Effect of Alloying Additions of Aluminium and Iron on the Creep Resistance of Ti-12Cr (wt. %)

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Abstract

Titanium (Ti) and its alloys are among the desired materials for biomaterial, material, and aerospace applications due to their excellent properties. Metastable beta titanium (β-Ti) alloys exhibit enhanced strengths and hardness values after thermomechanical processing (TMP) due to the presence of omega (ω) and alpha (α) phase precipitates in the beta (β) matrix. In this study, the creep properties of three different β-Ti alloys, Ti-12Cr-1Fe-3Al (wt. %), Ti-12Cr-3Al (wt. %), and Ti-12Cr (wt. %), were experimentally obtained at different applied stresses and at 683 K. The relationship between microstructure and creep properties was investigated. X-ray diffractometer (XRD), optical microscope (OM), and scanning electron microscope (SEM) were used to help characterize the microstructure before and after creep deformation. The hardness of alloys increased after heat treatment for 48 hrs at 410 °C due to the precipitation of the α and ω phases. The creep tests showed that Ti-12Cr-1Fe-3Al (wt. %) was the most creep resistant and Ti-12Cr (wt. %) was the least creep resistant.

Introduction

Titanium (Ti) is attractive compared to other metals due to its high specific strength, high corrosion resistance, high toughness, nontoxicity, and biological compatibility and thus it has significantly contributed to the aerospace, automotive, marine, and medical industries [1,2]. Ti alloys have been commercially used for over 50 years and are mostly classified based on their crystallography i.e., α, α+β, β (metastable) alloys. α-Ti alloys usually contain aluminum (Al), tin (Sn), or zirconium (Zr) and generally show more creep resistance than the other alloy types at high temperatures [3]. α+β alloys have one or more α and/or β stabilizing elements and possess balanced properties. Ti-6Al-4V (wt. %) is a commonly used α+β alloy. Being predominantly α phase (hcp structured), α and α+β alloy have some disadvantages, such as low cold workability, low age hardenability, and low fracture toughness [4]. β-Ti alloys usually contain V, Mo, and Nb and the bcc structure is stable at higher temperatures. The β phase can be maintained at room temperature (RT) through quenching after heat treatment [4]. Having good cold workability and considerable age hardening capabilities, β-Ti alloys are increasingly being used for aerospace applications.

TMP can transform metastable β phase alloys into other equilibrium and metastable phases. This was first seen by P.D. Frost et al. who observed the presence of transition phases, including ω, which were responsible for the hardening effects during aging [5]. In subsequent studies of Ti-V alloys, it was found that upon low-temperature aging, the β phase first decomposes into β + ω followed by ω + α and then finally to the α phase [6]. The intermediate metastable phase transition steps can be avoided by high temperature aging. According to Lütjering and Williams the most effective way to strengthen β-Ti alloys is by precipitation hardening [7]. Thermal and/or mechanical processing and alloying content have a strong influence on the morphology, volume fraction, size, and distribution of the ω and α precipitates formed in β-Ti alloys [8]. Precipitates obstruct the movement of dislocations and add strength and toughness. A significant amount of research has been done on near β and β-Ti alloys correlating the mechanical properties with the microstructural changes.

According to Dubinskiy et al., ω precipitates in Ti alloys are classified into three types based on their transformation behavior [9–12]:

- Athermal ω (ωath) – martensitic transformation caused during quenching
- Isothermal ω (ωiso) – diffusion-controlled process during aging
- ω – Induced by deformation process

Lütjering and Williams also found that ωiso has an ellipsoidal or a cuboidal shape [7].

The thermal effects on the strength of Ti-35Nb-7Zr-5Ta-xO (wt. %) was studied by Qazi et al. by solutionizing above the β transus temperature followed by an aging step [13]. For 0.06 O wt.%, ω-phase formation was observed at 700 K and this provided strengthening. The maximum strength was observed in a 0.46 wt.% O alloy after a 755 K heat treatment due to both α and ω precipitation. Similar strengthening has been observed in other β-Ti alloys during aging between 623 K and 873 K for about 12 days.

