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Coupled experimental and computational investigation of omega phase evolution in a high misfit titanium-vanadium alloy

D. Choudhuri [a], Y. Zheng [b], T. Alam [a], R. Shi [b], M. Hendrickson [a], S. Banerjee [c], Y. Wang [b], S.G. Srinivasan [a], H. Fraser [b], R. Banerjee [a, *]

[a] Department of Materials Science and Engineering, University of North Texas, Denton, TX 76191, USA
[b] Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 4310, USA
[c] Bhabha Atomic Research Centre, Mumbai, India

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ABSTRACT

Morphological and compositional evolution of omega (ω) precipitates in a model Titanium-20 wt%Vanadium (or 19 at.%V) alloy has been systematically investigated by coupling transmission electron microscopy and atom probe tomography with atomistic *ab initio* and continuum microelasticity computations. The initial water quenched microstructure comprised of a fine scale distribution of athermal ω precipitates, which form congruently from the β phase via a complete displacive collapse of $\{222\}_\beta$ planes, that has been rationalized based on DFT computations. Subsequent annealing at 300 °C, over progressively increasing time periods, resulted in isothermal evolution of the ω precipitates, whose morphology changes from ellipsoidal to cuboidal, accompanied with V rejection. The highly V-enriched β matrix consisted of short V–V bond lengths, further distorting the *bcc* lattice, and increasing the β/ω misfit. This facilitates the change in the morphology of omega precipitates from ellipsoidal to cuboidal resulting in a $\{001\}_\beta$ habit plane for these precipitates. The coupled experimental and computational approach permits rationalizing the evolution of ω precipitate morphology and composition in such high β–ω misfit β-Ti alloys.

1. Introduction

Omega (ω) phase formation is an interesting case of displacive or coupled displacive-diffusional transformation found in Group IV metals (e.g. Ti, Zr) and their alloys [1–7].

The past six decades has witnessed substantial amount of research effort to understand ω precipitation and its influence on the mechanical and superconducting properties [6]. In recent years, ω formation has gained renewed attention due to its role as a precursor to fine scale α phase precipitation in Ti-alloys [7–15], which results in higher strengths [16,17]. In pure Ti ω forms only under the influence of large compressive stress/pressures during hydrostatic or shock compression [1–5]. In contrast ω forms at ambient pressure only in *bcc* (β) Ti alloys containing β –stabilizing elements like Mo, V, Nb etc [6].

In β-stabilized Ti alloys, ω forms athermally by quenching form the β phase field (at high temperature), to a much lower temperature e,g, room temperature [6]. Athermal ω formation is typically with associated with an atomic shuffle mechanism [18–29], which, according to De Fontaine, can also be described as either $\frac{2}{3}\langle 111\rangle$ longitudinal or $\frac{1}{3}\langle 112\rangle$ transverse displacement wave in the bcc lattice [19,23]. The presence of this displacement wave was latter confirmed via neutron diffraction experiments, which showed $\frac{2}{3}\langle 111\rangle$ wave vector in the phonon spectra [30]. However, contrary to experimental observations, De Fontaine's harmonic lattice theory based mechanism also implied that β → ω transformation will reach completion [28]. Latter, Cook modified this mechanism by introducing anharmonicity to the lattice free energy, and expressed this energy as a Landau polynomial $F = A\eta^2 + B\eta^3 + C\eta^4 + \ldots$, where the constants A and C are positive definite and B is negative, and η planar displacement [24–26]. Crucially, the modified theory indicated an energy barrier leading to ω formation [24–27], which was recently confirmed via first principle calculations involving β → ω transformation in Ti-Mo alloys [31]. From an experimental point of view, these theoretical insights suggest that β → ω transformation is due to the collapse of neighboring $\{222\}_\beta$ planes, and several microscopy-based

* Corresponding author.
E-mail address: Raj.Banerjee@unt.edu (R. Banerjee).

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investigations have been carried out to observe this planar collapse.

Sukedai et al. carried out one of the first high-resolution imaging of ω in quenched Ti-11 at.%Mo and Ti-14 at.%Mo alloys by coupling high-resolution transmission electron microscopy (HRTEM) and image simulations [32–34]. Recently, Devaraj et al. examined the ω structure in Ti-9at.%Mo in unprecedented detail by using aberration corrected (Cs corrector in condenser lens [35,36]) high resolution scanning transmission electron microscopy (HRSTEM) fitted with high angle dark field (HAADF) detector [37,38]. The HAADF-STEM methodology allows one to image atomic columns with sub-atomic resolution, while simultaneously showing the differences in the average atomic number of such columns via contrast differences [31,35–37]. However, these atomically resolved examinations of the ω structure was carried out in only low misfit alloys exhibiting small difference in atomic radii of Ti and the solute atoms such as Mo atoms.

