

**STRESS-INDUCED MARTENSITIC TRANSFORMATION
ROLE ON MICROSTRUCTURE-MECHANICAL
PROPERTIES CORRELATION IN METASTABLE
 β TITANIUM ALLOYS**

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by

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to the



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Certificate

This is to certify that the thesis titled “**STRESS-INDUCED MARTENSITIC TRANSFORMATION ROLE ON MICROSTRUCTURE-MECHANICAL PROPERTIES CORRELATION IN METASTABLE β TITANIUM ALLOYS**” is being submitted by **Mr. ABHISHEK RASTOGI** to the Indian Institute of Technology Delhi for the award of the degree of **DOCTOR OF PHILOSOPHY**. This is a record of bonafide research work carried out by him under my supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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Abstract

Stress-induced martensitic transformations (SIMT) in retained metastable phase are known deformation mechanisms that provide additional plasticity in several metallic alloy systems. Iron-, titanium- and high entropy-alloy systems exhibit metastable phases that show transformation plasticity due to twinning or martensite formation. Metastable β -Ti alloys, in specific, show significant potential for martensitic transformation through microstructure modification promoting leading to transformation-induced plasticity (TRIP). Typically, β (austenite) $\rightarrow \alpha''$ (orthorhombic) and $\beta \rightarrow \alpha'$ (HCP) martensitic transformations are induced in them either by quenching or application of load. The two transformations differ from each other in terms of atomic shuffle displacement, with the former requiring less than the latter. As a result, $\beta \rightarrow \alpha''$ transformation can be considered as a crystallographically incomplete $\beta \rightarrow \alpha'$ transformation. Further, the influence of different alloying elements in metastable β -Ti alloys also plays an important role in driving the $\alpha'' \rightarrow \alpha'$ martensitic transformation. In addition, the microstructural state, in particular the β phase stability and β grain orientations, play an important role on the martensite transformation during deformation and eventual property enhancement in metastable β -Ti alloys.

This thesis work effectively demonstrates SIMT in metastable β Ti-10V-2Fe-3Al (Ti-1023) alloy resulting in enhanced cold deformability. The evidence of phase transformation from $\beta \rightarrow \alpha'' \rightarrow \alpha'$ martensites is observed in Ti-1023 alloy during continuous deformation. Microstructural characterization using electron backscattered diffraction (EBSD), X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis confirmed the transformation of α'' to α' . It is noted that the combined effect of lattice strain induced by cold rolling and the different alloying elements, drives the $\alpha'' \rightarrow \alpha'$ martensitic transformation. A correlation of the lattice strain and alloying elements on the transformation

of $\beta \rightarrow \alpha'' \rightarrow \alpha'$ in Ti-1023 has been established. The observations thus confirm stress-induced martensite (SIM) been the prime reason for achieving enhanced cold deformability (up to $\sim 43\%$). Significant fraction of SIM provides preferred nucleation sites for new strain-free grains upon recrystallization annealing. The thermomechanical treatment results in grain refinement by $\sim 93\%$ in Ti-1023 alloys. Further, the influence of grain size on the SIM transformability based on micro hardness variations has been deduced. In addition, the role of the stability of β phase on the SIM transformation is elucidated using Electron Probe Micro Analyzer (EPMA) in the Ti-1023 microstructure. EPMA confirms the influence of diffusivities of alloying element (such as Fe, Mo, V, Cr and Al) as a function of recrystallization time on the β phase stability.

