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Characterization of yttrium-rich precipitates in a titanium alloy weld

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ABSTRACT

The yttrium-rich (Y-rich) precipitates that form in the fusion zone (FZ) of a Ti–5Al–1Sn–1Zr–1V–0.8Mo (wt.%) alloy, or Ti-5111, gas-tungsten arc welds (GTAW) were characterized. The filler metal was modified by a small concentration of Y in order to refine the microstructure and thus improve the FZ ductility. A high number density of nanoscale Y-rich precipitates were characterized in the weld FZ by atom probe tomography (APT) and scanning transmission electron microscopy (STEM).

1. Introduction

Titanium (Ti) alloys are technologically important for diverse applications in many industries, such as aerospace, biomedical, naval, and energy production [1,2]. One titanium alloy designed for structural marine applications is Ti–5Al–1Sn–1Zr–1V–0.8Mo (wt.%), which is referred to as Ti-5111 [3]. It has intermediate strength, excellent corrosion resistance, high toughness, excellent stress-corrosion cracking resistance, and room temperature creep resistance [3]. This alloy has a near-α microstructure that consists of colonies of hexagonal close-packed (h.c.p.) α-phase plates (or lamella) with small quantities of retained body-centered cubic (b.c.c.) β-phase grains between the plates [4,5]. The h.c.p. α-phase colonies have an orientation relationship (OR) such that their {0001} basal planes are misoriented by 60° and share a common $\langle 11\bar{2}0 \rangle$ close-packed direction [5]. One limitation of this alloy is, however, that conventional welding processes may have a deleterious effect on the weld's ductility due to the embrittling effect of interstitial impurity elements, such as oxygen (O) [6,7], and the formation of coarse, columnar grains in the fusion zone (FZ) microstructure [8]. Oxygen atoms reside at the octahedral interstitial sites of the h.c.p. α-Ti lattice and act to strengthen the alloy thereby reducing its ductility and increasing its strength [6,7,9]. One approach to improve the weld ductility of alloys is microstructural refinement and sequestering of interstitial elements through compositional changes in the FZ by adding rare earth elements to the weld filler metal [10]. More specifically, Neuberger et al.'s recent approach to improve the FZ ductility was to modify the weld filler metal by adding small concentrations of yttrium (Y) [11].

In earlier reported results, Neuberger et al. [11] compared the mechanical properties and microstructure of Ti-5111 plates welded by filler metal matching the base metal (BM) composition, filler metal modified with 60 ppm Y, and filler metal modified with 268 ppm Y when employing a gas-tungsten arc welding (GTAW) procedure. Their results indicated that the FZ of both yttrium-modified filler metal welds exhibited greater ductility (percent reduction in area) of 21.2 ± 1.0% % and 17.4 ± 6.4%, when compared to the FZ of the matching BM filler metal weld ductility of 14.8 ± 7.5% and the BM ductility of 15.0 ± 3.3% [11,12]. Additionally, Vickers microhardness measurements indicated that the FZ of both yttrium-modified filler metal welds exhibited a lower hardness when compared to the FZ of the matching BM filler metal weld [11,12]. They also measured an improved tearing modulus, *T*, meaning that the FZ of both yttrium-modified filler metal welds exhibited more stable crack growth once a crack was initiated. Furthermore, their scanning electron microscope (SEM) observations of the fractured tensile specimens indicated that both yttrium-modified filler metal FZ fracture surfaces were more characteristic of failure by microvoid coalescence and dimpled rupture, whereas the matching BM filler metal FZ fracture surface was more characteristic of cleavage failure [11,12]. Neuberger et al. partially attributed this improved response to a smaller average grain diameter in the FZ of both yttrium-modified filler metal welds caused by the possible presence of Y-rich precipitates that inhibited columnar grain growth and promoted limited heterogeneous nucleation of the grains [11,12]. Their conventional transmission electron microscope (TEM) and selected area electron diffraction (SAED) pattern observations suggested the presence

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Table 1
Nominal compositions of the Ti-5111 base metal (BM) and yttrium-modified weld filler metal as reported in Ref. [11].

		Elements								
		Ti	Al	Y	Zr	V	Mo	Sn	O	C
High-Y weld filler metal (FM)	(wt.%)	Balance	4.40	0.0268	1.00	1.00	0.75	1.00	0.089	–
	(at.%)	Balance	7.70	0.014	0.51	0.92	0.37	0.40	0.261	–
Base metal (BM)	(wt.%)	Balance	4.92	–	1.05	1.00	0.80	1.00	0.094	0.009
	(at.%)	Balance	8.52	–	0.54	0.92	0.38	0.39	0.274	0.035

of small nanoscale precipitates in the FZ of the yttrium-modified filler metal welds that were not present in the FZ of the matching BM filler metal welds [11,12]. The crystal structure of the small precipitates could not, however, be definitively resolved, and their composition was not conclusively characterized. The authors suggested, however, that the precipitates were possibly face-centered cubic (f.c.c.) yttrium oxide (Y_2O_3) or trigonal yttrium oxysulfide (Y_2O_3S) based on the aforesaid observations and due to the strong affinity between Y and O or sulfur (S) that is related to their electronic structure leading to large negative values of enthalpy of formation ΔH_f, and even small concentrations can lead to the formation of oxides and sulfides [10,13,14].

