Pseudo-elastic deformation behavior in a Ti/Mo-based alloy

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Abstract

It is shown that the pseudo-elastic response in a series of Ti–Mo–V–Nb–Al alloys with 8–11 wt.% Mo is highly sensitive to both composition and heat treatment. Recovery of up to 3.0% strain has been observed but it appears that this may not be due to reversible formation of \(\alpha'\) martensite.

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1. Introduction

Commercial Ti alloys are generally classified into three categories, \(\alpha\), \(\alpha + \beta\), and \(\beta\) alloys depending on the composition, thermo-mechanical processing and the ultimate microstructure. The so-called \(\beta\)-alloys contain critical amounts of \(\beta\)-stabilizing elements, such as Mo, V, Nb, W, Ta and Fe, exhibit extended \(\beta\)-stability at high temperatures, and a reduction in \(\beta\) transus temperature with increasing elemental concentration. When a certain concentration level is achieved, the \(\beta\)-phase can be retained upon rapid cooling, although it is metastable. Most commercial Ti alloys possess high strength, low modulus, good toughness, high fatigue strength, and excellent corrosion properties. These materials are typically used in the two-phase \(\beta + \alpha\) condition, and are increasingly finding applications in aerospace, oil well systems and automotive parts [1]. Alloys in the metastable \(\beta\) condition are gaining acceptance for biomedical devices.

The stability of the \(\beta\)-phase can be expressed as the sum of the weighted averages of the elements in wt.% that comprise the alloy, often known as the Mo equivalent (Mo\(_{eq}\)) given by [2]:

\[
\text{Mo}_{eq} = 1.00\text{Mo} + 0.28\text{Nb} + 0.22\text{Ta} + 0.67\text{V} + 1.60\text{Cr} + 2.90\text{Fe} - 1.00\text{Al}
\]

Experimental data indicate that if the value of this parameter is less than 8 wt.%, an alloy can exhibit a martensitic transformation when quenched from temperatures above the \(\beta\) transus. The martensite has an HCP structure, designated \(\alpha'\) martensite, in dilute compositions or an orthorhombic \(\alpha''\) martensite in more solute-rich alloys [3]. For values larger than 8 wt.%, the \(\beta\)-phase can be retained in a metastable state. Over a rather narrow compositional range the material will transform to martensite under an applied stress. Based on limited observations, the \(\alpha''\) form of martensite appears to be thermally and mechanically reversible, giving rise to a shape memory effect and possible pseudo-elasticity [4]. These characteristics have been observed in Ti–10V–2Mo–3Fe [5], Ti–Mo–Al alloys [6], Ti–15.4V–4Al [7] and Ti–11Mo–4Nb–2V–3Al [8]. The latter alloy is the basis of the study described here, the preliminary composition being set in an earlier alloy-development program [8]. Alloys with this composition showed low modulus and good pseudo-elastic response. Moreover, it was demonstrated that this alloy exhibits excellent biocompatibility, being free of potentially toxic elements such as Ni, and is therefore a strong candidate for medical applications. As a preamble to scale-up and production, a supplemental alloy-screening program was conducted using Ti–10Mo–4Nb–2V–3Al as the base with Mo-contents (x) in the range of 7.5–11.5 wt.% (Mo\(_{eq}\) = 7.0–11.0 wt.%). Mechanical testing and microstructural characterization of this alloy to explore pseudo-elastic behavior constitutes the basis of this paper.
2. Experimental

Buttons of experimental alloys were prepared by double vacuum-arc melting. The chemistries of the alloys were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OE). The results are listed in Table 1 together with the Mo$_{eq}$ values. The alloy buttons were hot-rolled and solution-treated at 870 °C in air, followed by air-cooling. Surface oxides were subsequently removed by grinding to a final thickness of 1.3 mm. Test specimens were then cut or machined from the sheets. One alloy, XB22002, was rolled to rod and 3 mm diameter wire was drawn from this stock.