Cost is a major driving factor in Ti research. Processing Ti from its naturally occurring oxide state is expensive due to inert atmosphere requirements and post-processing costs. Replacing commonly used alloying elements like vanadium (V), niobium (Nb), and molybdenum (Mo) with lower cost alternatives like Chromium (Cr) and Iron (Fe) is a potential means to reduce the costs [1]. It is essential to understand the mechanical properties and their relationship with the microstructure. J. Ballor et al. studied microstructure-property relationships of four Ti-12Cr (wt. %) alloys and the effect of individual alloying elements was investigated [14]. This paper was intended to further the understanding of the mechanical properties of the same alloys. In this study, the creep properties of three different β-Ti alloys, Ti-12Cr-1Fe-3Al (wt. %) (TCFA), Ti-12Cr-3Al (wt. %) (TCA),
T-12Cr (wt. %) (TC), were melted and compared. The microstructures for these alloys were studied before and after creep using various characterization techniques.

**Materials and Methods**

All the studied alloys were levitation melted in a 2-kg, 90D×80L LEV levitation induction furnace. They were then hot forged into blocks of dimension 25 × 60 × 250 -mm³ at approximately 1320 K. The alloys were then subjected to homogenization annealing at 1173 K for 1 hour in vacuum. The quenching process was carried out at 3.47 K/s (Cooling rate) in ice water [14]. Maintaining a high cooling rate helps obtain a uniform β microstructure without the presence of the α-phase [15]. Table 1 provides the measured chemical compositions of each alloy. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to obtain the at. % and wt. % compositions of Cr, Al, and Fe in the alloys. Using nondispersive infrared spectroscopy (NDIR), the O, C, and N contents were determined by the Daido Steel Corporation (Nagoya, Japan).

For the purpose of creep testing, samples were electric-discharge machine (EDM) cut from the forged blocks into ‘dogbone’ shaped samples. The cut dogbones had a gage length of 35 mm ± 0.1 mm, width of 7 ± 0.2 mm, and thickness of 1.1 mm ± 0.2 mm. The contamination on the surface of the samples due to EDM cutting was removed by grinding using silicon carbide papers, progressively from 120 grit to 800 grit. Conventional constant load constant temperature creep tests were performed using Applied Test Systems (ATS) (Butler, PA) 2400 series creep frames. The creep frame was equipped with a high temperature split tube furnace with a maximum temperature of 2073 K, and a contact type extensometer attached to a linear variable differential transformer (LVDT) to measure the strain. The creep tests were conducted in an open-air environment. A gage length of 1 inch was used. The alloys were tested at the following stress levels – 200 MPa, 250MPa, 300 MPa, and 350 MPa, with a constant temperature of 683 K. All the alloys, prior to creep testing, were heat treated for 48 hrs inside the creep frame furnace at 683 K under no load. The approximate duration of the tests was about 336 hours (14 days), and all the tests were stopped in the secondary creep regime

Vickers microhardness testing was performed according to ASTM Standards E92-17 [16]. This testing was performed using a 500 g-force load and a dwell time of 10 s. Six readings were made at each of the locations and the hardness values (HV) were reported. The hardness testing was performed on the as-processed samples, the grips of the creep tested samples (subjected to heat treatment and minimal creep deformation), and the gage sections of the creep tested samples (subjected to both heat treatment and creep deformation).

X-Ray diffraction (XRD) was performed on the alloys with a Bruker - D2 PHASER diffractometer in the Bragg–Brentano orientation using Cu-Kα radiation with a characteristic wavelength of 1.54 Å and a Ni filter. Each sample scan used a step size of 0.02°/step, a count time of 1 second, and a 2θ range of 20° - 90°. All scans were conducted with a tube current of 35mA and a tube voltage of 35kV. Samples from the alloys were HT in a partially evacuated tube furnace at 683 K for 12hrs followed by air cooling. XRD was performed on the samples in the as-processed condition, after HT for 12 hrs, and post creep-deformation in the gage section (subjected to both heat treatment and creep deformation).

