

Development of Transformation-Induced Plasticity/Twinning-Induced Plasticity Ti Alloys

Subjects: Materials Science, Characterization & Testing

Contributor: Yu Fu, Yue Gao, Wentao Jiang, Wenlong Xiao, Xinqing Zhao, Chaoli Ma

Metastable β -type Ti alloys that undergo stress-induced martensitic transformation and/or deformation twinning mechanisms have the potential to simultaneously enhance strength and ductility through the transformation-induced plasticity effect (TRIP) and twinning-induced plasticity (TWIP) effect. These TRIP/TWIP Ti alloys represent a new generation of strain hardenable Ti alloys, holding great promise for structural applications. Nonetheless, the relatively low yield strength is the main factor limiting the practical applications of TRIP/TWIP Ti alloys. The intricate interplay among chemical compositions, deformation mechanisms, and mechanical properties in TRIP/TWIP Ti alloys poses a challenge for the development of new TRIP/TWIP Ti alloys.

Keywords: TRIP ; TWIP ; Ti alloys ; solid solution strengthening ; precipitation strengthening ; grain refinement strengthening

1. Introduction

The utilization of Ti alloys as high-strength components, such as landing gears, calls for high-strength metastable β -Ti alloys with strength exceeding 1200 MPa. This level of strength is primarily attained through α precipitation strengthening and solid solution strengthening mechanisms [1][2][3]. However, the successful development of high-strength Ti alloys inevitably comes at the cost of decreased ductility and strain hardening capability owing to the restricted dislocation activity, which is typically faced in the materials' development. For example, the 0.2% yield strength of the most widely used Ti-6Al-4V (weight percentage hereafter unless otherwise specified) can be as high as ~1000 MPa, but its fracture elongation is only 12%, and its strain hardening rate is rather limited [4]. In comparison, a high ductility of 35% and high strain hardening ability (ultimate tensile strength minus yield strength) of about 730 MPa were obtained in a TRIP/TWIP Ti-8Cr-1.5Sn alloy [4]. In addition to high strength, especially the high yield strength required to prevent the alloy from plastic yielding during stress loading, combined high ductility and high strain hardening are also crucial for Ti alloys to increase the absorbable work before abrupt material fracture, thereby improving the overall service reliability [5].

A feasible way to mitigate the low ductility and limited work hardening observed in high-strength Ti alloys is to introduce additional deformation modes that can accommodate the plastic strain during dynamic deformation. These deformation mechanisms include stress-induced martensite transformation and deformation twinning, which can be achieved by tailoring the phase stability of the body-centered cubic β phase [6][7][8]. As historically observed in steels, the dynamic phase transformation and twinning during deformation lead to simultaneous improvement in strength, ductility, and strain hardening, a mechanism known as the transformation-induced plasticity (TRIP) effect and twinning-induced plasticity (TWIP) effect [9][10][11].

Since the first report of Ti-12Mo alloy combining TRIP and TWIP effects in 2012 [12], TRIP/TWIP Ti alloys have attracted increasing interest in the field of Ti science. They constitute an important class of Ti alloy due to their ability to achieve an outstanding combination of high strength, high ductility, and high strain hardening capability. Ongoing efforts are dedicated to designing new TRIP/TWIP Ti alloys with improved yield strength, ultimate tensile strength, and total elongation by manipulating the activation sequence of the various deformation modes [4][8][13][14][15]. Understanding the intrinsic correlation between the compositional design strategy (specifically, β phase stability), deformation mechanisms, and mechanical properties is essential for the design and development of new TRIP/TWIP Ti alloys that can simultaneously offer high yield strength, high strain hardening capability, and high ductility to meet the ever-growing demands for high-strength Ti alloy in advanced structural applications.

Since the first publication of Ti-12Mo TRIP/TWIP Ti alloy by Marteleur et al. in 2012 [12], which was designed using d -electron theory, there has been growing interest in these alloys over the past decade due to their remarkable combination of high strength, high ductility, and high strain hardening rate. Inspired by the compositional design method and complex

combination of deformation mechanisms observed in Ti-12Mo alloy, including stress-induced β -to- α' martensitic transformation, stress-induced β -to- α'' martensitic transformation, and $\{332\}_\beta$ deformation twinning [12][16][17], a variety of new TRIP/TWIP Ti alloys with promising mechanical properties were designed using *d*-electron theory. Examples of these alloys include Ti-9Mo-6W [18], Ti-8Cr-1.5Sn [4], and Ti-12Mo-5Zr [19]. These alloys have demonstrated simultaneously enhanced strength and ductility as a result of stress-induced martensitic phase transformation (TRIP) and deformation twinning (TWIP).

For instance, the TRIP/TWIP Ti-8.5Cr-1.5Sn exhibited 3–4 times greater ductility than Ti-6Al-4V and a 50% higher yield strength than Fe-22Mn-0.6C TWIP steel [4]. Nevertheless, the yield strength of Ti-8.5Cr-1.5Sn is about 520 MPa, and it is about 480 MPa for Ti-12Mo [4]. The design and development of new TRIP/TWIP Ti alloys have recently been a significant research focus in the Ti community. In addition to ternary alloys, Ti-Mo [20][21][22], Ti-Nb [8][23], Ti-V [13][24][25], and Ti-Cr [20][26] based multi-component alloys have been developed, such as Ti-6Cr-4Mo-2Al-2Sn-1Zr (Ti-64221) [14], Ti-3Al-5Mo-7V-3Cr (Ti-3573) [13], and Ti-3Mo-3Cr-2Fe-2Al [20]. More detailed information about the chemical compositions, deformation mechanisms, and mechanical properties of these developed TRIP/TWIP Ti alloys can be found in References [27][28][29].