Furthermore, the surface characterization of micro indents using EBSD technique highlights that only a few grain orientations on the top surface showed the formation of stress-induced martensitic laths after micro indentation, suggesting that the SIMT is influenced by the grain orientations. Therefore, nanoindentation has been used to elucidate the grain orientation relationship on the SIM transformation behaviour during deformation and their eventual effect on the mechanical properties of Ti-1023. Austenite grains with specific crystallographic orientations of near $\langle 001 \rangle$, $\langle 101 \rangle$ and $\langle 111 \rangle$ are chosen. Nanoindentation is performed with two different diamond indenters viz. Berkovich and cono spherical. Nanoindentation reveals dominant stress-induced martensitic (of α'' type) transformation in the grains with near $\langle 111 \rangle$ crystallographic orientation, which contrasts with near $\langle 001 \rangle$ orientations showing only the presence of slip at the surface. In addition, lowest hardness (~ 4.1 GPa) is observed for near $\langle 111 \rangle$ grain orientations, while the hardness increased further for the near $\langle 101 \rangle$ and $\langle 001 \rangle$ grain orientations (~ 4.3 GPa). The observations confirm that near $\langle 111 \rangle$ grain orientation is the most favoured grain orientation, followed by near $\langle 101 \rangle$ for enhanced SIM, while the near $\langle 001 \rangle$ grain orientation is the least

favoured. Therefore, deformation micro-mechanisms across various length scales have been established by study of local deformation behaviour at the nanoscale.

Plastic deformation characteristics has been studied through different modes of localised deformation like micro and nanoindentation, however, the influence of SIMT on the overall material's mechanical behaviour is critical. Thus the influence of SIMT on the tensile deformation properties has been evaluated. The alloy show SIM transformation with strength enhancement, and the triggering stress variation with β grain size. However, the % strain to failure shows a significant decrease. Furthermore, the dual impact of SIM on the deformation and fracture behaviour is found, wherein the presence of SIM induces embrittlement during the plastic deformation, which resulted in absence of necking, despite enhancing the overall strength of the alloy by double yielding. Consequently, also providing indication for the absence of necking followed by non-uniform elongation during tensile deformation, which can be attributed to the embrittling actions of SIM. Since β grain size mainly governs the martensitic lath spacing and width, grain boundary engineering serves the foundation for creating high-performance Ti alloys.

Overall, the study highlights that the SIMT has successfully shown to result in achievement of the enhanced cold deformability. Furthermore, the high cold deformability is attributed to the orthorhombic- α'' martensites coupled with strain-induced $\alpha'' \rightarrow \alpha'$ martensitic transformations resulting in enhanced plasticity. SIM also acted as nucleating sites and eventually promoted grain refinement. Additionally, indentation studies have demonstrated the influence of grain orientations on the SIM transformability, providing confirmation that near $\langle 111 \rangle$ grain orientations are most favored, followed by near $\langle 101 \rangle$ for enhanced SIM, while the near $\langle 001 \rangle$ grain orientations are the least favored. Finally, the dual impact of SIM on deformation and fracture behaviour is found, wherein, the presence of SIM induced embrittlement during the plastic deformation despite enhancing the overall ductility

of the alloy by double yielding. Additionally, also provided indication for the absence of necking followed by non-uniform elongation during tensile deformation, which is ascribed to the embrittling actions of SIM. Consequently, the study evidently elucidates that β grain size and triggering of multiple variant martensites control the SIM transformability during plastic deformation. The study further demonstrates that effective control of SIM transformation potentially could provide strength-ductility enhancement via transformation-induced plasticity in metastable β titanium alloys.