The microstructural analysis was performed using a field emission gun (FEG) Tescan Mira3 scanning electron microscope (SEM). Both secondary electron (SE) images and back-scattered electron (BSE) images were captured using a beam voltage of 20 KeV. The samples were cut using a low-speed diamond saw, mounted using a conductive resin, and ground and polished using silicon carbide (SiC) papers progressively from 120 grit to 2400 grit. 3 μm, 1 μm, 0.5 μm, and 0.25 μm diamond paste were used to obtain a mirror finish. The final polishing step used a 5:1 ratio of Streurs OP-S Colloidal silica (0.02–0.04 micron) and 30% hydrogen peroxide. All the samples were etched using Kroll’s reagent (2-mL HF, 6-mL, nitric acid, 92-mL distilled water) for approximately 1 minute at RT. The average β-phase grain size was measured from the SEM images according to ASTM standard E112-12 (ASTM International) [16].

| Table 1. Measured compositions of the alloys studied** |
|----------------|----------------|-------|-------|-------|-------|-------|-------|
| **Alloy**       | **Chemical composition** |
|                 | **Ti** | **Cr** | **Fe** | **Al** | **C** | **O** | **N** |
| Ti-12Cr (TC)    | Bal.   | 12.1   | 0.02   | 0.01   | 0.004 | 0.059 | 0.004 |
|                 | wt.%   |        |        |        |       |       |       |
|                 | at.%   | Bal    | 11.2   | 0.02   | 0.02  | 0.02  | 0.18  | 0.01  |
| Ti-12Cr-3Al (TCA) | Bal    | 12.3   | 0.02   | 3.06   | 0.003 | 0.062 | 0.004 |
|                 | wt.%   |        |        |        |       |       |       |
|                 | at.%   | Bal    | 11.2   | 0.02   | 5.35  | 0.01  | 0.18  | 0.01  |
| Ti-12Cr-1Fe-3Al (TCFA) | Bal    | 12.4   | 0.93   | 3.02   | 0.003 | 0.11  | 0.004 |
|                 | wt.%   |        |        |        |       |       |       |
|                 | at.%   | Bal    | 11.3   | 0.79   | 5.28  | 0.01  | 0.32  | 0.01  |

**Table taken from Ballor et al. 2019**
Results and Discussion

Microstructure Characterization

The XRD results for the as-processed materials revealed peaks corresponding to the \( \beta \) phase (see Figure 1).

![XRD Data for TCFA, TCA, and TC](image)

**Figure 1:** XRD data in the form of Integrated intensity vs 2\( \theta \) for the studied alloys which exhibited only \( \beta \) phase peaks

From the integrated intensity values, TCA exhibited a (211) \( \beta \)-phase peak which was almost three times greater than that of the other two alloys. The addition of Al may be responsible for the observed texturing. The further addition of Fe to Ti-12Cr-3Al (wt. %) seems to reduce the peak intensity for (211) \( \beta \)-phase peak. The changes in the atomic radii of the individual elements was likely the cause for the slight shift in the \( \beta \)-phase peak positions for the three alloys. The lattice parameters for the \( \beta \)-Ti was calculated for the three different alloys using Bragg’s law (refer to Eq. 1).

\[
\lambda = 2 \times d \times \sin (\theta)
\]

A decrease of about 0.02 Å was found going from the pure Ti (Theoretical value – ASM Handbook, vol. 9, pp. 899–917) to TC. Similarly, a decrease of 0.04 Å was found on addition of Al to TC, and a decrease of 0.02 Å on addition of both, Al and Fe to TC. Although the change observed in the lattice parameter was small it may have influenced the hardness and the strength of the alloys.

The XRD patterns of the samples after heat treatment for 12 hrs at 683 K indicates possible \( \omega \) and \( \alpha \) phase peaks. The peak locations for the \( \alpha \), \( \omega \), and TiCr\(_2\) phases found in the literature [15,17–19] for metastable \( \beta \)-Ti alloys was used to identify the peaks as shown in Figure 2. To improve the qualitative analysis, peaks below 5% of the background intensity were set to zero.

![XRD Data for TCFA, TC, and TCA](image)

**Figure 2:** XRD data in the form of Integrated intensity vs 2\( \theta \) for the studied alloys HT at 683 K for 12 hrs

More \( \omega \) phase peaks were observed for TC and TCA alloys as compared to TCFA. It appears that the addition of Fe to TCA has reduced the number and the intensity of the \( \omega \) phase peaks. Fe being a \( \beta \)-phase stabilizer could possibly reduce the amount of the \( \omega \)-phase precipitation at this temperature. The aging duration could also play an important role in the number of secondary phase peaks and their intensities. The XRD pattern indicates the possible precipitation of both the \( \omega \) and \( \alpha \) phases similar to what was reported by Li et al. after isothermal aging of Ti-29Nb-13Ta-4.6Zr (wt. %) for 48 hrs between 573 K to 673 K [20].