Table 1 summarizes some recent findings on TRIP/TWIP Ti alloys and their mechanical properties. Researchers are committed to discovering new TRIP/TWIP Ti alloys through compositional design and studying their deformation mechanisms and mechanical properties. Despite the excellent combination of high strength, high ductility, and high strain hardening capability, one of the limitations of the TRIP/TWIP Ti alloys is the inherently soft nature of the parent β phase, which leads to low yield strength (**Table 1**) owing to the low trigger stress required to initiate stress-induced martensitic transformation and deformation twinning. TRIP/TWIP Ti alloys typically tend to exhibit a yield strength below 600 MPa, for example, Ti-12Mo (~480 MPa) [12], Ti-10V-4Cr-1Al (~420 MPa) [25], and Ti-8.5Cr-1.5Sn (520 MPa) [4], as stress-induced β -to- α'' martensitic transformation is activated at low applied stress. Therefore, the primary challenge lies in enhancing the yield strength of TRIP/TWIP Ti alloys while preserving large ductility and high strain hardenability. Several strategies are proposed to address this challenge and improve the yield strength of TRIP/TWIP Ti alloys. These strategies include solid solution strengthening [7][13][14], the precipitation of secondary phases [15][30][31][32], oxygen interstitial strengthening [16][33][34][35][36], and grain refinement [30][37].

Table 1. Summary of the main findings achieved in TRIP/TWIP Ti alloys in recent years with their mechanical properties, including yield strength (YS, MPa), engineering ultimate tensile strength (UTS, MPa), and uniform elongation (uEL).

| Alloy (wt.%) | Year | Researchers | Research Findings | YS | UTS | uEL | Ref. |
|-------------------------------|------|----------------------|---|-----|------|------|------|
| Ti-12Mo (TRIP/TWIP) | 2012 | M. Marteleur, et al. | Developing a new family of TRIP/TWIP Ti alloys based on <i>d</i> -electron alloy design | 485 | 661 | 0.35 | [12] |
| Ti-12Mo (TRIP/TWIP) | 2013 | F. Sun, et al. | Unveiling the deformation mechanisms at the early deformation stage in TRIP/TWIP Ti alloy | - | - | 0.4 | [6] |
| Ti-15Mo (TWIP) | 2013 | X. Min, et al. | Quantitative evaluation of $\{332\}_\beta$ twinning at various tensile strains | 504 | 765 | 0.24 | [38] |
| Ti-10Mo-0.2O (TRIP/TWIP) | 2014 | X. Min, et al. | Strengthening TRIP/TWIP Ti alloy by oxygen interstitials | 800 | 852 | - | [39] |
| Ti-15Mo (TWIP) | 2015 | X. Min, et al. | Strengthening TWIP Ti alloy by pre-strain-induced twins and ω_{iso} | 760 | - | 0.15 | [40] |
| Ti-9Mo-6W (TRIP/TWIP) | 2015 | F. Sun, et al. | Outstanding work hardening and uniform elongation by stress-induced β -to- α'' and β -to- ω transformation and $\{332\}_\beta$ twinning | 528 | 791 | 0.33 | [18] |
| Ti-9Cr-0.2O (TRIP) | 2015 | H. Liu, et al. | TRIP by stress-induced β -to- ω transformation | 850 | 1025 | 0.2 | [41] |
| Ti-27Nb (at.%) (TRIP/TWIP) | 2016 | P. Castany, et al. | Origin of $\{332\}_\beta$ as a result of reversion of a parent $\{130\}<310>_{\alpha''}$ twinning | - | - | - | [42] |
| Ti-12Mo (TRIP/TWIP) | 2017 | F. Sun, et al. | Strengthening TRIP/TWIP Ti alloy through low-temperature aging | 730 | 793 | 0.38 | [32] |
| Ti-6Cr-4Mo-2Al-2Sn-1Zr (TWIP) | 2018 | L. Ren, et al. | Ultrahigh product of strength and elongation (42.6 GPa%) by $\{332\}_\beta$ and $\{112\}_\beta$ twinning and reverse ω transformation | 670 | 820 | 0.31 | [14] |
| Ti-12Mo-5Zr (TRIP/TWIP) | 2018 | J. Zhang, et al. | Improving yield strength by increasing critical resolved shear stress (CRSS) of stress-induced β -to- α' transformation | 656 | 733 | 0.31 | [19] |