Subsequent solution treatments were conducted on encapsulated specimens, which were water quenched. Aging treatments were carried out in a nitride/nitrate salt bath. Elastic spring-back characteristics were determined quantitatively by bend testing. Strip specimens, 0.5 mm × 1.3 mm × 63.5 mm, were bent 180° into a “U” shape around a mandrel of 12.2 mm diameter. This geometry yields a 4% outer fiber strain. The recovery ratio was calculated as explained in Ref. [8]. The tensile properties were determined using an Instron model 5565 testing frame with appropriate extensometry. Microstructures were characterized by optical microscopy with a Nikon Macrophot inverted metallurgical microscope and by scanning electron microscopy utilizing a JEOL JSM 6335F, equipped with a field-emission electron source for high-resolution imaging. X-ray diffraction (XRD) analysis was performed on a Bruker AXS D5005 diffractometer. Most of the results cited are for 2θ values around 40°.

3. Bend properties

The recovery ratios were determined by bend testing after solution treatment and air cooling (as-received condition) on these alloys with different Mo$_{eq}$ [9]. While alloys at the extremes of the range exhibited a recovery ratio of approximately 50%, the compositions between 7.5 and 9.5 wt.% Mo$_{eq}$ clearly demonstrated improved elasticity. The peak recovery ratio was 80% occurring at ~8.8 wt.% Mo$_{eq}$ [9].

4. Tensile properties

For the as-received materials, the tensile strength is relatively constant at around 750–825 MPa for all the compositions studied. In contrast, the yield strength falls with decreasing Mo$_{eq}$ for values below about 10 wt.% [9], dropping gradually from 790 MPa at 10.15 wt.% Mo$_{eq}$ (XB1174) to 440 MPa at 7.39 wt.% Mo$_{eq}$ (XB2067). Individual tensile stress/strain curves for sheet specimens from lower (XB2067), intermediate (XB2002) and higher (XB22002) Mo content alloys for up to 4% total strain are shown in Fig. 1. Other high Mo content alloys (Mo$_{eq}$ > 9.6 wt.%) exhibited very similar

![Graph showing tensile stress vs. strain for alloys XB2067, XB2002, and XB22002.]

Fig. 1. The tensile response of the alloys XB2067, XB2002 and XB22002 in the as-received condition.

Table 1

Chemical composition and Mo$_{eq}$ in wt.% of the experimental alloys

<table>
<thead>
<tr>
<th>Alloy no.</th>
<th>Ti</th>
<th>Mo</th>
<th>Nb</th>
<th>V</th>
<th>Al</th>
<th>Mo$_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XB2067</td>
<td>Bal.</td>
<td>8.03</td>
<td>3.89</td>
<td>2.03</td>
<td>3.09</td>
<td>7.39</td>
</tr>
<tr>
<td>Xb2001</td>
<td>Bal.</td>
<td>8.97</td>
<td>3.86</td>
<td>1.95</td>
<td>3.03</td>
<td>8.53</td>
</tr>
<tr>
<td>XB2002</td>
<td>Bal.</td>
<td>9.34</td>
<td>3.79</td>
<td>1.95</td>
<td>3.01</td>
<td>8.70</td>
</tr>
<tr>
<td>XB22002*</td>
<td>Bal.</td>
<td>9.59</td>
<td>3.98</td>
<td>1.99</td>
<td>3.13</td>
<td>9.62</td>
</tr>
<tr>
<td>XB1173</td>
<td>Bal.</td>
<td>10.35</td>
<td>3.83</td>
<td>1.99</td>
<td>3.02</td>
<td>9.93</td>
</tr>
<tr>
<td>XB1174</td>
<td>Bal.</td>
<td>10.74</td>
<td>3.88</td>
<td>2.01</td>
<td>3.02</td>
<td>10.15</td>
</tr>
</tbody>
</table>

Unit: wt.%.

*Alloy XB22002 also contains 0.25 wt.% Fe.
tensile behavior to XB22002 for up to 4% strain. Compared to the bend results on the same alloys described above, the magnitude of the recovery is clearly higher for bend tests for reasons that are not clear. It could be postulated that the compression stress element in bend may influence the results.