The XRD patterns of the post-creep tested samples is indicated in Figure 3. The results showed peaks corresponding to the \( \alpha \), \( \omega \), and TiCr\(_2\) phases. The intensity of the \( \alpha \) peaks were higher for TCA compared to both TC and TCFA, which could be due to the presence of Al which is an \( \alpha \)-phase stabilizer. The further addition of Fe seems to have reduced the \( \alpha \)-phase peak intensity. The presence of the \( \omega \)-phase has been reported to be the possible cause for the nucleation of the \( \alpha \)-phase [20–27].
A larger number of the $\omega$-phase peaks were observed after the HT compared with the creep tested samples. Conversely, a larger number of $\alpha$-phase peaks were observed in the creep tested samples as compared to the HT samples. It has been well documented that the $\alpha$-phase nucleates from the $\omega$-phase [22]–[28]. It is possible that during creep deformation, the $\alpha$-phase nucleated from the $\omega$-phase which could explain the differences observed in Figures 2 and 3.

Figure 3: XRD data in the form of Integrated intensity vs 2$\theta$ for the creep samples tested at 350 MPa and 683 K

Figures 4 and 5 show the microstructures of the alloys in the as-processed and 683 K 12 hr heat-treated conditions respectively. The average grain size for $\beta$ phase in the as-processed condition was compared with the grain sizes from the creep tested samples. In the as-processed alloys, the addition of Al increased the grain size almost by a factor of 2.5 compared to the TC alloy. The addition of both Fe and Al only resulted in an increase by a factor of 1.6 compared to the TC alloy. The addition of Al alone had a more pronounced effect on the grain size. After creep testing, the grain size for the TC alloy slightly increased by a factor of 1.6 compared to the as-processed TC alloy. But, the grain sizes for TCA and TCFA showed a decrease by a factor of about 1.5 and 1.1 respectively compared to their as-processed conditions. The grain sizes of TCA and TCFA went down by a factor of 1.3 and 1.5 from the grip to the gage section. Table 2 summaries the observed grain size results. The observed decrease may be due to the possible phase transformations occurring during creep testing in the gage section. All the observed grain size changes were within a factor of 1.6 for the studied alloys going from the as-processed to the creep tested conditions. TC exhibited the largest grain size while TCFA exhibited the smallest grain size after creep.
Table 2: Summary of the grain sizes of the as-processed (BCC) and creep tested (transformed BCC) microstructures

<table>
<thead>
<tr>
<th></th>
<th>Average grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TC</td>
</tr>
<tr>
<td>As-processed</td>
<td>33.9</td>
</tr>
<tr>
<td>Heat treated (grip section post creep)</td>
<td>57.7</td>
</tr>
<tr>
<td>Creep tested in the gage section</td>
<td>56.1</td>
</tr>
<tr>
<td>Percentage change from as-processed to creep tested</td>
<td>70.2</td>
</tr>
</tbody>
</table>

Figure 4: BSE SEM photomicrographs of the cross section of the as-processed microstructures of a.) TC b.) TCA and c.) TCFA alloys
Representative BSE SEM images of the as-processed alloys are provided in Figure 6. The SE SEM images for the creep tested gage section are provided in Figure 7. The SE images show pit-like nanoscale structures with visible topographical contrast suggesting possible secondary phase(s). Based on the XRD results which show the presence of α-phase ω-phase, it is expected that these fine features in Figure 7 were α and/or ω precipitates. Future Transmission electron microscopy (TEM) analysis is intended to verify the phase(s) observed.

Figure 5: BSE SEM photomicrographs of the cross section of the grip sections of a.) TC b.) TCA and c.) TCFA alloys after creep testing at 350 MPa and 683 K

Figure 6: BSE SEM photomicrographs of the as-processed a.) TCA and b.) TCFA alloys
Mechanical Properties

The Vickers hardness testing and the results are represented in Figure 8. The alloys show an increase in the HV after creep testing. TCFA showed a 75% increase, followed by TCA with a 68%, and then by TC with a 50% increase. This could be due to the precipitation hardening effects observed in β-Ti alloys which strongly hinders the movement of dislocations. Due to the aging process, precipitates nucleate and change in volume fraction, size, and geometry leading to an increase in the strength and hardness of β-Ti alloy [7,28–32]. B.S. Hickman et al. found that the β-phase to ω-phase transformation occurs in the temperature range of 373 K and 773 K in β-Ti alloys[33]. The hardness values increase is likely a result of the ω and α phase precipitate formation. The gage section hardness values were 5-10% larger than those in the grip section. This is expected to be a result of the increased dislocation content in the gage as compared to the grip.