| Alloy (wt.%) | Year | Researchers | Research Findings | YS | UTS | uEL | Ref. |
|-------------------------------|------|----------------------|---|-----|------|------|--------------|
| Ti-3Al-5Mo-7V-3Cr (TRIP/TWIP) | 2018 | S. Sadeghpour et al. | Increasing yield strength by solid-solution strengthening | 750 | 1100 | 0.19 | [13] |
| Ti-6Mo-4Zr (at.%) | 2018 | C. Wang, et al. | Introducing a semi-empirical approach based on the average electron-to-atom ratio (e/a) and atomic radius difference (Δr) to predict the deformation behaviors of metastable β -Ti alloys | 475 | - | - | [43] |
| Ti-10V-2Fe-3Al (TRIP/TWIP) | 2019 | Y. Danard, et al. | Developing design strategy to reach ($\alpha + \beta$) dual-phase TRIP/TWIP Ti alloy | 670 | - | 0.30 | [15] |
| Ti-18Mo-13Zr (TWIP) | 2019 | J. Zhang et al. | Multimodal twinning by microscale $\{332\}_\beta$, nanoscale $\{112\}_\beta$, and novel $\{5811\}<135>_\beta$ | 800 | - | 0.18 | [44] |
| Ti-4Al-4Fe-0.25Si-0.1O (TRIP) | 2019 | S. Lee, et al. | Stress-induced β -to- α' transformation mediated by the O' phase resulted in an excellent combination of strength and ductility | 600 | 1352 | 0.3 | [45] [46] |
| Ti-11Mo-5Sn-5Nb (TWIP) | 2019 | G. Zhao, et al. | Building a multiscale dislocation-based model to describe microstructural evolution and strain-hardening of $\{332\}_\beta$ TWIP Ti alloy | 490 | 788 | 0.24 | [27] |
| Ti-16Nb-8Mo (TRIP/TWIP) | 2020 | D.M. Gordin, et al. | Designing strain transformable Ti alloy for biomedical applications | 420 | 650 | - | [47] |
| Ti-4Mo-3Cr-1Fe (TWIP) | 2020 | L. Ren, et al. | Ultrahigh yield strength and ductility harnessed by a stress-induced nano-scale hierarchical twin structure and ω_{ath} -to- β reversion | 870 | 1092 | 0.27 | [7] |
| Ti-15Nb-5Zr-4Sn-1Fe (TRIP) | 2020 | Y. Fu, et al. | Designing TRIP Ti alloy with stress-induced β -to- α' transformation | 546 | 939 | 0.17 | [8] |
| Ti-10V-2Fe-3Al (TRIP) | 2021 | B. Ellyson, et al. | $\beta + \omega$ TRIP Ti | - | - | - | [5] |
| Ti-12Mo (TRIP/TWIP) | 2021 | B. Qian, et al. | Determining transformation pathways in TRIP/TWIP Ti alloy | - | - | - | [48] |
| Ti-6Mo-3.5Cr-1Zr (TRIP) | 2022 | K. Chen, et al. | Designing TRIP Ti alloy with stress-induced β -to- ω transformation | 698 | 1242 | 0.32 | [49] |
| Ti-12Mo (TRIP/TWIP) | 2022 | B. Qian, et al. | Strengthening TRIP/TWIP Ti alloy by grain refinement and ω_{iso} | 865 | - | 0.35 | [30] |
| Ti-15Nb-5Zr-4Sn-1Fe (TRIP) | 2023 | Y. Fu, et al. | Natural aging in TRIP Ti alloy led to simultaneously enhanced yield strength and uniform elongation | 683 | 987 | 0.17 | [50] |
| Ti-12Mo-0.3O (TRIP/TWIP) | 2023 | Y. Chong, et al. | Strengthening TRIP/TWIP Ti alloy by grain refinement and oxygen interstitials | 826 | 1064 | 0.24 | [51] |

2. Solid Solution Strengthening

Solid-solution strengthening by adding substitutional and interstitial elements is a feasible way to improve the yield strength of TRIP/TWIP Ti alloys. The advantages of solid solution strengthening are twofold. The increased yield was obtained in Ti-12Mo-5Zr (656 MPa) [19] and Ti-12Mo-0.18O (623 MPa) [16], compared to baseline Ti-12Mo (480 MPa) due to the solid-solution strengthening effect of Zr and O, respectively. A multi-element Ti-3Al-5Mo-7V-3Cr TRIP/TWIP alloy with an enhanced yield strength of up to 750 MPa was designed based on considering the solid-solution strengthening effect of alloying elements [13]. Furthermore, a TWIP Ti-4Mo-3Cr-1Fe alloy, boasting a high yield strength of 870 MPa, which is the highest among the currently developed TRIP/TWIP Ti alloys [52], was designed by Ren et al. by combined addition of strong solid solution strengthening elements Mo + Cr + Fe [7].

The enhanced yield strength by solid-solution strengthening is also related to the reduced probability or even fully suppressed stress-induced martensitic transformation as a result of improved β phase stability [53]. Therefore, the addition of strengthening elements should be carefully tailored utilizing d -electron theory and $[Mo]_{\text{eq}}$ to ensure the occurrence of TRIP and/or TWIP effects. A small amount of oxygen interstitial doping can effectively enhance the yield strength by suppressing stress-induced martensitic transformation and deformation twinning in metastable β -Ti alloys [33][39][54], i.e., the interstitial oxygen acts as a strong β -stabilizing element in metastable β -Ti alloys. Doping 0.3 wt.% oxygen combined with grain refinement was successfully employed by Chong et al. to substantially improve the yield strength of Ti-12Mo-0.3O to 826 MPa while maintaining a high strain hardening ability and high uniform elongation [51]. The beneficial role of O

interstitial strengthening is also reported in Ti-32Nb [55], Ti-38Nb [36][55], and Ti-20V [34]. However, oxygen is excluded by the calculation of electron parameters \overline{Bo} , \overline{Md} , and $\overline{e/a}$, while it is treated as an α -stabilizer in calculating the $[Mo]_{eq}$, meaning that the β -stabilizing effect of interstitial oxygen is not considered in the current semi-empirical alloy design approaches. So do the neutral elements Zr and Sn. Consequently, the current d -electron theory, $[Mo]_{eq}$, and electron-to-atom ratio approach need to be modified to fully harness the benefits of the β -stabilizing effect of oxygen, Zr, and Sn, and their interaction with other β -stabilizers.