सार

तनाव-उत्पन्न मार्टेन्सिटिक परिवर्तन (SIMT) में रखी गई मेटास्टेबल फेज में जोड़ी जाने वाली विकृति यांत्रिकी हैं जो कई धातुयुक्त एलॉय प्रणालियों में अतिरिक्त प्लास्टिसिटी प्रदान करती हैं। लोहा, टाइटेनियम, और उच्च एंट्रोपी-एलॉय प्रणालियाँ मेटास्टेबल फेज को दिखाती हैं जो ट्विनिंग या मार्टेन्साइट निर्माण के कारण परिवर्तन प्लास्टिसिटी दिखाती हैं। विशिष्ट रूप से, मेटास्टेबल बीटा-टाइटैनियम एलॉयज, मार्टेन्सिटिक परिवर्तन के लिए महत्वपूर्ण संभावना दिखाती हैं जो माइक्रोस्ट्रक्चर संशोधन के माध्यम से परिवर्तन-उत्पन्न प्लास्टिसिटी (TRIP) को प्रमोट करता है। सामान्यतः बीटा (ऑस्टेनाइट) → एल्फा" (ऑर्थोरोम्बिक) और बीटा → एल्फा' (एचसीपी) मार्टेन्सिटिक परिवर्तनों को उनमें या तो केंचिंग या लोड लगाने से प्रेरित किया जाता है। इन दो परिवर्तनों में एटमिक शफल विस्थापन के परिप्रेक्ष्य में अंतर होता है, जिसमें पहला दूसरे से कम की आवश्यकता है। इस परिणामस्वरूप, बीटा→एल्फा" परिवर्तन को क्रिस्टलोग्राफिकली अधूरा बीटा→एल्फा' परिवर्तन के रूप में विचारा जा सकता है। इसके अलावा, मेटास्टेबल बीटा-टाइटैनियम एलॉयज में विभिन्न आलॉयिंग तत्वों का प्रभाव भी अभिविन्नता पैदा करता है जो एल्फा" → एल्फा' मार्टेन्सिटिक परिवर्तन को निर्देशित करने में महत्वपूर्ण भूमिका निभाता है। इसके अलावा, माइक्रोस्ट्रक्चरल स्थिति, विशेषकर बीटा फेज स्थिरता और बीटा दान की दिशाएँ, मेटास्टेबल बीटा-टाइटैनियम एलॉयज में परिवर्तन के दौरान और अंत में संपत्ति सुधार में महत्वपूर्ण भूमिका निभाती हैं।

यह थीसिस काम मेटास्टेबल बीटा Ti-10V-2Fe-3Al (Ti-1023) एलॉय में SIMT को प्रभावी रूप से प्रदर्शित करती है, जिससे ठंडी प्लास्टिसिटी में सुधार होता है। Ti-1023 एलॉय में $\beta \rightarrow \text{एल्फा}'' \rightarrow \text{एल्फा}'$ मार्टेन्साइट्स के स्थानांतरण का साक्षात्कार सतत परिवर्तन के दौरान होता है। इलेक्ट्रॉन बैकस्कैटर्ड डिफ्रैक्शन (EBSD), एक्स-रे डिफ्रैक्शन (XRD), और ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोप (TEM) विश्लेषण का उपयोग करके माइक्रोस्ट्रक्चरल विश्लेषण ने एल्फा" से एल्फा' का परिवर्तन स्पष्ट किया। यह नोट किया गया है कि ठंडे रोलिंग से पैदा हुए ग्रेड स्ट्रेन और विभिन्न आलॉयिंग तत्वों का संयुक्त प्रभाव,

एल्फा" → एल्फा' मार्टेनसिटिक परिवर्तन को प्रेरित करता है। बीटा→एल्फा"→एल्फा' में Ti-1023 में ग्रिड स्ट्रेन और आलॉयिंग तत्वों के परिवर्तन पर लैटिस स्ट्रेन और आलॉयिंग तत्वों के सहयोग से एक संबंध स्थापित किया गया है। इस अवलोकन से यह स्पष्ट होता है कि तनाव-उत्पन्न मार्टेनसाइट (SIM) उच्चतम स्थिति की प्राप्ति के लिए प्रमुख कारण है (लगभग ~ 43 % तक की)। SIM का साइनिफिकेंट भाग रिक्रिस्टलाइजेशन एनीलिंग पर नए स्ट्रेन-फ्री ग्रेन्स के लिए प्राथमिक न्यूक्लियेशन साइट्स प्रदान करता है। थर्मोमैकेनिकल ट्रीटमेंट से Ti-1023 एलॉयज में ग्रेन रिफाइनमेंट लगभग ~ 93 % होता है। इसके अलावा, माइक्रो हार्डनेस विविधताओं पर आधारित SIM परिवर्तनीयता पर ग्रेन साइज के प्रभाव की गुमान लगाई गई है। इसके अलावा, बीटा फेज स्थिरता पर SIM परिवर्तन का प्रभाव को Ti-1023 के माइक्रोस्ट्रक्चर में इलेक्ट्रॉन प्रोब माइक्रो एनालाइजर (EPMA) का उपयोग करके स्पष्ट किया गया है। EPMA ने आलॉयिंग तत्व की डिफ्यूजिविटी का प्रभाव (जैसे कि Fe, Mo, V, Cr, और Al) पर बीटा फेज स्थिरता के समय के साथ बीटा फेज स्थिरता पर पुष्टि की है।

