NASA/TM—2012-216044

Processing Issues for Preliminary Melts of the Intermetallic Compound 60-NITINOL

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November 2012

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Abstract

The effect of various high temperature heat treatments and cooling rates on the hardness of cast 60-NITINOL (60wt%Ni-40wt%Ti) was studied. The hardness ranged from approximately 33 HRC for annealed specimens to 63 HRC for water quenched specimens. Aging did not have a further effect on the hardness of the heat-treated and quenched material. The issue of material contamination and its possible effect on quench cracking during heat treatment above 1000 °C was explored. The Charpy impact energy of the material was found to be relatively low (ranging from 0.4 to 1.0 J) and comparable to that of cast magnesium. Selection of service environments and applications for this material based on these findings should consider the processing route by which it was produced.

Introduction

60-NITINOL is an intermetallic compound composed of 60wt%Ni and 40wt%Ti. Since it was discovered that this material has high hardness, good dimensional stability, high specific strength, excellent corrosion resistance and exceptional tribological properties, it is being evaluated for advanced gears and bearings (Refs. 1 and 2). 60-NITINOL is an ordered intermetallic with the B2 crystal structure. In this arrangement, atoms of one type (i.e., Ni) are at the eight corners of a cubic cell and an atom of another type (i.e., Ti) sits at the center of the cube, as depicted schematically in Figure 1. Though composed of metallic atoms, the high degree of atomic ordering in this material causes it to behave more like a covalently bonded ceramic with intrinsic brittleness. Charpy impact testing was used as a screening test to evaluate the impact energy of this material as well as its mode of fracture after various heat treatments.

During preliminary research on this material, several of the prototype components ruptured during the water-quenching step of the heat treatment process. Initially, it was thought that this quench cracking was initiated by high residual stresses that were concentrated at stress risers within the components such as fillets with high radii of curvature. A study to optimize the hardness of the material produced several more occurrences of this quench cracking phenomenon with specimens that only had relatively simple geometries. The crack typically propagated through the specimen resulting in two separate pieces. The purpose of this paper is to report the results of the heat treatment study and to present preliminary observations of samples affected by quench cracking. To better understand the behavior of the material, the impact energy was also studied.

Materials and Procedures

60-NITINOL is a Ni-rich version of the well-known shape memory alloy, *55-NITINOL* (55wt%Ni-45wt%Ti). The studied compound is composed of 60wt% Ni and 40wt% Ti and was fabricated by vacuum induction skull melting with a water-cooled copper crucible (Ref. 3). The crucible was coated with a zirconia-based lining to increase crucible durability. The cast material was subsequently hot isostatically pressed for 2 hr at 900 °C and 100 MPa to diminish porosity.

Heat treatment can be used to modify the strength and hardness of 60-NITINOL. The heat treatments used in this study are described in Table I. They were designed to determine the temperature necessary to produce maximum hardness by dissolving all of the second phase Ni_3Ti to produce austenitic NiTi based on the nickel-titanium phase diagram (Ref. 4). High-temperature heat treatment followed by furnace cooling was designed to relieve residual stresses in the material but this technique typically provides the least strength and hardness due to the enhanced growth of the incoherent second phase Ni_3Ti. The solution heat treatment is designed to dissolve the Ni_3Ti into the parent NiTi phase and transform all of the material into austenitic NiTi. The austenitic NiTi is a homogeneous supersaturated solid solution that has high hardness. The aging heat treatment is designed to grow crystallographically coherent Ni_4Ti_3 precipitates that further increase the strength and hardness of the material to a condition that is desirable for bearing applications.

Heat treatment can, however, produce internal stresses that can lead to dimensional distortion and, in extreme cases, quench cracking, where thermally-induced stresses exceed the tensile strength of the material. The purpose of the heat treatment investigation was to determine the thermal processing necessary to maximize the hardness of the material. When quench cracking was observed, this issue was studied more systematically. The specimens used for the heat treatment investigation were approximately 12- by 12- by 50-mm. A well-preserved heat treatment specimen that cracked during water quenching (WQ) was examined by field-effect scanning electron microscopy (SEM).

The setup of the Charpy impact test is shown schematically in Figure 2. The test measures the energy required to fracture a specimen by determining the difference between the initial height *h* and final height *h*′ when the hammer (or striker) on the pendulum impacts the specimen. The fractured surface of the specimen can then be analyzed to determine the type of fracture the specimen underwent. Though fracture takes place in a fraction of a second, the mechanisms are assumed to be the same as if the specimen were subjected to a tensile test (Ref. 5). The impact energy of the specimen is, therefore, thought of as somewhat analogous to the area under the stress-strain curve (or toughness). The test articles used in this portion of the study were U-notched, 55 mm long by 10 mm wide by 10 mm high specimens as specified in ASTM E23-07a$^{\varepsilon 1}$ (Ref 6). A schematic representation of the Charpy specimen is shown in Figure 3. The Charpy specimens were heat treated using the conditions listed in Table II (these heat treatments vary slightly from the heat treatments used to study hardness). The averages of three impact tests per heat treatment condition were reported. The fractured surfaces were examined by SEM.