3. Precipitation Strengthening

3.1. α Precipitation Strengthening

The yield strength can also be enhanced by developing TRIP/TWIP Ti alloys from the single β phase alloys to $\beta + \alpha$ and $\beta + \omega$ dual-phase alloys, which can be achieved by utilizing equiaxed α phase or nanoscale ω phase precipitation to strengthen the least stable β matrix. The yield strength (760 MPa) of 20% α strengthened Ti-7Cr-1.5Sn dual-phase alloy is 200 MPa higher than that of the Ti-8.5Cr-1.5Sn single β phase alloy while maintaining the TRIP/TWIP effects [56]. A transition from TRIP to TRIP/TWIP in Ti-10V-2Fe-3Al accompanied by remarkably enhanced yield strength was achieved by precipitating the 20% α phase [15]. Simultaneously enhanced yield strength, ultimate tensile strength, and ductility were observed in a 4 vol.% α containing $\alpha + \beta$ dual-phase Ti-3Mo-3Cr-2Fe-2Al TRIP/TWIP alloy as compared to its single-phase counterpart [20]. The precipitation of the α phase leads to solute-atom partitioning, enriching the β matrix with β -stabilizers and thus enhancing its phase stability, which results in a transition of deformation mechanism from TRIP to TWIP or even the complete suppression of the TRIP/TWIP effect. It appears that a small fraction of no more than 20 vol.% α should be ensured to maintain the TRIP/TWIP effects in $\alpha + \beta$ dual-phase Ti alloys [46][57][58][59]. The volume fraction of α precipitates and the resultant transition of deformation mode in $\alpha + \beta$ dual-phase TRIP/TWIP Ti alloys can be guided by coupling the Calphad calculation and $\overline{Bo} - \overline{Md}$ diagram [15][56]. The α precipitation strengthening opens a new branch of TRIP/TWIP Ti alloy development from single β phase alloys to $\alpha + \beta$ dual phase alloys.

3.2. ω Precipitation Strengthening

Controlling the development of ω phase has also been shown to be quite effective in increasing the yield strength of TRIP/TWIP Ti alloys while reserving their promising strain hardening, leading to the development of ω strengthened $\beta + \omega$ dual-phase TRIP/TWIP Ti alloys [30][32]. Sun et al. [32] conducted low-temperature short-time aging (150 °C for 60 s) to control the development of the isothermal ω phase in Ti-12Mo without causing any discernible compositional partitioning. This method takes full advantage of the precipitation hardening of the ω phase while minimizing its harmful effect on suppressing stress-induced martensitic transformation and deformation twinning. The result was a substantial increase in yield strength from 480 MPa to 730 MPa while maintaining the original high ductility. Low-temperature short-time aging (200 °C for 60 s) combined with grain refinement was employed by Qian et al. [30] to achieve high yield strength as high as 990 MPa in Ti-12Mo without significantly sacrificing the ductility. Enhanced uniform elongation in the Ti-15Mo TWIP alloy was achieved by Min et al. through coupling pre-strain-induced twins and isothermal ω (ω_{iso}) precipitation, as compared to the counterpart with only ω_{iso} precipitation [40][60][61]. These works have highlighted the potential of tuning the ω phase precipitation to enhance the mechanical properties of TRIP/TWIP Ti alloys.

It is worth mentioning that the athermal ω (ω_{ath}) phase formed during quenching is not harmful to the mechanical properties of TRIP/TWIP Ti alloys, contrary to the isothermal ω phase. It is reported that the ω_{ath} disappeared after the formation of stress-induced martensite and deformation twinning, which is believed to be reversed back to the parent β phase during deformation [7][8][62]. The excellent combination of high yield strength of 870 MPa, ultimate tensile strength of 1092 MPa, and excellent ductility with a fracture elongation of 41% observed in Ti-4Mo-3Cr-1Fe is likely related to the dynamic ω_{ath} -to- β reversion during tensile deformation, which promotes the formation of stress-induced nano-scale hierarchical twinning structures [7].

The ω_{ath} -to- β reversion ability during deformation makes it possible to tune the deformation mechanisms and mechanical properties of TRIP/TWIP Ti alloys by regulating the development of ω_{ath} . This can be realized by low-temperature short-time aging [5][30][32] and room-temperature aging [5][50]. Accordingly, substantially increased yield strength without obviously sacrificing ductility or even enhanced ductility was achieved in Ti-12Mo, Ti-10V-2Fe-3Al, and Ti-15Nb-5Zr-4Sn-1Fe [5][30][32][50]. Especially, a high yield strength of 683 MPa, which is comparable to most of the TRIP/TWIP Ti alloys, was reported in a TRIP Ti-15Nb-5Zr-4Sn-1Fe TRIP Ti alloy after regulating the ω_{ath} by nature aging [50]. These results demonstrate a new opportunity to enhance the mechanical properties of TRIP/TWIP Ti alloys via engineering the ω_{ath} . Future efforts may be dedicated to revealing the evolution of ω_{ath} during aging and its influence on the deformation mechanisms and mechanical properties of TRIP/TWIP Ti alloys.