इसके अतिरिक्त, EBSD तकनीक का उपयोग करके माइक्रो इंडेंट्स की सतह का विश्लेषण दिखाता है कि केवल कुछ अशी ग्रेन ओरिएंटेशन्स शीर्ष सतह पर माइक्रो इंडेंटेशन के बाद तनाव-उत्पन्न मार्टेनसिटिक लैक्स का निर्माण दिखाती हैं, इस से सिद्ध होता है कि SIMT ग्रेन ओरिएंटेशन्स पर प्रभावित है। इसलिए, ग्रेन ओरिएंटेशन के बारे में जानकारी प्राप्त करने के लिए नैनोइंडेंटेशन का उपयोग किया गया है, जिससे विकृति के दौरान SIM परिवर्तन की व्यवहारिकता और उनके अंत में Ti-1023 की यांत्रिक गुणमें आने वाले प्रभाव को स्पष्ट किया जा सकता है। निकट $\langle 001 \rangle$, $\langle 101 \rangle$ और $\langle 111 \rangle$ के क्रिस्टलोग्राफिक ओरिएंटेशन के साथ ऑस्टेनाइट ग्रेन्स को चुना गया है। नैनोइंडेंटेशन को दो विभिन्न डायमंड इंडेंटर्स, यानी Berkovich और cono spherical के साथ किया गया है। नैनोइंडेंटेशन में निकट $\langle 111 \rangle$ क्रिस्टलोग्राफिक ओरिएंटेशन के ग्रेन्स में प्रमुख तनाव-उत्पन्न मार्टेनसिटिक (प्रकार एल्फा") परिवर्तन का प्रमुख होता है, जो $\langle 001 \rangle$ क्रिस्टलोग्राफिक ओरिएंटेशन्स में केवल सतह पर स्लिप की उपस्थिति दिखा रहा है। इसके अतिरिक्त, निकट $\langle 111 \rangle$ ग्रेन ओरिएंटेशन्स के लिए सबसे कम हार्डनेस

(~ 4.1 जीपीए) होती है, जबकि हार्डनेस निकट $\langle 101 \rangle$ और $\langle 001 \rangle$ ग्रेन ओरिएंटेशन के लिए आगे बढ़ जाती है (~ 4.3 जीपीए)। इससे सिद्ध होता है कि निकट $\langle 111 \rangle$ ग्रेन ओरिएंटेशन सबसे पसंदीदा ग्रेन ओरिएंटेशन है, जिसे निकट $\langle 101 \rangle$ के लिए बढ़ावा होता है, जबकि निकट $\langle 001 \rangle$ ग्रेन ओरिएंटेशन सबसे कम पसंदीदा है। इसलिए, विभिन्न लंबाई मापों पर यांत्रिक विकृतियों का अध्ययन करके विभिन्न स्तरों पर रूप विकृतियों को स्थापित किया गया है।