Deformation features in plastically strained samples were observed to be a function of composition. The most dilute alloy deformed predominantly by the formation of martensite during plastic deformation, as shown in Fig. 2(a). In contrast, the other two materials are seen to deform by slip and, possibly, twinning as shown in Fig. 2(b). No martensite was found in the XB22002 specimen with 4% strain or even in the specimens with much higher strains (>10%). A more detailed analysis of the specific morphological and crystallographic features of plastic deformation will be presented elsewhere.

Examination of the deformed specimens by X-ray diffraction confirmed the metallographic observations. The spectrum for 2θ near 40°, from an un-deformed specimen of alloy XB2067 showed the presence of only the β-phase (Fig. 2(c)). As the strain increases, the β peak diminishes and new peaks emerge. At 4%, the pattern indicates complete conversion to orthorhombic martensite (a = 0.301 nm, b = 0.491 nm, and c = 0.453 nm) as shown in Fig. 2(c). The other two alloys (XB22002 and XB1174) also exhibited a single-phase beta structure before deformation and retained this structure at 4% strain.

Wire product was received in an as-drawn condition after a reduction in area of ~50%. The stress–strain relationship for this as-received material for up to 3% strain, which is close to the fracture-limit, is shown in Fig. 3. The modulus of the material is quite low, and therefore the material shows good strain recovery, but with little evidence of classic pseudo-elastic response.

5. Influence of heat treatment on pseudo-elastic response

Based on the pseudo-elastic performance observed in bend testing, the alloy XB22002, which is near the center of the composition range, was selected for a comprehensive study of thermal exposure effects. Both wire and sheet product forms of the alloy were evaluated.

Fig. 2. (a) and (b) Secondary electron SEM micrographs showing the surface morphology of; (a) the as-received XB2067 alloy after 4% tensile strain, (b) the as-received XB22002 alloy after >10% tensile strain. (c) X-ray diffraction spectrum for the alloy XB2067 after 4% strain showing extensive formation of α’ martensite.
Material was re-solution treated at 900 °C and water-quenched. The tensile responses of the cold-worked and solution-treated wires were very different since the material has recrystallized from the cold-worked condition (Fig. 3). The yield strength is reduced with respect to the as-received material, however, the biggest change is in the recovery exhibited on stress removal which is ~3%, most of which can be attributed to pseudo-elastic behavior. For the alloy XB22002, solution-treated sheet also showed a much better pseudo-elastic response than as-received sheet, as can be seen from Fig. 3, which shows that the recovery is slightly smaller in this case.

XRD and metallographic methods were used to examine the surfaces of the bend specimens in order to provide information on the deformation modes and potential phase changes that occurred during straining. The same areas were subsequently examined when the stress had been released. An example from alloy XB22002, which showed good elastic response, is shown in Fig. 4(a) illustrating deformation features at the highest strain location while Fig. 4(b) shows the same area in the relaxed condition. There appears to be little difference between the two images indicating that any reverse deformation is limited. The initial structure before testing was single β-phase and this was the only phase found in bend specimens under stress as shown in Fig. 4(c).

It was also found that aging at lower temperatures after solution treatment can amplify the pseudo-elastic response. Specimens were held at temperatures between 350 and 550 °C for times up to 10 s. Ageing treatments resulted in a maximum 15% of recovery ratio at 550 °C for 10 s over the initial as-received materials. In all cases XRD analysis revealed only the β-phase after testing and the deformation features were similar to the as-received material.

6. Influence of strain cycling on pseudo-elastic response

The tensile properties of the as-received wire, reported above, were somewhat unexpected, in that the modulus was considerably lower than for the solution-treated material. To gain insight into the influence of strain on properties, wire samples were subjected to repeated strain cycles in tension tests between predetermined limits. The results for 3% total strain are shown in Fig. 5. It can be seen that, after the first loop, a small level of residual strain is registered, but this is not observed for the subsequent cycles. In addition, the shape of the curve changes with the flow strength, and the apparent modulus, which is defined here as the ratio of stress to strain over the pseudo-elastic range (i.e. 3% strain), decreases to ~26 GPa for the third loop. This value is similar to, but lower than, that exhibited by the as-received wire. Similar effects were observed at other strain limits, but the curve shapes became more complex as the strain range increased.