4. Grain Refinement Strengthening

The role of grain refinement strengthening in increasing the yield strength of TRIP/TWIP Ti alloys has received little attention. This might be attributed to the fact that the critical resolved shear stress for stress-induced martensitic phase transformation and deformation twinning is not very sensitive to changes in grain size [63][64][65]. A higher yield strength was observed in coarser-grained TRIP Ti alloys [66][67][68]. Accordingly, the impact of grain refinement on the yield strength of TRIP/TWIP Ti alloys is limited. It is challenging to refine the grain size of metastable β -Ti alloys to the ultrafine grain scale after undergoing severe plastic deformation. This difficulty is related to the rapid recrystallization and grain growth kinetics during the annealing of Ti alloys above the β transus temperatures [51][64].

Chong et al. [51] demonstrate that significantly refining the grain size from 50 μm to 4.5 μm in Ti-12Mo only slightly increased the yield strength by 43 MPa. A similar result has also been reported in Ti-13.3Nb-4.6Mo (at.%) [37]. This is because substantial grain refinement promotes the occurrence of stress-induced martensitic phase transformation, leading to a reduction in the ultimate tensile strength and ductility. However, combining grain refinement with other strengthening methods, such as α phase precipitation [20], ω phase precipitation [30], and oxygen addition [16], has shown the potential to significantly increase the yield strength while maintaining high ductility and a high work-hardening rate. Therefore, the combination of grain refinement with other strengthening methods is worthy of further research and exploration.

References

1. Banerjee, D.; Williams, J.C. Perspectives on titanium science and technology. *Acta Mater.* 2013, 61, 844–879.
2. Devaraj, A.; Joshi, V.V.; Srivastava, A.; Manandhar, S.; Moxson, V.; Duz, V.A.; Lavender, C. A low-cost hierarchical nanostructured beta-titanium alloy with high strength. *Nat. Commun.* 2016, 7, 11176.
3. Cotton, J.D.; Briggs, R.D.; Boyer, R.R.; Tamirisakandala, S.; Russo, P.; Shchetnikov, N.; Fanning, J.C. State of the art in beta titanium alloys for airframe applications. *Miner. Met. Mater. Ser.* 2015, 67, 1281–1303.
4. Brozek, C.; Sun, F.; Vermaut, P.; Millet, Y.; Lenain, A.; Embury, D.; Jacques, P.J.; Prima, F. A β -titanium alloy with extra high strain-hardening rate: Design and mechanical properties. *Scr. Mater.* 2016, 114, 60–64.
5. Ellyson, B.; Klemm-Toole, J.; Clarke, K.; Field, R.; Kaufman, M.; Clarke, A. Tuning the strength and ductility balance of a TRIP titanium alloy. *Scr. Mater.* 2021, 194, 113641.
6. Sun, F.; Zhang, J.Y.; Marteleur, M.; Gloriant, T.; Vermaut, P.; Lailé, D.; Castany, P.; Curfs, C.; Jacques, P.J.; Prima, F. Investigation of early stage deformation mechanisms in a metastable β titanium alloy showing combined twinning-induced plasticity and transformation-induced plasticity effects. *Acta Mater.* 2013, 61, 6406–6417.
7. Ren, L.; Xiao, W.; Kent, D.; Wan, M.; Ma, C.; Zhou, L. Simultaneously enhanced strength and ductility in a metastable β -Ti alloy by stress-induced hierarchical twin structure. *Scr. Mater.* 2020, 184, 6–11.
8. Fu, Y.; Xiao, W.; Kent, D.; Dargusch, M.S.; Wang, J.; Zhao, X.; Ma, C. Ultrahigh strain hardening in a transformation-induced plasticity and twinning-induced plasticity titanium alloy. *Scr. Mater.* 2020, 187, 285–290.
9. Zhang, Y.; Song, R.; Wang, Y.; Cai, C.; Wang, H.; Wang, K. C-modified stacking-fault networks inducing the excellent strength- plasticity combinations of medium manganese steel by simple two-stage warm rolling without annealing. *Scr. Mater.* 2023, 229, 115372.
10. Zhi, H.; Li, J.; Li, W.; Elkot, M.; Antonov, S.; Zhang, H.; Lai, M. Simultaneously enhancing strength-ductility synergy and strain hardenability via Si-alloying in medium-Al FeMnAlC lightweight steels. *Acta Mater.* 2023, 245, 118611.
11. Gao, J.; Jiang, S.; Zhang, H.; Huang, Y.; Guan, D.; Xu, Y.; Guan, S.; Bendersky, L.A.; Davydov, A.V.; Wu, Y.; et al. Facile route to bulk ultrafine-grain steels for high strength and ductility. *Nature* 2021, 590, 262–267.
12. Marteleur, M.; Sun, F.; Gloriant, T.; Vermaut, P.; Jacques, P.J.; Prima, F. On the design of new β -metastable titanium alloys with improved work hardening rate thanks to simultaneous TRIP and TWIP effects. *Scr. Mater.* 2012, 66, 749–752.
13. Sadeghpour, S.; Abbasi, S.M.; Morakabati, M.; Kisko, A.; Karjalainen, L.P.; Porter, D.A. A new multi-element beta titanium alloy with a high yield strength exhibiting transformation and twinning induced plasticity effects. *Scr. Mater.* 2018, 145, 104–108.
14. Ren, L.; Xiao, W.; Ma, C.; Zheng, R.; Zhou, L. Development of a high strength and high ductility near β -Ti alloy with twinning induced plasticity effect. *Scr. Mater.* 2018, 156, 47–50.

