On the eutectoid transformation behavior of the Ti-Zn system and its metastable phases

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Abstract
To date, Zn has not been used as an alloying addition in structural Ti alloys. The main obstacle has been the disparity between their melting and vaporization temperatures. A novel processing technique was developed to create a Ti-Zn compound. The equilibrium phases and microstructures were studied by electron microscopy and x-ray diffraction techniques. Results show the presence of pearlitic domains of α-Ti (hexagonal closed packed crystal structure) and Ti2Zn (body center tetragonal structure) in regions that have a near eutectoid composition. Solutionizing and water quenching results in the formation of martensite along with intermetallic laths, suggesting that the eutectoid transformation is active.

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**On the eutectoid transformation behavior of the Ti-Zn system and its metastable phases**


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6 key words  
Pearlite, TEM, omega, martensite, zinc, titanium

**Abstract**

To date, Zn has not been used as an alloying addition in Ti has never been used in a structural Ti alloy. The main obstacle for this has been the disparity between the melting and vaporization temperatures of the two elements. A novel processing technique was developed to create a Ti-Zn compound. From the material produced, equilibrium phases and microstructures were studied through the use of electron microscopy techniques and x-ray diffraction technique. Results show the presence of pearlitic domains of $\alpha$-Ti (hexagonal closed packed crystal structure) and Ti$_2$Zn (body center tetragonal structure) for regions that have a composition close to that of the eutectoid point. Solutionizing and water quenching the material results the formation of martensite along with intermetallic laths, suggesting that the eutectoid transformation is active.

**Introduction**

The primary use of Ti-Zn system is seen in grain refinement of Zn-Al alloys through the use of Ti and in the galvanization of steels[1, 2]. Most of the existing literature regarding the Ti-Zn system discusses the Zn–rich compositions, and has led to an ongoing debate regarding high Zn-containing intermetallic phases with particular stoichiometric compositions (in particular TiZn$_{16}$ and TiZn$_{15}$[2, 3]).

The use of Zn in Ti metallurgy has been restricted to laboratory settings. The reason for this is due to the disparity between the melting point of Ti (1660°C) and boiling point of Zn (917 °C). Recent assessments [2, 3] of the Ti-rich side of the Ti-Zn phase diagram suggest that the solubility of Zn in $\alpha$-Ti is larger than previously thought. As an addition to Ti, Zn is a $\beta$-Ti eutectoid stabilizer with a relatively high eutectoid transformation temperature of ~620 °C [4].

The eutectoid transformation of this has been studied previously. Most titanium based eutectoid systems in can be described as “sluggish” or “active,” where the “sluggish” transformation
results the transformation of β-Ti parent phase into α-Ti, and some retained β-Ti due to slow transformation (or sluggish). In contrast, an active system describes a eutectoid transformation in which the parent β-Ti phase is completely and rapidly transformed to the product phases (i.e., α-Ti + intermetallic). The work by Franti et al.[5] demonstrates that most eutectoid systems are sluggish (e.g. Ti-Cr, Ti-Fe, Ti-Mn, etc). A few systems, such as Ti-Cu, are active. Additionally, the assessment of metastable phases upon quenching (martensite) has never been studied for this system.

Because the Ti-Zn system has been neglected, this study aims to understand simple facts about the Ti-Zn system. Particularly, the authors are interested in understating the ability of the Ti-Zn system to produce precipitates that may act as reinforcement to the material, and to classify the eutectoid transformation of the system as “active” or “sluggish.”

**Procedure**

The conditions under which the Ti and Zn can alloy together and allow the assessment of this binary system represent a significant experimental challenge. The vaporization of Zn must be avoided (907°C), yet it is desirable for the Ti to exist in its BCC b-Ti phase.

To produce conditions that would allow Ti and Zn to react with one another, the vaporization of Zn (907 °C) had to be avoided, and the Zn would have to come in contact with β-Ti (882 °C). To this end, a reaction vessel was constructed to house Zn and Ti in an inert Ar atmosphere (to avoid oxidation) at 900 °C. The design of the vessel is presented in Figure. 1(a).

The vessel consisted of a steel tube with each end capped. Inlet and outlet holes allow the flow of Ar gas through the reaction vessel. To prevent unwanted reactions between the metal inner surface and the reactants, an alumina sleeve with caped ends was placed in the chamber. On the capped end of the sleeve, titanium powder was placed in Ti foil. Zinc was introduced as pellets and held on top of the powder within an alumina cradle. As the temperature increased, the Zn became molten, fell onto the Ti powder and reacted, as shown in Figure 1. To ensure that the internal inert atmosphere was not contaminated, the vessel was sealed with an alumino-silicate high temperature cement prior to reaction. Once the cement hardened, the chamber was purged with Ar for 10 minutes to evacuate any gases present. Reaction between molten Zn and Ti took place at 900 °C for two different exposure times of 1 hrs (run 1) and 5 hrs (run 2).