7. Discussion of results

The presence of elastic recovery clearly depends on a number of alloy, test and process factors. It is obvious from the bend test data that alloys near the middle of the composition range studied showed the best properties. However, tensile tests on the same as-received material showed no pseudo-elastic effect. Pseudo-elastic response could be induced by rapid cooling from the solution treatment temperature, and here again the best response was in alloys containing ~8.9 wt.% Mo eq. The level of recovery can be further enhanced by flash annealing at intermediate temperatures. These observations indicate that the state of stress (tension and/or compression) may influence the response, and certainly the condition established by the heat treatment cycle could also be important. One practical finding is that a fully recovered strain of 3% can be achieved in the right alloy with the correct process cycle, and this may be expanded by a pre-deformation step.

The pseudo-elastic effect in NiTi is due to a stress-induced martensitic transformation in the austenitic phase. The change in the fractions of martensitic domains due to displacement of interdomain boundaries enables an easy mode of deformation accompanied with quite remarkable reversible strains. The recovery levels for the alloys reported here are less spectacular than...
those exhibited by NiTi alloys, but certainly adequate for many medical applications. However, the experimental results in this study have failed to identify $\alpha''$ martensite as a key feature of the pseudo-elastic response. For alloys that showed good response, no $\alpha''$ martensite was detected by X-ray methods either under stress or in the relaxed state. Metallographic observations have failed to reveal any clear relaxation process, at least near the surface of specimens.

Another phase that may form within the $\beta$-phase in this class of alloys during cooling is the ubiquitous “athermal omega” phase. There are several features of the behavior which indicate that this phase may contribute to the observed pseudo-elastic response. This phase forms most readily during rapid cooling from the beta field. The critical temperature for formation has been reported as 400 °C for one alloy [10]. If the growth of the pre-existing athermal omega contributes to the strain reversibility then it could be crucial to cool at a rate that retains the optimum amount of this phase and to avoid any decomposition at higher temperature.

The fact that the as-received material softens after quenching may be an indication that some such decomposition had occurred during the original air-cooling. In addition, the beneficial effect of flash annealing above 300 °C may be a result of modifying the athermal omega phase fraction and distribution. Much

Fig. 4. Deformation in the alloy XB22022: (a) and (b) surface topographies exhibited; (a) whilst under 4% strain in a bend test, (b) the same region after unloading. (c) X-ray diffraction spectrum showing that the alloy exhibits a single beta phase after 4% strain.

Fig. 5. Tensile response for solution-treated XB22002 wire under cyclic straining. The origins for each cycle are offset for clarity.
additional work is needed not only to confirm the presence of the phase in these alloys, but also to prove that its formation is both stress-dependent and reversible.

8. Summary

A preliminary study has been performed on the pseudo-elastic response in a series of Ti–Mo–V–Nb–Al alloys with different Mo-contents. All of the as-received alloys in sheet form show at least 50% elastic recovery in bend testing to 4% peak strain with >80% recovery for alloys with a Mo<sub:eq</sub> of 9.0 wt.%. The same alloys show no evidence of pseudo-elasticity in tensile tests. Resolution treatment of sheet material with 9.5 wt.% Mo gave a pronounced pseudo-elastic response in tension and improved elastic recovery in bend tests. Subsequent flash annealing at lower temperatures gave yet higher recovery values in bend tests. The response of as-received wire specimens was also modified by solution treatment, from a low modulus material with large elastic displacements to a pseudo-elastic material similar to the sheet. The low modulus condition could be induced in multiple cycle tests. There is no clear evidence for the formation of α<sup>′</sup> martensite during pseudo-elastic deformation. Further work is underway to establish clearly the mechanisms that determine this behavior, and hence to elucidate the effects of prior microstructural condition upon pseudo-elastic response.

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