15. Danard, Y.; Poulain, R.; Garcia, M.; Guillou, R.; Thiaudière, D.; Mantri, S.; Banerjee, R.; Sun, F.; Prima, F. Microstructure design and in-situ investigation of TRIP/TWIP effects in a forged dual-phase Ti-10V-2Fe-3Al alloy. *Materialia* 2019, 8, 100507.
16. Bortolan, C.C.; Campanelli, L.C.; Paternoster, C.; Giguère, N.; Brodusch, N.; Bolfarini, C.; Gauvin, R.; Mengucci, P.; Barucca, G.; Mantovani, D. Effect of oxygen content on the mechanical properties and plastic deformation mechanisms in the TWIP/TRIP Ti-12Mo alloy. *Mater. Sci. Eng. A* 2021, 817, 141346.
17. Zhang, J.Y.; Li, J.S.; Chen, Z.; Meng, Q.K.; Sun, F.; Shen, B.L. Microstructural evolution of a ductile metastable β titanium alloy with combined TRIP/TWIP effects. *J. Alloys Compd.* 2017, 699, 775–782.
18. Sun, F.; Zhang, J.Y.; Marteleur, M.; Brozek, C.; Rauch, E.F.; Veron, M.; Vermaut, P.; Jacques, P.J.; Prima, F. A new titanium alloy with a combination of high strength, high strain hardening and improved ductility. *Scr. Mater.* 2015, 94, 17–20.
19. Zhang, J.; Li, J.; Chen, G.; Liu, L.; Chen, Z.; Meng, Q.; Shen, B.; Sun, F.; Prima, F. Fabrication and characterization of a novel β metastable Ti-Mo-Zr alloy with large ductility and improved yield strength. *Mater. Charact.* 2018, 139, 421–427.
20. Lee, S.W.; Park, C.H.; Hong, J.-K.; Yeom, J.-T. Development of sub-grained $\alpha+\beta$ Ti alloy with high yield strength showing twinning- and transformation-induced plasticity. *J. Alloys Compd.* 2020, 813, 152102.
21. Gao, J.; Knowles, A.J.; Guan, D.; Rainforth, W.M. ω phase strengthened 1.2GPa metastable β titanium alloy with high ductility. *Scr. Mater.* 2019, 162, 77–81.
22. Xu, Y.; Gao, J.; Huang, Y.; Rainforth, W.M. A low-cost metastable beta Ti alloy with high elastic admissible strain and enhanced ductility for orthopaedic application. *J. Alloys Compd.* 2020, 835, 155391.
23. Li, Q.; Liu, T.; Li, J.; Cheng, C.; Niinomi, M.; Yamanaka, K.; Chiba, A.; Nakano, T. Microstructure, mechanical properties, and cytotoxicity of low Young's modulus Ti-Nb-Fe-Sn alloys. *J. Mater. Sci.* 2022, 57, 5634–5644.
24. Wang, W.; Zhang, X.; Mei, W.; Sun, J. Role of omega phase evolution in plastic deformation of twinning-induced plasticity β Ti-12V-2Fe-1Al alloy. *Mater. Des.* 2020, 186, 108282.
25. Liliensten, L.; Danard, Y.; Brozek, C.; Mantri, S.; Castany, P.; Gloriant, T.; Vermaut, P.; Sun, F.; Banerjee, R.; Prima, F. On the heterogeneous nature of deformation in a strain-transformable beta metastable Ti-V-Cr-Al alloy. *Acta Mater.* 2019, 162, 268–276.
26. Danard, Y.; Martin, G.; Liliensten, L.; Sun, F.; Seret, A.; Poulain, R.; Mantri, S.; Guillou, R.; Thiaudière, D.; Freiherr von Thüngen, I.; et al. Accommodation mechanisms in strain-transformable titanium alloys. *Mater. Sci. Eng. A* 2021, 819, 141437.
27. Zhao, G.-H.; Xu, X.; Dye, D.; Rivera-Díaz-del-Castillo, P.E.J. Microstructural evolution and strain-hardening in TWIP Ti alloys. *Acta Mater.* 2020, 183, 155–164.
28. Castany, P.; Gloriant, T.; Sun, F.; Prima, F. Design of strain-transformable titanium alloys. *C. R. Phys.* 2018, 19, 710–720.
29. Zhao, G.; Li, X.; Petrinic, N. Materials information and mechanical response of TRIP/TWIP Ti alloys. *NJP Comput. Mater.* 2021, 7, 91.
30. Qian, B.; Mantri, S.A.; Dasari, S.; Zhang, J.; Liliensten, L.; Sun, F.; Vermaut, P.; Banerjee, R.; Prima, F. Mechanisms underlying enhanced strength-ductility combinations in TRIP/TWIP Ti-12Mo alloy engineered via isothermal omega precipitation. *Acta Mater.* 2023, 245, 118619.
31. Zhang, J.Y.; Chen, G.F.; Fu, Y.Y.; Fan, Y.; Chen, Z.; Xu, J.; Chang, H.; Zhang, Z.H.; Zhou, J.; Sun, Z.; et al. Strengthening strain-transformable β Ti-alloy via multi-phase nanostructuring. *J. Alloys Compd.* 2019, 799, 389–397.
32. Sun, F.; Zhang, J.Y.; Vermaut, P.; Choudhuri, D.; Alam, T.; Mantri, S.A.; Svec, P.; Gloriant, T.; Jacques, P.J.; Banerjee, R.; et al. Strengthening strategy for a ductile metastable β -titanium alloy using low-temperature aging. *Mater. Res. Lett.* 2017, 5, 547–553.
33. Min, X.; Bai, P.; Emura, S.; Ji, X.; Cheng, C.; Jiang, B.; Tsuchiya, K. Effect of oxygen content on deformation mode and corrosion behavior in β -type Ti-Mo alloy. *Mater. Sci. Eng. A* 2017, 684, 534–541.
34. Wang, X.L.; Li, L.; Xing, H.; Ou, P.; Sun, J. Role of oxygen in stress-induced ω phase transformation and $\langle 113 \rangle$ mechanical twinning in β Ti-20V alloy. *Scr. Mater.* 2015, 96, 37–40.
35. Ramarolahy, A.; Castany, P.; Prima, F.; Laheurte, P.; Peron, I.; Gloriant, T. Microstructure and mechanical behavior of superelastic Ti-24Nb-0.5O and Ti-24Nb-0.5N biomedical alloys. *J. Mech. Behav. Biomed. Mater.* 2012, 9, 83–90.
36. Li, Q.; Ma, D.; Li, J.; Niinomi, M.; Nakai, M.; Koizumi, Y.; Wei, D.; Kakeshita, T.; Nakano, T.; Chiba, A.; et al. Low Young's Modulus Ti-Nb-O with High Strength and Good Plasticity. *Mater. Trans.* 2018, 59, 858–860.