Specimens for microstructural examination were sectioned with an abrasive cut-off saw using a resin bonded aluminum oxide blade. The wheel rotated at 3820 rpm with a traverse speed of 0.1 mm/s. The specimens were prepared using standard

TABLE I.—HEAT TREATMENTS USED TO STUDY CAST 60-NITINOL HARDENABILITY

Designation	Heat treatment	Hardness, HRC
Furnace-cooled	2 hr at 900 °C/furnace cool (FC)[a]	37 ± 1
	2 hr at 1000 °C/FC	33 ± 2
	2 hr at 1050 °C/FC	33 ± 2
Water-quenched (partially solution treated)	2 hr at 900 °C/WQ[b]	56 ± 2
	2 hr at 1000 °C/WQ	63 ± 2
	2 h at 1050 °C/WQ	63 ± 1
Partially solution treated and aged	2 hr at 900 °C/WQ/1 hr at 400 °C/WQ	58 ± 1
	2 hr at 1000 °C/WQ/1 hr at 400 °C/WQ	61 ± 3
	2 hr at 1050 °C/WQ/1 hr at 400 °C/WQ	62 ± 1

[a] Furnace cooling was done by shutting off the power to the furnace and allowing it to cool to room temperature. This took approximately 24 hr.

[b] Water quenching was done in still room temperature water. The specimen was swirled about in the water.

TABLE II.—HEAT TREATMENTS AND RESULTANT ROCKWELL HARDNESS OF CAST-60NITINOL CHARPY SPECIMENS

Heat treatment	Conditions	Hardness, HRC	Impact energy, J
Furnace annealed	70 min at 1040 °C/furnace cool	32 ± 0	1.0
Solution treated	90 min at 980 °C/WQ	61 ± 0	0.4
Aged	90 min at 980 °C/WQ/60 min at 400 °C/WQ	63 ± 1	0.5

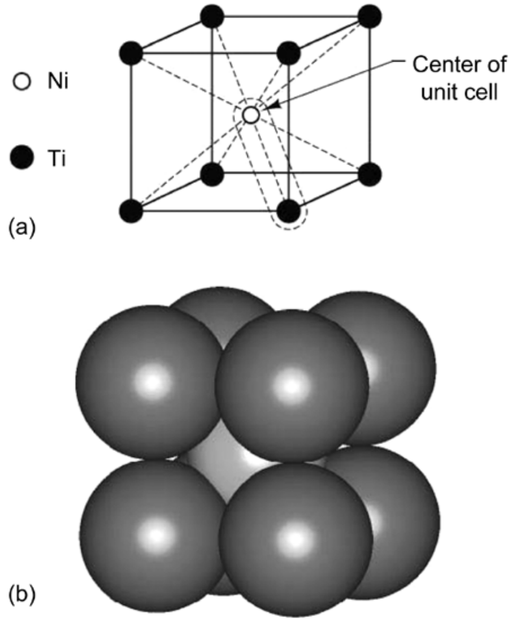

Figure 1.—60-NITINOL B2 unit cell showing (a) atomic arrangement and (b) relative size of atoms in the unit cell. (Image generated with Materials Studio modeling package from Accelrys Software, Inc.)

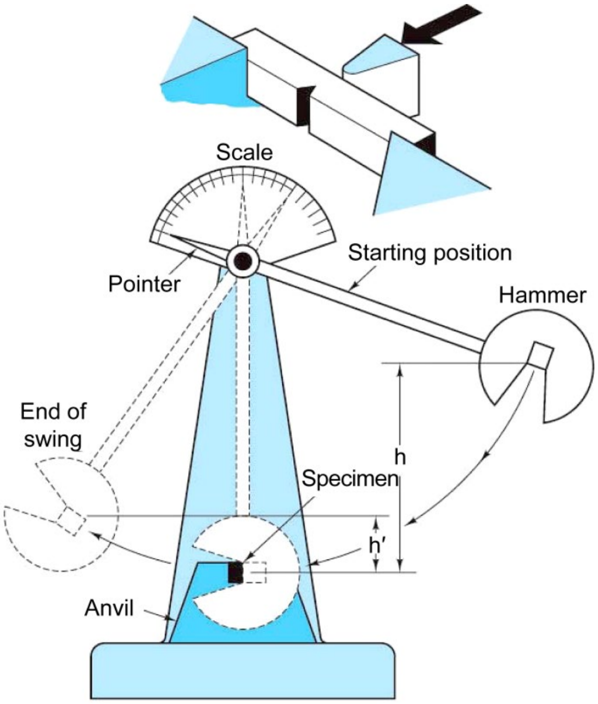

Figure 2.—Charpy test of impact energy (Ref. 5).

