Acta Materialia 131 (2017) 410–422

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Effect of chemistry on martensitic phase transformation kinetics and resulting properties of additively manufactured stainless steel

Zhuqing Wang, Allison M. Beese*

Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 15 January 2017
Received in revised form
5 April 2017
Accepted 9 April 2017
Available online 11 April 2017

Keywords:
Additive manufacturing
Austenitic stainless steels
Austenite-to-martensite phase transformation
Elemental vaporization

ABSTRACT

Here we investigate the effect of chemistry, including initial powder chemistry and spatial chemical variations due to vaporization during fabrication, on strain-induced martensitic phase transformation in 304L stainless steel components fabricated by directed energy deposition (DED) additive manufacturing (AM). The austenite stability was altered by mixing pre-alloyed 304L stainless steel powder with Fe powder, which promoted martensitic phase transformation and resulted in an increase in ultimate tensile strength and elongation to failure over pure 304L walls deposited by DED AM. The chemical composition variation with position, due to spatial variations in thermal history, was quantified, showing that austenite stabilizing elements Cr, Mn, and Ni were preferentially vaporized during deposition. We present a martensitic transformation kinetics equation that describes the evolution of martensite volume fraction with respect to plastic strain as a function of chemistry. This allows for the prediction of strain-induced martensite evolution as a function of strain, nominal chemistry, and heterogeneous chemistry due to vaporization within additively manufactured components.

1. Introduction

In laser-based, powder-based directed energy deposition (DED) additive manufacturing (AM), 3D components are fabricated through a repetitive process of generating a melt pool on a substrate or previous layer with a laser and delivering powder feedstock directly to the melt pool through nozzles. As the laser beam travels, the melt pool rapidly solidifies and fuses to the layer below [1–3]. Each location in the build undergoes rapid heating and cooling cycles with the addition of new layers. The complex thermal history results in heterogeneous and anisotropic microstructures and mechanical properties in additively manufactured components that are different from traditionally wrought materials [4–6].

In this work, the microstructure and tensile mechanical properties of AISI type 304L austenitic stainless steel (SS304L) fabricated by DED were studied. When austenitic stainless steels are plastically deformed, the relatively soft austenitic phase has the potential to transform to a harder martensitic phase, which forms at nucleation sites created by dislocation interactions. This deformation-induced, or 'strain-induced,' phase transformation, often referred to as the TRansformation Induced Plasticity (TRIP) effect, results in an increase in the macroscopic strain hardening rate and a crystallographic volume expansion of 2–4 vol.% [7–17]. The strain-induced martensitic phase transformation in this study is fundamentally different from thermally-induced, or stress-induced, martensitic phase transformation in which austenite-to-martensite phase transformation occurs in the elastic region of austenite, and martensite forms at pre-existing nucleation sites within the austenite matrix [9,11]. The rate of strain-induced martensitic phase transformation with respect to increment in plastic strain is influenced by the chemical composition, stress state, strain, strain rate, and temperature [8,10,11].

The ability for an austenitic stainless steel to undergo strain-induced phase transformation depends on the material's chemical composition, as this affects the stacking fault energy (SFE) of austenite [18]. The addition of alloying elements that increase the SFE of austenite, decrease the width of stacking faults, promoting cross-slip instead, and increase the stability of austenite. A stacking fault in face-centered cubic (fcc) austenite changes the stacking sequence of the {111} planes from ABCABC to ABAB, which is the stacking sequence of a hexagonal close-packed (hcp) structure [18]. Therefore, stacking faults in austenite act as nucleation sites for hcp ε-martensite, which is an intermediate phase for the formation of

---

* Corresponding author.
E-mail address: amb961@psu.edu (A.M. Beese).

http://dx.doi.org/10.1016/j.actamat.2017.04.022
1359-6454/

body-centered cubic (bcc) strain-induced α' martensite from austenite [9,19]. Consequently, a decrease in the width of stacking faults suppresses the generation of energetically favorable nucleation sites for strain-induced martensite [18]. Talonen and Hänninen [20] studied strain-induced martensitic phase transformation in 304 stainless steel and 301LN stainless steel, showing that the rate of phase transformation with respect to plastic strain depends on composition and temperature. Angel [8] investigated the effect of chemistry on strain-induced martensitic phase transformation in austenitic stainless steels and showed that carbon, nitrogen, chromium, nickel, silicon, manganese, and molybdenum increased austenite stability, and therefore, decreased the strain-induced martensite finish temperature. Tomimura et al. [21] found that the amount of strain-induced martensite increased with the increase in the weight fraction of chromium and nickel in cold rolled austenitic stainless steels.