37. Zhang, B.; Huang, M.; Chong, Y.; Mao, W.; Gong, W.; Zheng, R.; Bai, Y.; Wang, D.; Sun, Q.; Wang, Y.; et al. Achieving large super-elasticity through changing relative easiness of deformation modes in Ti-Nb-Mo alloy by ultra-grain refinement. *Mater. Res. Lett.* 2021, 9, 223–230.
38. Min, X.; Chen, X.; Emura, S.; Tsuchiya, K. Mechanism of twinning-induced plasticity in β -type Ti-15Mo alloy. *Scr. Mater.* 2013, 69, 393–396.
39. Min, X.H.; Emura, S.; Tsuchiya, K.; Nishimura, T.; Tsuzaki, K. Transition of multi-deformation modes in Ti-10Mo alloy with oxygen addition. *Mater. Sci. Eng. A* 2014, 590, 88–96.
40. Min, X.; Emura, S.; Zhang, L.; Tsuzaki, K.; Tsuchiya, K. Improvement of strength–ductility tradeoff in β titanium alloy through pre-strain induced twins combined with brittle ω phase. *Mater. Sci. Eng. A* 2015, 646, 279–287.
41. Liu, H.; Niinomi, M.; Nakai, M.; Cho, K. β -Type titanium alloys for spinal fixation surgery with high Young's modulus variability and good mechanical properties. *Acta Biomater.* 2015, 24, 361–369.
42. Castany, P.; Yang, Y.; Bertrand, E.; Gloriant, T. Reversion of a parent $\langle 310 \rangle \alpha''$ martensitic twinning system at the origin of $\langle 113 \rangle \beta$ twins observed in metastable β titanium alloys. *Phys. Rev. Lett.* 2016, 117, 245501.
43. Wang, C.H.; Russell, A.M.; Cao, G.H. A semi-empirical approach to the prediction of deformation behaviors of β -Ti alloys. *Scr. Mater.* 2019, 158, 62–65.
44. Zhang, J.; Sun, F.; Chen, Z.; Yang, Y.; Shen, B.; Li, J.; Prima, F. Strong and ductile beta Ti-18Zr-13Mo alloy with multimodal twinning. *Mater. Res. Lett.* 2019, 7, 251–257.
45. Lee, S.; Park, C.; Hong, J.; Yeom, J.-t. The role of nano-domains in twinned martensite in metastable titanium alloys. *Sci. Rep.* 2018, 8, 11914.
46. Lee, S.W.; Oh, J.M.; Park, C.H.; Hong, J.-K.; Yeom, J.-T. Deformation mechanism of metastable titanium alloy showing stress-induced α' -Martensitic transformation. *J. Alloys Compd.* 2019, 782, 427–432.
47. Gordin, D.M.; Sun, F.; Lailé, D.; Prima, F.; Gloriant, T. How a new strain transformable titanium-based biomedical alloy can be designed for balloon expandable stents. *Materialia* 2020, 10, 100638.
48. Qian, B.; Liliensten, L.; Zhang, J.; Yang, M.; Sun, F.; Vermaut, P.; Prima, F. On the transformation pathways in TRIP/TWIP Ti-12Mo alloy. *Mater. Sci. Eng. A* 2021, 822, 141672.
49. Chen, K.; Fan, Q.; Yao, J.; Yang, L.; Xu, S.; Lei, W.; Wang, D.; Yuan, J.; Gong, H.; Cheng, X. Composition design of a novel Ti-6Mo-3.5Cr-1Zr alloy with high-strength and ultrahigh-ductility. *J. Mater. Sci. Technol.* 2022, 131, 276–286.
50. Fu, Y.; Xiao, W.; Kent, D.; Rong, J.; Zhao, X.; Ma, C. Natural aging of a metastable β -type titanium alloy to simultaneously enhance yield strength and uniform elongation. *Scr. Mater.* 2023, 234, 115569.
51. Chong, Y.; Gholizadeh, R.; Guo, B.; Tsuru, T.; Zhao, G.; Yoshida, S.; Mitsuhashi, M.; Godfrey, A.; Tsuji, N. Oxygen interstitials make metastable β titanium alloys strong and ductile. *Acta Mater.* 2023, 257, 119165.
52. Zhang, C.; Liu, S.; Zhang, J.; Zhang, D.; Kuang, J.; Bao, X.; Liu, G.; Sun, J. Trifunctional nanoprecipitates ductilize and toughen a strong laminated metastable titanium alloy. *Nat. Commun.* 2023, 14, 1397.
53. Qian, B.; Zhang, J.; Fu, Y.; Sun, F.; Wu, Y.; Cheng, J.; Vermaut, P.; Prima, F. In-situ microstructural investigations of the TRIP-to-TWIP evolution in Ti-Mo-Zr alloys as a function of Zr concentration. *J. Mater. Sci. Technol.* 2021, 65, 228–237.
54. Liu, H.; Niinomi, M.; Nakai, M.; Cong, X.; Cho, K.; Boehlert, C.J.; Khademi, V. Abnormal Deformation Behavior of Oxygen-Modified β -Type Ti-29Nb-13Ta-4.6Zr Alloys for Biomedical Applications. *Metall. Mater. Trans. A* 2016, 48, 139–149.
55. Wang, J.; Xiao, W.; Ren, L.; Fu, Y.; Ma, C. The roles of oxygen content on microstructural transformation, mechanical properties and corrosion resistance of Ti-Nb-based biomedical alloys with different β stabilities. *Mater. Charact.* 2021, 176, 111122.
56. Liliensten, L.; Danard, Y.; Poulain, R.; Guillou, R.; Joubert, J.M.; Perrière, L.; Vermaut, P.; Thiaudière, D.; Prima, F. From single phase to dual-phase TRIP-TWIP titanium alloys: Design approach and properties. *Materialia* 2020, 12, 100700.
57. Fu, Y.; Xiao, W.; Wang, J.; Zhao, X.; Ma, C. Mechanical properties and deformation mechanisms of Ti-15Nb-5Zr-4Sn-1Fe alloy with varying α phase fraction. *J. Alloys Compd.* 2022, 898, 162816.
58. Chong, Y.; Gao, S.; Tsuji, N. A unique three-stage dependence of yielding behavior and strain-hardening ability in Ti-10V-2Fe-3Al alloy on phase fraction. *Mater. Sci. Eng. A* 2021, 821, 141609.
59. Liao, Z.; Luan, B.; Zhang, X.; Liu, R.; Murty, K.L.; Liu, Q. Effect of varying α phase fraction on the mechanical properties and deformation mechanisms in a metastable β -ZrTiAlV alloy. *Mater. Sci. Eng. A* 2019, 772, 138784.
60. Min, X.; Xiang, I.; Li, M.; Yao, K.; Emura, S.; Cheng, C.; Tsuchiya, K. Effect of $\langle 113 \rangle$ Twins Combined with Isothermal ω -Phase on Mechanical Properties in Ti-15Mo Alloy with Different Oxygen Contents. *Aata Metall. Sinica* 2018, 54,

