system.



Fig. 3—Ti-22.2 pct Zr alloy; 675°C, 1464 hr; ice-brine-quenched; "A" etch, 10 sec; equiaxed α ; X375. Enlarged approximately 28 pct for reproduction.

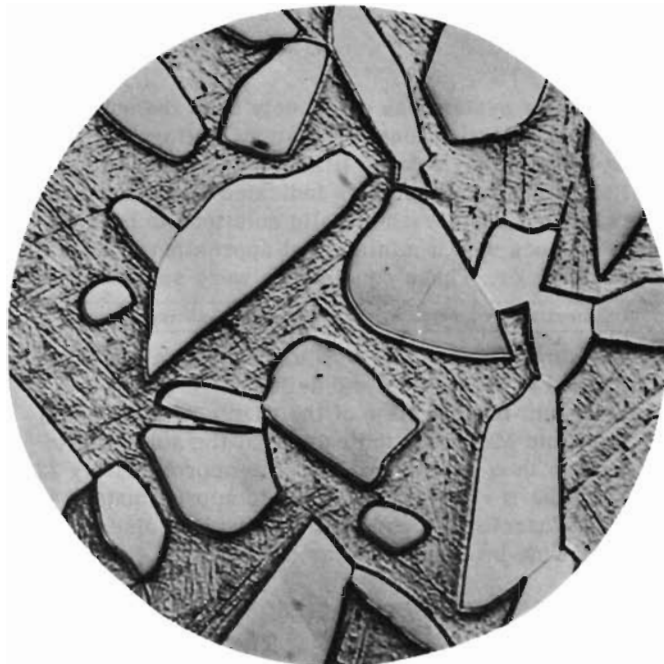


Fig. 4—Ti-39.6 pct Zr alloy; 675°C, 1464 hr; ice-brine-quenched; "A" etch, 10 sec; $\alpha + \beta$; X600. Enlarged approximately 28 pct for reproduction.

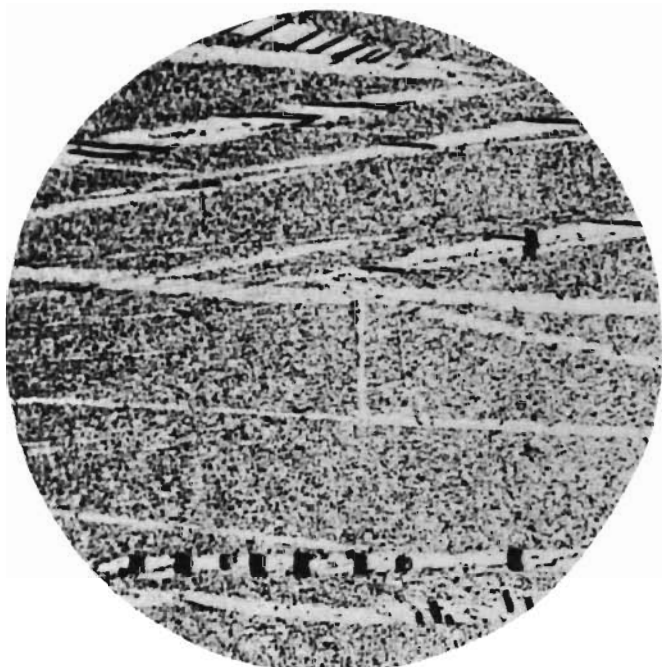


Fig. 5—Ti-50 pct Zr alloy; 675°C, 1464 hr; ice-brine-quenched; "A" etch, 10 sec; transformed β ; X600. Enlarged approximately 28 pct for reproduction.

as indicating that what was a single-phase β alloy at the temperature of heat treatment had nearly completely transformed upon cooling. However, as only one hexagonal phase was detected,⁶ where two would logically be expected if a eutectoid-type reaction were to be encountered and nearly all the β had transformed, it is reasonable to assume that the system must be one of continuous solubility in both the α and β phases. Therefore, it would seem that the alternate explanation that the alloy had not reached equilibrium

at the temperature of final heat treatment and the β which was detected was that which remained following the vacuum-annealing treatment would seem to be preferred. The alloys used in this investigation, however, were not given any β treatment after cold working. Recrystallization in the α field at 600° and 700°C was completed in the annealing times used. It was noted, however, that at lower temperatures recrystallization was not completed even with the extremely long annealing times used in this investigation.