The temperature range for the phase transformations from β-phase to α and/or ω phase(s) in a Ti-12Cr-1Fe-3Al (wt. %) (TCFA) alloy was found to be 653 K to 723 K [34]. For this study, the creep tests were conducted at 683 K which is in the temperature range.

Figure 8: Hardness values for the alloys in the different conditions showing an increase from as-processed to the heat-treated grip section and a further increase in the crept gage section

Figure 9 compares the creep strain vs time curves for TCFA as a function of applied stress. The curves indicate an increase in the creep strain as the stress was increased. Similar trends were observed for the other two alloys.

Figure 7: SE SEM photomicrographs of a.) TCA and b.) TCFA alloys after creep testing at 350 MPa exhibiting the β phase matrix with pit-like structures indicating presence of secondary phase(s)
Figure 9: Creep strain vs time plots for TCFA alloy at 683 K and varying applied stress levels

Figure 10 compares the creep strain versus time plots for the three alloys at each of the applied stress levels. At 200 MPa, TCFA exhibited greater creep resistance followed by TCA and then TC as observed in Figure 10. This trend in the creep resistances was consistently seen over all the four applied stress values. This indicates that the addition of both 3 wt. % Al and 1 wt. % Fe to Ti-12Cr (wt. %) provided the greatest creep properties among the alloys.

Although each of the creep samples were heat treated at the creep temperature (683 K) for 48 hrs prior to loading, it is possible that the phase transformations were not complete. Therefore, the microstructure may still have been evolving during the subsequent creep exposure.

The hardness results followed the same trend as the creep resistance trend. Further analysis into the creep mechanism is required to clearly ascertain the microstructure-creep property relationships. TEM studies of the microstructure, determining the volume fraction, size distribution and geometry of the secondary phases (α and ω) are required to gain a deeper understanding of the effects of the alloying elements on the observed creep trends.

Figure 10: Creep strain vs time plots for the three alloys tested at 683 K and a.) 200 MPa, b.) 250MPa, c.) 300 MPa, d.) 350 MPa showing a consistent creep resistance trend.
Summary and Conclusions

A set of Fe and Al modified Ti-12Cr (wt. %) alloys were heat-treated and the resulting microstructure, hardness, and the creep properties were characterized. The results were compared with the as-processed alloys to observe the effects of microstructure on the mechanical properties.

The as-processed XRD results showed the presence of β-phase peaks. After heat-treatment at 683 K for 12 hrs, the XRD results showed peaks corresponding to α and ω secondary phase(s). The SE SEM images of the creep tested samples revealed nanoscale pit-like structures suggesting the presence of secondary phase(s).

The grain size measurements in the as-processed state showed that the addition of Al to Ti-12Cr (wt. %) increased the average grain size by a factor of almost three and the addition of both Al and Fe resulted in an increase by a factor of 1.6 compared to the TC alloy. Addition of Al displayed a noticeable difference in the grain size measurement in the as-processed alloys. All grain size changes from the as-processed to the creep tested conditions were within a factor of 1.6 for the alloys. TC exhibited the largest grain size while TCFA exhibited the smallest grain size after creep.

The addition of Al and Fe did not contribute to a significant change in the Vickers hardness of the as-processed alloys. Post heat-treatment, the Vickers hardness exhibited an increase for all the alloys when compared to the as-received material indicating possible phase transformations during the aging process. TCFA exhibited the highest hardness followed by TCA and then TC. A slight increase of about 5%-10% in the hardness values was observed going from the grip to the gage sections of the creep tested alloys and can be the result of the higher expected dislocation content in the gage section.

The creep strength results followed the same trend as the hardness results. TCFA exhibited the greatest creep resistance followed by TCA and then TC.

Determining other mechanical properties like tensile strength, elongation-to-failure, fatigue strength and correlating them with the microstructural changes is crucial in developing an understanding of the influence of alloying elements on properties. Such studies will be important in developing cheaper alternatives to the current Ti alloys commercially being used.

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References