61. Min, X.; Tsuzaki, K.; Emura, S.; Tsuchiya, K. Enhanced uniform elongation by pre-straining with deformation twinning in high-strength β -titanium alloys with an isothermal ω -phase. *Philos. Mag. Lett.* 2012, 92, 726–732.
62. Xiao, J.F.; Nie, Z.H.; Tan, C.W.; Zhou, G.; Chen, R.; Li, M.R.; Yu, X.D.; Zhao, X.C.; Hui, S.X.; Ye, W.J.; et al. Effect of reverse β -to- ω transformation on twinning and martensitic transformation in a metastable β titanium alloy. *Mater. Sci. Eng. A* 2019, 759, 680–687.
63. Church, N.L.; Hildyard, E.M.; Jones, N.G. The influence of grain size on the onset of the superelastic transformation in Ti-24Nb-4Sn-8Zr (wt%). *Mater. Sci. Eng. A* 2021, 828, 142072.
64. Wang, J.; Xiao, W.; Fu, Y.; Ren, L.; Ma, C. Dependence of mechanical behavior on grain size of metastable Ti-Nb-O titanium alloy. *Prog. Nat. Sci. Mater. Inter.* 2022, 32, 63–71.
65. Cai, M.-H.; Lee, C.-Y.; Lee, Y.-K. Effect of grain size on tensile properties of fine-grained metastable β titanium alloys fabricated by stress-induced martensite and its reverse transformations. *Scr. Mater.* 2012, 66, 606–609.
66. Ma, X.; Chen, Z.; Xiao, L.; Lu, W.; Luo, S.; Mi, Y. Compressive deformation of a metastable β titanium alloy undergoing a stress-induced martensitic transformation: The role of β grain size. *Mater. Sci. Eng. A* 2020, 794, 139919.
67. Bhattacharjee, A.; Bhargava, S.; Varma, V.K.; Kamat, S.V.; Gogia, A.K. Effect of β grain size on stress induced martensitic transformation in β solution treated Ti-10V-2Fe-3Al alloy. *Scr. Mater.* 2005, 53, 195–200.
68. Xiao, J.F.; Shang, X.K.; Hou, J.H.; Li, Y.; He, B.B. Role of stress-induced martensite on damage behavior in a metastable titanium alloy. *Inter. J. Plast.* 2021, 146, 103103.