Once the specimens were prepared, they were cross-sectioned using a TechPress2™ (Allied High tech, USA). The resulting specimens were polished using abrasive SiC paper with grit ranging from 240-800. This was followed by a final polish using polyurethane cloths with 0.04 μm colloidal silica. Subsequently, the specimens were cleaned in an ultrasonic bath, using acetone, distilled water, ethanol, and methanol. Once the specimens were cleaned, they were
placed in a vacuum furnace at 50 °C to dry and remained there until the characterizations was performed.

Scanning electron microscopy (SEM) imaging was conducted using an FEI Nova 230 NanoSEM field emission gun scanning electron microscope equipped with an electron backscattered detector (BSED). TEM specimens were prepared using FEI Nova Nanolab 200 DualBeam™ focused ion beam (FIB)/SEM. The TEM specimens were examined using FEI Tecnai G2 F20 TEM field emission gun transmission electron microscope operating at 200 keV. The TEM was equipped with a high angle annular dark field scanning transmission electron microscope (HAADF STEM) and an energy dispersive x-ray spectrometer.

Results and Discussion

a) Microstructure, Composition and Phases

The microstructural evolutions for both runs are presented in Fig 2. Quantification of chemical composition via EDS revealed that the Zn content decreases with increasing distance from the surface of the produced specimen (as described in Fig 1(b)). This observation is expected because the liquid Zn first interacts with the powder particles at the top and then flows downwards. Pearlitic domains have formed in both specimens from both runs. Micrographs from Run1 (see Fig 2(a-b)) specimen consistently show dark centers surrounded by pearlitic domains with a Zn–rich phase. Figure 2 shows images with z-contrast, indicating that the dark centers are rich in Ti and the brighter features are Zn-rich. The aforementioned deduction is validated through an EDS measurements presented in Fig 3 and Table 2. Additionally, the compositional measurements (see Fig 3 spots 3-6) indicated a larger Zn composition within α-Ti (17wt% Zn) than the negligible solubility for Zn in α-Ti reported in Okamoto’s assessment [4]. However, the assessment by Ghosh et al. agrees with the compositional measurements presented in this study showing a maximum solubility of 14wt% Zn (~10 at% Zn) in α-Ti [3]. Similarly, the specimen produced in run 2 displays pearlitic domains within the Ti powder particles; however, the pearlitic domains from run 2 have formed at the centers of the powder particles (see Fig 2(c-d)). The formation of Zn-rich phases at the center of the powder particles is anomalous because it indicates that the Zn diffuses to the center and continues to diffuse until the center of the particle is Zn enriched. There are two possible explanations for the concentration of Zn at the center of the powders from run2: (1) The diffusion of Zn can be affected by the presence of a stress field. Work by Shemon shows atoms can move faster due to the existence of stress-drift that is superimposed over the drift due to the compositional gradient[6]. (2) Oxygen presence near the surface of the particles. Oxygen in Ti is an α-Ti stabilizer and displays a large solubility within α-Ti [7]. Therefore, the presence of O would stabilize the α-Ti and expel other solute atoms out of solution from the α-Ti phase, and concentrating the expelled Zn into the center of the powder particle.

In order to identify the phases, x-ray spectra of run1 and run2 specimens were recorded (see Fig 4) at positions near the center at the top and bottom (as defined in Fig 2 (b)). α-Ti and Ti₂Zn phases (with a MoSi₂ structure) were detected. This is in agreement with both Ghosh et al. and Okamoto. One unintended consequence came from the use of cement in the construction of the
reaction chamber was the inclusion of Al$_2$SiO$_5$ with the reactants, as its correspondent peaks emerged in XRD spectra and are identified as Al$_2$SiO$_5$. The pattern used to index the XRD peaks of Ti$_2$Zn was calculated using the prototype crystal structure of MoSi$_2$; consequently, to confirm the presence of Ti$_2$Zn was confirmed by TEM microscopy. The foil was taken from the pearlitic regions that formed within the run2 specimen (see Fig 2(d)). TEM results presented in Fig 5 show that the laths/lamellae microstructure correspond to an assembly of Ti$_2$Zn intermetallic phase and $\alpha$-Ti.