Fig. 6—Ti-29.0 pct Zr alloy; 600°C, 2616 hr; ice-brine-quenched; "R" etch, 15 sec; equiaxed α ; X600. Enlarged approximately 28 pct for reproduction.

In order to check this hypothesis, the 50 pct Zr alloy, which after heat treatment at 525°C for 3040 hr gave the coarse "transformation" structure shown in Fig. 8, was heated to 675°C for 48 hr and then water-quenched. This treatment gave the fine transformation structure shown in Fig. 9. From this experiment and a similar one on the 58 pct Zr alloy it can be concluded that the original coarse transformation structure was



Fig. 8—Ti-50 pct Zr alloy; 525°C, 3048 hr; ice-brine-quenched; "R" etch, 5 sec; unrecrystallized α ; X250. Enlarged approximately 28 pct for reproduction.



Fig. 7—Ti-39.6 pct Zr alloy; 600°C, 2616 hr; ice-brine-quenched; "R" etch, 15 sec; partially recrystallized $\alpha + \beta$; X600. Enlarged approximately 28 pct for reproduction.



Fig. 9—Ti-50 pct Zr alloy; 525°C, 3048 hr; ice-brine-quenched; 675°C, 48 hr; ice-brine-quenched; "A" etch, 15 sec; transformed β ; X250. Enlarged approximately 28 pct for reproduction.

caused by growth in the α field during the 525°C heat treatment. Upon heating to the higher temperature, in the β field, the alloy transformed to β , and upon subsequent quenching the fine transformation structure shown in Fig. 9 was produced. Therefore it must be concluded that the 50 and 58 pct alloys were not in the β field at 525°C and that the diagram as presented in Fig. 1 is the proper representation of the phase relations in this system.

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Thermodynamics of the Thermal Decomposition of Nickel(II) Sulfate: The Ni-S-O System from 1000° to 1150°K

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The thermal decomposition of Nickel(II) sulfate was examined by determining the total pressure of SO₃, SO₂, and O₂ developed over a sample when it was heated in an evacuated system fitted with a Pyrex-bellows mercury manometer. The equilibrium pressures were combined with previously published data on the oxide and sulfide systems to establish a predominance volume diagram for the Ni-S-O system over the normal range of roasting temperature and gas composition used in the treatment of nickel minerals. The protective coating of NiSO₄ which forms on the oxide during roasting, and which causes the sulfation reaction to almost cease, may be disengaged readily by temperature cycling.

WHEN nickel sulfide is roasted in air, either nickel sulfate or nickel oxide may be formed by altering the experimental conditions. Because of the differing stabilities of various metal sulfates and oxides, possibilities exist for separating some of the constituents of mineral mixtures by the technique of selective sulfation and oxidation roasting. The experimental information required to make reasonable predictions of the possibilities of this technique is incomplete and, in some cases, in conflict. As part of a general program of providing some of the required information, a study

was made of the decomposition of NiSO₄ into NiO, SO₃, SO₂, and O₂ in accord with the equilibria:



EXPERIMENTAL

Materials, Apparatus, and Procedure. Fisher certified reagent-grade nickel sulfate hexahydrate was used in the source material for both nickel sulfate and nickel oxide. The manufacturer's analysis indicated: 0.001 pct Fe, 0.005 pct Cu, 0.003 pct Co, 0.001 pct Cl, other 0.15 pct.

The material was dehydrated, before use, by heating at 420°C for 5 hr. The oxide was prepared by roasting the sulfate in an open tray in a muffle furnace for 10 hr at 950°C. Preliminary experiments which were made by thermogravimetric analysis and X-ray diffraction analysis established that only one crystal form of nickel oxide and one of nickel sulfate were involved in the equilibrium shown in Eq. [1].

The apparatus used in the experiments was described previously.¹⁻³ The main feature is a corrosion-resistant, flexible Pyrex bellows which is used to protect the mercury in a u-tube manometer. Before a run was begun, the apparatus was washed thoroughly with hot hydrochloric acid and water and dried by heating under vacuum. The mixed sulfate-oxide sample was contained in a platinum boat rest-

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