This investigation characterizes the possible Y-rich precipitates that form in the FZ of the high yttrium-modified filler metal weld, which improve its ductility. We employ state-of-the-art atom probe tomography (APT) and scanning transmission electron microscopy (STEM) and report the first direct visualization of these precipitates and confirm that they are enriched in Y. The sub-nanometer spatial resolution and high elemental sensitivity of the APT technique [15] permits three-dimensional (3-D) visualization of nanoscale precipitates [16], while STEM permits analysis of a wider field-of-view (FOV) than APT via both high-angle annular dark-field (HAADF) imaging and -Xray energy dispersive spectroscopy (XEDS). We also discuss the local distribution of O and S in the weld FZ matrix phase and the Y-rich precipitates.

2. Experimental Procedures

2.1. Material

The nominal composition of the yttrium-modified filler metal containing 268 ppm Y and the base metal as measured by Timet Co. are given in Table 1. Details regarding the BM alloy plate fabrication and yttrium-modified filler metal fabrication are found in Refs. [11,12]. The BM has a nominal thickness of approximately 25.4 mm (1-inch). A summary of the GTAW procedure is presented here and additional details are also found in Refs. [11,12]. Welding was performed by Tricor Metals, Inc. The double-V butt weld joint was fabricated by GTAW inside a glove box using nominally pure (>99.99 at.%) argon (Ar) shielding gas. A total of 12 weld passes were performed on each side using a nominal arc voltage of ~15 V, a nominal weld current of ~225 amps (A), and a travel speed of 3.4 mm/s for each pass.

2.2. Atom Probe Tomography (APT)

Specimens with a needle-shaped geometry necessary for APT analysis were fabricated using a FEI[1] Nova 600 dual-beam scanning electron microscope/focused ion beam (SEM/FIB) instrument following standard lift-out and annular milling procedures [17,18]. The *in situ* site-specific specimen preparation technique was performed on metallographic mounts to take APT specimen blanks in the weld FZ. Details regarding fabrication of the mounts are presented in Refs. [11,12]. A platinum (Pt) protective layer was deposited over a region of interest (ROI) using established procedures. Annular milling was performed employing a 30 keV gallium ion (Ga^+) beam and sequentially decreasing probe current following standard procedures after transfer of the ROI to silicon (Si) microtip posts with an Omniprobe micromanipulator [19]. A low keV ion beam of 5 keV was allowed to raster over the specimen tip to remove material that had been damaged by the 30 keV Ga^+ ion beam annular milling operation [20]. The final apex of the specimen tips had a radii of ~50 nm suitable for APT analysis.

A CAMECA Local-Electrode Atom Probe (LEAP®) 4000 instrument in the Si configuration was used to perform pulsed-voltage APT. Data acquisition was performed at a specimen tip base temperature of 70 K, a pulse frequency of 200 kHz, and a pulse-to-standing DC voltage ratio of 20% in order to promote field evaporation. The evaporation rate was maintained at a constant 0.5% or 0.005 ions per pulse. The background pressure was an ultra-high vacuum (UHV) of 1.1×10^{-8} Pa (8.1×10^{-11} Torr). Data reconstruction and analysis was performed using the CAMECA Integrated Visualization and Analysis Software (IVAS), version 3.6.6.

2.3. Scanning Transmission Electron Microscopy (STEM)

Specimens taken from the weld FZ were also prepared for analysis by STEM-HAADF imaging and XEDS elemental characterization using standard dual-beam SEM/FIB instrument lift-out techniques [21]. Analysis was performed using a FEI Titan 80–300 STEM operating at 300 kV and a probe current of approximately 0.1 nA. For XEDS analysis, the microscope was also equipped with an EDAX Sapphire r-TEM side-entry Si(Li) spectrometer with super ultra thin window, a nominal solid angle of collection of 0.1 sr, an energy resolution of 134 eV as measured for the Mn-K_α X-ray peak, and an active detector area of 30 mm^2. The XEDS hyperspectral images were acquired using a higher probe current of 0.3 nA from a 300 nm × 250 nm area of the specimen that contained several precipitates. A 5 nm × 5 nm pixel size was used and the spectra were integrated for 1 s. Phase analysis was performed using the Sandia National Laboratory (SNL) Automated eXpert Spectral Image Analysis (AXSIA) multivariate statistical analysis software [22], and spectral analysis was performed using the National Institute of Standards and Technology (NIST) Desk Top Spectrum Analyzer (DTSA) II software [23].

3. Results and Discussion

3.1. Yttrium-rich (Y-rich) Precipitates

The APT reconstruction, Fig. 1(a), illustrates nanoscale spheroidal Y-rich particles (red isoconcentration surfaces) that are distributed in the weld FZ matrix phase (blue atoms) with a high number density, N_V, of ca. 3.0×10^{24} particles/m^3, where the theoretical atomic density is ca. 42.5 atoms/nm^3 for this Ti alloy, which is used to determine the volume. The FZ contains predominantly Ti atoms (blue), as discussed below. These particles have a mean spherical volume equivalent radius, $\langle r \rangle = 0.85 \pm 0.05$ nm, where the $\pm 2\sigma$ error is given by standard error of the mean and the spheroid volumes are provided by interface analysis in the IVAS software. A normal probability plot, Fig. 1(b), demonstrates that these particles deviate from linearity that is expected of local statistical compositional fluctuations in a random solid-solution

[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.