**b) Phase transformations**

**b-1) Eutectoid transformation**

The lamellar arrangement of $\alpha$-Ti and Ti$_2$Zn laths is seen throughout specimens produced from run1 and run2. The Pearlite formation is the result of cooperative growth, where the rejection of solute from one of the phases promotes the formation of the second phase. In this case, the transformation of $\beta$-Ti into $\alpha$-Ti causes the rejection of Zn from $\alpha$-Ti and it accumulates at the phase $\alpha/\beta$ boundary, and the increased Zn concentrations allows the decomposition of $\beta$-Ti to Ti$_2$Zn to occur.

In titanium, many binary systems exhibit a eutectoid transformation; however, most systems do not produce pearlitic domains and instead retain the parent $\beta$-Ti phase and only precipitate $\alpha$-Ti. These systems are termed “sluggish” [8]. Franti et al. [5] and Lin at al. [9] show that only Ti-Cu and Ti-Ni systems produce pearlitic microstructures, where the parent phase is transformed to the eutectoid product phases. These systems are described as “active”.

Owing to the lack of work on Ti-Zn, the nature of the eutectoid transformation is unknown. The pearlitic domains that formed (see Fig 2 (a-d)) within the specimens would indicate that this system exhibits an active eutectoid transformation. However, the particular experimental setup caused the cooling time for these materials to be extended, and may have allowed enough time for the pearlitic structure to form.

Comparing Zn to Cu, both elements display a similar electron configuration, similar alloying behavior with Ti, i.e. both are eutectoid $\beta$-Ti stabilizers with relatively high eutectoid transformations. Given that Zn and Cu are chemically similar, it can be expected that the Ti-Zn system would exhibit an active eutectoid transformation. To test this, a specimen from run2 was solutionized at 975 °C for 4 hours and then water quenched. As seen in Fig 6, upon solutionizing and water quenching finer intermetallic laths have formed (see Fig 6(a)) along with Zn-rich domains that display fine laths that resemble a martensitic microstructure (see Fig 6 (b)). The presence of the lamellar domains (see Fig 6 (a)) would indicate that the decomposition of $\beta$-Ti happens quickly and gives credence to the hypothesis that Ti-Zn is an active eutectoid.

**b-2) Martensite and omega**

The microstructure from the water quenched specimen shows the formation of two distinct features: (1) martensitic (see Fig 6(a)) laths and (2) intermetallic lath domains (see Fig 6(b)).
Compositional measurements from these regions (see table 3) show that the (shown to be slightly brighter in Fig 6) intermetallic laths contain 30-38wt% Zn (24-30at% Zn). The compositional measurements indicate that the laths must be Ti$_2$Zn phase; however, the measured compositions (see Table 3) are slightly lower than the expected composition of ~40wt% (~33at% Zn) Zn this must be due to the volume the electron beam is interacting with Zn lean regions. Alternatively, the variation in compositions measured could indicate that the Ti$_2$Zn phase could exhibit a nonstoichiometric composition.

Compositional measurements from the central bright regions (see Fig 6 (b)) show fine laths with a composition that ranges between 22-33 wt% Zn (see Table 3). The fine martensitic laths (within a given powder particle in Fig 6(a)) have little variation in composition would suggest that this is a martensitic phase. Martensite forms due to large cooling rate that results in the formation of a distorted crystal structure that have the composition of the parent phase. Previous EDS measurements of $\alpha$-Ti phase (see Table 2) show that the composition reaches 17 wt% Zn. The increased Zn composition (27 wt% Zn) is a further evidence of a martensitic transformation having taken place because it indicates retention of solute upon quenching. It should be noted that the presence of both pearlite and martensite microstructures suggests that there is a competition between the formation of martensite and pearlite features. This means that the formation of Ti$_2$Zn takes place during quenching and its rate of formation can be compared to the transformation of the parent $\beta$-Ti phase. Consequently, this indicates that the eutectoid transformation is fast enough to be considered as an active eutectoid system.

The compositional measurements presented above show that martensite can form at compositions far past the eutectoid composition (15wt% Zn). Consequently, the retention of beta is not expected even at large Zn concentration unlike most $\beta$-stabilizers where at a large enough solute concentration, the formation martensite is suppressed. The schematic of a proposed martensite start temperature within the Ti-Zn system (Fig 7) shows that one could expect martensite to form up to the Ti$_2$Zn composition. Another consequence of a wide range of compositions capable of forming martensite is the inability to form athermal $\omega$ because the formation of martensite suppresses athermal $\omega$ formation [10].