The elemental composition of additively manufactured components depends on the chemistry of the initial powder, any absorption of oxygen, nitrogen, or argon from the chamber environment during fabrication, or elemental vaporization during deposition, and can vary with location within components [2,22–24]. A previous study by the authors on SS304L components produced by DED showed that when using pre-alloyed SS304L powder gas atomized in nitrogen, the 4 wt.% increase in N with respect to traditionally annealed SS304L, stabilized the austenite, resulting in no phase transformation in the additively manufactured materials, while phase transformation was apparent in the annealed SS304L with plastic deformation [2]. Rafi et al. [24] studied the influence of build environment on microstructure and mechanical properties of additively manufactured 17-4 PH stainless steel. They found that the components contained a mixture of retained austenite (50–75 vol.%) and thermally-induced martensite (25–50 vol.%) when built in nitrogen, and mostly thermally-induced martensite (92 vol.%) when built in argon. The component built in nitrogen had a higher fracture toughness than the component built in argon due to the strain-induced austenite-to-martensite phase transformation present in the former.

In addition to depending on the powder composition and build environment, the chemical composition of components made by AM can vary from the initial powder composition, and as a function of position, if volatile elements vaporize from the molten pool during deposition [25]. The amount of elemental depletion is affected by the temperature of the molten pool, which is dependent on the temperature of the layer onto which new material is being added, as well as the energy input [26]. The most volatile elements in SS304 are Cr, Ni, and Mn [27], all of which are austenite stabilizers; therefore, depletion of these elements should impact the propensity for strain-induced martensitic phase transformation.

The strain-induced martensitic phase transformation in traditionally annealed or rolled austenitic stainless steels has been well studied [7–15], but little is known about the martensitic phase transformation kinetics in additively manufactured stainless steels. The aim of this work was to investigate the effect of initial powder chemistry, and spatial chemical composition changes due to vaporization, on the strain-induced martensitic phase transformation in SS304L made by DED. The chemistry as a function of location and starting composition was quantified, and the resulting phase transformation was characterized during uniaxial tension tests using *in situ* magnetic permeability measurements confirmed with time of flight neutron diffraction. A phase transformation kinetics equation that describes the amount of strain-induced martensite as a function of plastic strain, and in which the parameters depend on chemistry through the martensite finish temperature, is proposed and calibrated for the additively manufactured 304L stainless steel.

2. Experimental

Two geometrically similar walls measuring 140 mm long x 104 mm tall x 14 mm thick were deposited on annealed 304L stainless steel substrates (ASTM A479 standard [28]) using laser based DED with powder feedstock. During the deposition of each wall, the substrate was clamped with 4 bolts to an aluminum fixture, and a thermocouple was attached to the bottom of the stainless steel substrate to measure the temperature during the build process. In order to isolate the effect of powder chemistry on microstructure and mechanical properties, the two walls were fabricated using the same processing parameters, but with different powder compositions by mixing pre-alloyed SS304L powder and pure Fe powder as shown in Table 1. The pre-alloyed SS304L powder was gas atomized in nitrogen (Carpenter Powder Products, Corp.), and had the elemental composition given in Table 2. The Fe powder was hydrogen reduced (Atlantic Equipment Engineers) with a purity of 99.8%. The SS304L powder and Fe powder were sieved to +325/-100 mesh, resulting in a powder diameter range of 45 μm–145 μm.

To mix the powders, the pre-alloyed SS304L powder and pure Fe powder were combined in a sealed container filled with argon and put in a Type T2C Turbula mixer (Willy A. Bachofen AG Maschinenfabrik, Switzerland), which moved in three dimensions for 1 h to ensure random mixing of the two powder types.

One wall was built using a mixture of 80 vol.% SS304L pre-alloyed powder and 20 vol.% Fe powder, referred as the 80% SS304L wall; the other wall was built using a mixture of 90 vol.% SS304L pre-alloyed powder and 10 vol.% Fe powder, referred as the 90% SS304L wall. EDS mapping of different regions from the 80% and 90% SS304L walls showed no elemental segregation (Fig. 1), which was indicative of sufficient mixing of the powders.

A custom-built DED system with an ytterbium fiber laser (IPG Photonics® YLR-12000-L) operating at a wavelength from 1070 to 1080 nm was used to fabricate the components. The components were deposited in a chamber purged with ultra-high purity argon to minimize oxygen contamination. Pre-mixed powder was delivered by a four-nozzle system in which the nozzles were about 10 mm above the substrates, and a laser spot size of 4 mm in diameter was used in a defocused condition. The processing

Table 1
AM processing parameters used to fabricate 80%, 90%, and 100% SS304L walls.

	80% SS304L wall	90% SS304L wall	100% SS304L wall
Powder composition	80 vol.% SS304L powder + 20 vol.% Fe powder	90 vol.% SS304L powder + 10 vol.% Fe powder	100 vol.% SS304L powder
Laser power (W)	2000	2000	2300
Scanning speed (mm/s)	10.6	10.6	8.5
Linear heat input (J/mm)	189	189	277
Powder flow rate (g/min)	15.5	15.5	18
Hatch spacing (mm)	2.5	2.5	2.5
Layer height (mm)	1.1	1.1	1.2