प्लास्टिक विकृति विशेषताएँ माइक्रो और नैनोइंडेंटेशन की तरह स्थानीय विकृति के विभिन्न प्रकारों के माध्यम से अध्ययन की गई हैं, हालांकि, SIMT का सम्पूर्ण सामग्री के यांत्रिक व्यवहार पर प्रभाव महत्वपूर्ण है। इसलिए, SIMT के प्रभाव को खींचने के लिए तन्तुवाती विकृति गुणों का मूल्यांकन किया गया है। यह एलॉय स्ट्रेथ एन्हांसमेंट के साथ SIM परिवर्तन दिखाती है, और बीटा ग्रेन साइज के साथ ट्रिगरिंग स्ट्रेस विभिन्नता है। हालांकि, % विकृति के लिए स्ट्रेन में एक सार्थक घटना है। इसके अतिरिक्त, SIM के द्वय द्वारा विकृति और फ्रैक्चर व्यवहार पर SIM के द्वय का प्रभाव मिलता है, जिसमें SIM की हस्तक्षेप के दौरान एम्ब्रिटलमेंट को उत्पन्न करता है, जिसके परिणामस्वरूप लोहे की अभाव की परिभाषा होती है, हालांकि एलॉय की समग्र स्थिति को दोहरे यील्डिंग के साथ मजबूती प्रदान करता है। इसके परिणामस्वरूप, एक साइटिंग के अभाव की सूचना भी प्रदान करता है जो टैंसाइल डिफॉर्मेशन के दौरान गलबी अभिवृद्धि के अभाव का कारण हो सकता है, जो SIM के एम्ब्रिटलिंग क्रियाओं का लाभ उठाने के लिए जाता है। क्योंकि बीटा ग्रेन साइज मुख्य रूप से मार्टेन्सिटिक लैथ स्पेसिंग और चौड़ाई को शासित करता है, ग्रेन बाउंडरी इंजीनियरिंग उच्च प्रदर्शन टाइ एलॉय्स की नींव प्रदान करती है।

समग्र, अध्ययन में यह प्रमुख बातें हैं कि तनाव-उत्पन्न मार्टेन्सिटिक परिवर्तन (SIMT) ने ठंडी प्लास्टिसिटी की सफलतापूर्वक प्राप्ति में साबित होता है। इस बढ़ी हुई ठंडी प्लास्टिसिटी का कारण ऑर्थोरोम्बिक-एल्फा" मार्टेन्साइट्स के होने के साथ-साथ तनाव-उत्पन्न एल्फा " → एल्फा' मार्टेन्सिटिक परिवर्तनों का है, जिससे प्लास्टिसिटी में सुधार होती है। SIM ने भी न्यूक्लियेटिंग साइट्स के रूप में कार्य किया और अंत में ग्रेन रिफाइनमेंट को प्रोत्साहित किया। इसके अतिरिक्त, इंडेंटेशन अध्ययन ने ग्रेन

ओरिएंटेशन पर SIM ट्रांसफॉर्मैबिलिटी पर प्रभाव को प्रदर्शित किया है, जिससे स्पष्ट होता है कि निकट $\langle 111 \rangle$ ग्रेन ओरिएंटेशन सबसे पसंदीदा हैं, जिस पर निकट $\langle 101 \rangle$ के लिए बढ़ावा है, हालांकि निकट $\langle 001 \rangle$ ग्रेन ओरिएंटेशन सबसे कम पसंदीदा हैं। इसके अलावा, अध्ययन ने विकृति और भंग व्यवहार पर SIM के द्वय प्रभाव की पहचान की है, जिसमें, SIM की मौजूदगी प्लास्टिक विकृति के दौरान एम्ब्रिटलमेंट को उत्पन्न करती है, हालांकि एलॉय की कुल सुप्लेक्सिटी में डबल यील्डिंग के साथ वृद्धि होने के बावजूद। इसके अतिरिक्त, यांत्रिक विकृति के दौरान नैन-यूनिफॉर्म एलॉन्गेशन के अभाव की सूचना प्रदान करने के लिए भी सूचना प्रदान करता है, जो SIM के एम्ब्रिटलिंग क्रियाओं के लिए आस्थानित किया जा सकता है। इस परिणामस्वरूप, अध्ययन स्पष्टता से स्पष्ट करता है कि बीटा ग्रेन साइज और मल्टीपल वेरिएंट मार्टेनसाइट्स को कैसे तनाव-उत्पन्न मार्टेनसाइट ट्रांसफॉर्मैबिलिटी को नियंत्रित करते हैं प्लास्टिक विकृति के दौरान। अध्ययन यह भी प्रदर्शित करता है कि SIM परिवर्तन को प्रभावी रूप से नियंत्रित करने से मेटास्टेबल बीटा टाइटेनियम एलॉय में ट्रांसफॉर्मेशन-इंड्यूस्ड प्लास्टिसिटी के माध्यम से स्ट्रेच-डक्टिलिटी वृद्धि प्रदान की जा सकती है।