An interesting result from the SEM images (see Fig 6) is the higher brightness of the central martensitic regions in comparison to the more Zn enriched Ti$_2$Zn laths. Because the images were taken with a backscattered detector the brightness of the phases is representative of the atomic number of the constituent atoms. Thus the brighter central regions should have a larger Zn concentration than the Ti$_2$Zn laths present, but the compositional measurements presented in Table 3 show the exact opposite. Analyzing the densities of each phase (Ti$_2$Zn, Martensite and $\beta$-Ti) shows that the martensitic region should have a larger density than Ti$_2$Zn and $\alpha$-Ti thus the interaction volume of the electron with the material is smaller which is resulting in a brighter image for the martensite.

**Conclusions**
A study on the eutectoid transformation of Ti-Zn has been conducted. The salient conclusions are as follows:

- It was shown that the rudimentary reaction chamber made for this study was capable of producing a specimen that contained Ti and Zn.
- From compositional measurements it is found that the $\alpha$-Ti phase displays a much larger solubility than reported in the equilibrium phase diagram as presented by Okamoto[4].
- Anomalous diffusion of Zn into the center of the particles was seen for specimen produced from *run2*. This could be a result of oxygen contamination or the presence a stress field within the powder particles.
- The eutectoid transformation of the Ti-Zn system is active. This is concluded from the pearlitic microstructures (composed of $\alpha$-Ti and Ti$_2$Zn) that are displayed in all specimens including the water quenched specimen.
- EDS measurements of the intermetallic laths suggest that the Ti$_2$Zn phase could display a nonstoichiometric composition.
- The formation of pearlitic regions shows that the system can readily produce precipitates, and would suggest that a supersaturated $\alpha$-Ti solution could be manipulated into precipitating dispersed intermetallic precipitates that may reinforce the material.
- The formation of martensite along with pearlite further supports the hypothesis that Ti-Zn is an active system because it clearly shows that the eutectoid composition can compete with the fast martensitic transformation. Additionally, the large Zn composition measured from the martensitic laths indicates that martensite may be stable up to the formation of the intermetallic Ti$_2$Zn. This would suggest that the Ti-Zn system may suppress the formation of athermal $\omega$.

Acknowledgements

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References

Table 1. Description of reactant materials used in the study.

<table>
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<th>Element</th>
<th>Provider</th>
<th>Purity(%)</th>
<th>Description</th>
</tr>
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<tr>
<td>Ti</td>
<td>Alfa Aesar</td>
<td>99.99</td>
<td>Powder -150 mesh</td>
</tr>
<tr>
<td>Zn</td>
<td>Alfa Aesar</td>
<td>99.993</td>
<td>Pellet</td>
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Table 2. EDS spot scan results presented in Fig 3.

<table>
<thead>
<tr>
<th>Location</th>
<th>wt% Zn</th>
<th>at% Zn</th>
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<tbody>
<tr>
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<td>0</td>
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<td>2</td>
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<tr>
<td>7</td>
<td>31</td>
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Table 3. Compositions measured from spots shown in Fig 6.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Zn (wt%)</th>
<th>Zn (at%)</th>
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<tbody>
<tr>
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<td>12</td>
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Figure 1. (a) Schematic of the reaction vessel used in this study, all measurements are in mm. (b) Schematic showing Molten Zn interacting with Ti powder to produce specimens. The areas 1-4 are placed to denote a compositional difference caused by the flow of the molten Zn into the Ti where 1 (top) is the highest concentration and 4 (bottom) the lowest.
Figure 2. SEM backscattered images of the reaction product from run 1 (a and b) and run2 (c and d)
Figure 3. Chemical analyses performed on specimen produced in run1 with. (a) Spot scans performed on the specimen (b) Line scan across powder particle showing Ti(red) and Zn(blue).

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Figure 4. XRD spectra taken from run1 (a) 20 wt% Zn (b) 10 wt% Zn and run 2 (c) 15 wt% Zn (d) 10 wt% Zn are presented.

Figure 5. Backscattered SEM image showing the areas of interest examined using bright field TEM and SAD for (a) $\alpha$-Ti grain and (b) Ti$_2$Zn lath within pearlitic domain.

Figure 6. Backscattered SEM images of Run2 specimen solutionized and water quenched showing (a) intermetallic lamellar domains along with (b) martensitic laths within Zn enriched central region. Spots 1 through 9 show places where compositional measurements were performed.
Figure 7. Schematic view of Ti-rich side of Ti-Zn system as presented by Okamoto[4] showing possible martensite start temperature ($M_s$).