One of the earliest study on as-quenched high misfit Ti-V alloys was performed by McCabe et al. [20]. Their observations indicated that ω structure consist of fully collapsed $\{222\}_\beta$ planes, corresponding to "ideal" ω structure (symmetry P6/mmm), even at very high levels of solute concentration e.g 19 at.%V compared to Ti-Mo alloys [20]. They deduced the presence of an ideal ω structure from selected area electron diffraction patterns (SADPs) recorded along $[011]_\beta$ zone axis [7,20–22]. Furthermore, higher alloy compositions (25–33 at.%) produced pronounced reciprocal lattice streaking (RLS) suggesting the presence of partially collapsed $\{222\}_\beta$, while very faint RLS was noted at concentrations in excess of 33 at.%V [20]. Regardless, a conclusive experimental evidence of full/partial $\{222\}_\beta$ collapse of athermal ω in quenched Ti-V alloys is yet to be presented [18–38]. More importantly, it is unclear why athermal ω is still observed at such high levels of solute concentration in Ti-V alloys, and not in Ti-Mo with comparable levels of solute atoms. Nevertheless, we believe that the displacement wave mechanism is likely responsible for the athermal ω formation in both alloys. However, displacement mechanism [19,24–26,30], or other recent theoretical works [5,31,39–43] offer little physical insight into the formation of athermal or isothermal ω at high/low levels of solute concentrations in beta-stabilized ω-forming Ti-alloys.

The differences in high and low misfit β-Ti alloys become even more prominent when they are exposed to annealing below their ω-solvus temperatures [7,18–29]. Such long-term annealing results in fully developed ω precipitates, called isothermal ω, that are rich in Ti and lean on solute elements [7,18–29]. While, isothermal ω in low misfit systems retain ellipsoidal morphology, but in high misfit alloys they eventually acquire cuboidal morphology [7,18–29]. The formation of isothermal ω for low misfit systems has been well established via a model Ti-Mo alloy [7,18–29,37]. By coupling structural and compositional observations obtained through HRSTEM and Atom Probe Tomography (APT) respectively, Devaraj et al. demonstrated that isothermal ω precipitates form in a compositionally phase-separated β-matrix [37,38]. In contrast, a conclusive mechanism for the nucleation and growth of isothermal ω is yet to be resolved in case of Ti-V system. Using conventional TEM of Ti-50 at.%V and thermodynamic calculations, Koul et al. suggested that compositional fluctuations in the β phase cannot be associated with the formation of isothermal ω [44]. Furthermore, the role of prior athermal ω on isothermal ω formation cannot be deduced from their work [44]. In a latter study on Ti-10 V-2Fe-3Al (wt%) or Ti-9.3V-1.7Fe-5Al (at%), Duerig et al. proposed that compositional fluctuations near the "quasi-static" athermal ω particles plays a role in the formation of isothermal ω precipitates [27,28]. Their proposition was primarily based on microstructures observed via dark-field TEM imaging [27,28], and not by measuring the composition of ω and β phases at different stages of annealing. Recently, Ng et al. reported compositional fluctuations preceding isothermal ω formation during a slow continuous cooling of a Ti-9.6V-4.6Cu (at%) alloy [45]. However, isothermal ω stability regime/or temperature is rather difficult to establish because of the continuous cooling rate employed in this work [45].

A systematic understanding of compositional evolution in Ti-V alloys during the formation and coarsening of ω will allow us to understand the role of misfit strains on morphological evolution of isothermal ω from ellipsoids (oriented along $\langle 111\rangle_\beta$ [7,19]) to the final cuboidal shape with faces parallel to $(001)_\beta$ [7,27,28]. It is expected that misfit strains, due to changing ω and β lattice parameters during annealing may play a key role in the observed change in morphology [7,27,28]. In fact the dependence of ω and β lattice parameters on V concentration was demonstrated by Aureloi et al. by using neutron diffraction [46]. These extensive results mandated coupling lattice and compositional information (from e.g APT [37,38,46]) to reexamine the role of V concentration on the isothermal ω morphology.

The present study is a systematic investigation of athermal and isothermal ω precipitation in a model Ti-20 wt%V or Ti-19 at.%V alloy, by water quenching and subsequent isothermal annealing to 256 Hrs. Ti-19 at.%V was chosen because it forms ω in the quenched-in condition [20] and, reportedly, phase separates upon isothermal annealing [27,28]. Microstructural characterization was carried out by coupling state-of-the-art aberration corrected HAADF-STEM microscopy, conventional TEM, and APT. The experimental results were complimented by density functional theory (DFT)-based first principle calculations, and microelasticity theory based strain energy calculations [48]. By combining the experimental observations with the computational results, we addressed the following salient aspects of ω precipitation in high β–ω misfit alloys:

1. The degree of $\{222\}_\beta$ collapse and the composition of ω precipitates in the as-quenched condition.
2. Examined systematically ω morphology and volume fraction, and solute partitioning between ω and β during isothermal annealing.
3. Established electronic and ground state structures of ω and β phases for relevant solute concentrations.
4. Characterized the effect of solute partitioning between ω and β on the habit plane of the ω precipitates.

2. Experimental and computational methods

Vacuum arc melted Ti-20 wt%V or Ti-19 at.%V samples were obtained from Air Force Research Laboratory, Dayton, OH. The alloy ingots were produced by arc-melting Ti sponge and V pellets mixed in appropriate proportions inside a vacuum furnace. For heat treatments, the samples were first cut into $3 \times 2 \times 10$ mm coupons, then wrapped in Ti foils along with small pieces of sponge Ti. The wrapped specimens were beta solutionized at 900 °C for 1 h in a tube furnace with flowing Argon atmosphere and followed by water quenching to room temperature. The water quenched coupons were subsequently annealed at 300 °C for 1, 64 and 256 h; followed by water quenching. For annealing experiments, each sample was wrapped in the same procedure described above. To probe the early stages of ω precipitation, cylindrically cut β-solutionized specimens were annealed for 1 and 10 min at 300 °C inside a LINSEIS RITA L78 Quenching dilatometer maintained in He environment. The dilatometer allowed a strict control, via