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List of abbreviation

TWIP	Twinning induced plasticity
TRIP	Transformation induced plasticity
SIM	Stress-induced martensite
SIMT	Stress-induced martensitic transformation
CP	Commercially pure
HCP	Hexagonal close-packed
BCC	Body centered cubic
Y.S.	Yield strength
T.S.	Tensile strength
El	Elongation
Mo Eq.	Molybdenum Equivalency
Ti-1023	Ti-10V-2Fe-3Al
Ti-5553	Ti-5Al-5Mo-5V-3Cr
TMP	Thermo-mechanical processing
CV	Correspondence variants
SAED	Selected area electron diffraction
M_s	Martensite start temperature
FIB	Focused ion beam
AFM	Atomic force microscopy
SEM	Scanning electron microscope
ASTM	American standards for testing of materials
ST	Solution treatment
WQ	Water quenching
CR	Cold rolled
EBSD	Electron backscattered diffraction
XRD	X-ray diffraction
TEM	Transmission electron microscope
LAM	Local average misorientation
IPF	Inverse pole figure
EPMA	Electron probe micro-analyzer
UTM	Universal testing machine
QCSM	Quasi-continuous stiffness measurement

Glossary

α phase	Phase stable at temperature below T_{β}
α stabilizer	Alloying elements that stabilizes the α phase
α'' phase	Martensites with orthorhombic structure
α' phase	Martensites with HCP structure
β phase	Phase stable at temperature above T_{β}
β stabilizer	Alloying elements that stabilizes the β phase
β' phase	Phase formed via phase separation reaction in solute lean alloys
δ	Atomic shuffle displacements
T_{β}	Temperature above which β phase remains stable
ω-phase	Fine uniformly distributed particles in β phase, acts as source of embrittlement
Athermal	Phase transformation induced during quenching, independent of time
Beta fleck	Defect that occurs due to fast diffusion of iron in Ti alloys during aging.
Delta glaze	Silicon based organic glass, used to provide protective coating against oxidation on Ti alloys during heat treatments
Double yielding	Characteristic of stress strain curve exhibited by Ti alloys showing SIMT
Isothermal	Phase transformation induced during ageing, dependent on the time
Lattice correspondence variants	Different variants of a phase oriented in different crystallographic directions

Martensite start temperature	Temperature during cooling at which martensite formation starts
Martensitic transformation	Formation of martensites induced either by quenching or deformation
Martensite variants	Martensites oriented in different crystallographic directions
Metastable β	β phase retained at room temperature without martensitic transformation after quenching from above T_{β} .
Molybdenum equivalency	Measure of stability of β phase
Strain-induced martensite	Primary martensite formed from the parent grain provides nucleation sites for martensite formation during deformation
Stress-induced martensite	Martensite formation from the parent grain during deformation
Thermo-mechanical processing	Process that combines mechanical or plastic deformation processes with thermal processes like heat-treatment, water quenching.
Trigger stress	Threshold stress beyond which SIM forms
Twin	In twinning, the portion of crystals takes up an orientation associated with the orientation of the rest of the untwinned lattice in a symmetrical and defined way