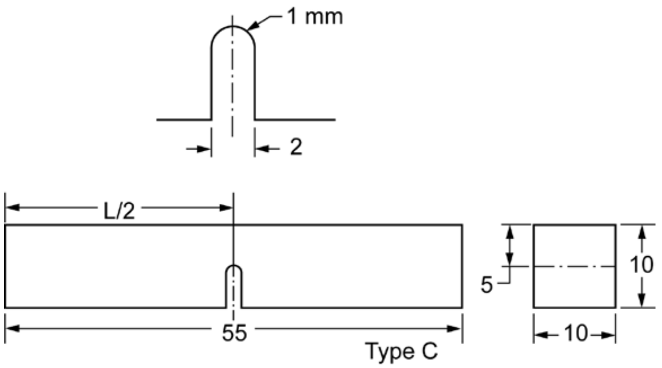

Figure 3.—Schematic of U-notched Charpy specimen used in this study (Ref. 6).

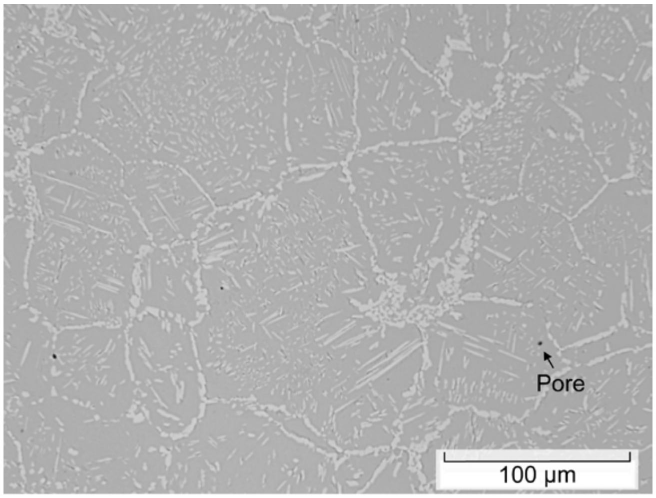

Figure 4.—Microstructure of the as-received cast 60-NITINOL.

metallographic procedures. About 1mm of the specimen was removed during the grinding and polishing procedure. The final polish used colloidal silica on a vibratory polisher. These specimens were analyzed by optical microscopy, SEM and energy-dispersive x-ray spectroscopy (EDS).

Results and Discussion

Table I lists the average Rockwell hardness of the cast 60-NITINOL based on the heat treatment used. Heat treatment followed by furnace cooling produced the softest specimens. Also, the hardness of the furnace-cooled material tended to decrease with increasing heat treatment temperature. The hardness of the water-quenched specimens ranged from 56 to 63 HRC, with the hardness increasing with increasing heat-treatment temperature. Partial solution treatment (defined here as the high-temperature heat treatment and water-quenched condition) followed by aging resulted in hardness ranging from 58 to 62 HRC. Based on the statistical variation, the hardness obtained by the partial solution treatment and by partial solution treatment with aging is essentially identical for each of the studied heat-treatment temperatures.

The microstructure of the as-received material is shown in Figure 4. EDS was used to confirm that the dark grey parent phase is NiTi and the light grey second phase, decorating the grain boundaries and in a lath pattern within the grains, is Ni_3Ti. A few pores are present in the microstructure, one of which is indicated on the photomicrograph (see Figure 4). Microstructures obtained from each heat treatment are shown in Figure 5. These photomicrographs show that the presence of Ni_3Ti is decreased considerably with heat treatment above 900 °C, but it is not eliminated, even after heat treatment at 1050 °C (which is the reason these heat treatments are referred to as “partial” solution treatments). A higher temperature is required to completely dissolve the Ni_3Ti. However, quench cracking was found to occur most often after heat treatments at 1000 °C and greater. Further work is needed to optimize the solution temperature without causing quench cracking. In addition, the amount of the (hardening) Ni_4Ti_3 precipitate phase produced by aging has not yet been quantified. Current work is underway to optimize the precipitation of this hardening precipitate.

Quench Cracking

A quench cracked specimen that was recovered in good condition was examined. The mating fracture surfaces of this specimen were either convex or concave. A cross-section of the concave surface is shown in Figure 6. Examination of the concave fracture surface by SEM revealed classical chevron patterns indicating brittle fracture and the location of the fracture initiation site (see in Figure 7). The fracture origin for quench crack specimens was relatively rough and had areas that statically charged in the SEM. EDS was used to partially identify the bright areas, which were zirconia-rich, though no source of zirconium was known at the time. Later it was realized that these particles were probably contamination from the zirconia lining used to coat the induction crucible. Bulk chemical analysis also detected 20 ppm of zirconium along the fracture surface and at the fracture initiation site.

Charpy Impact Testing

The hardness of Charpy specimens after heat treatment is listed in Table II. As expected, the furnace-cooled material has the lowest hardness (32 HRC), while the quenched material is considerably harder (61 HRC), being approximately the same hardness as the partially solution treated and aged material (63 HRC). The hardness obtained following each heat treatment is essentially the same as that for the comparable 1000 and 1050 °C heat treatments listed in Table I.

Table III shows the impact energy of the studied specimens compared to values for some common engineering alloys (Ref. 5) and for arc-melted 60-NITINOL (Ref. 7). The data for the studied specimens are comparable to those of cast partially solution treated or partially solution treated and aged magnesium, which is to say that their impact energy is very low. Inspection of the fracture surfaces revealed differences in

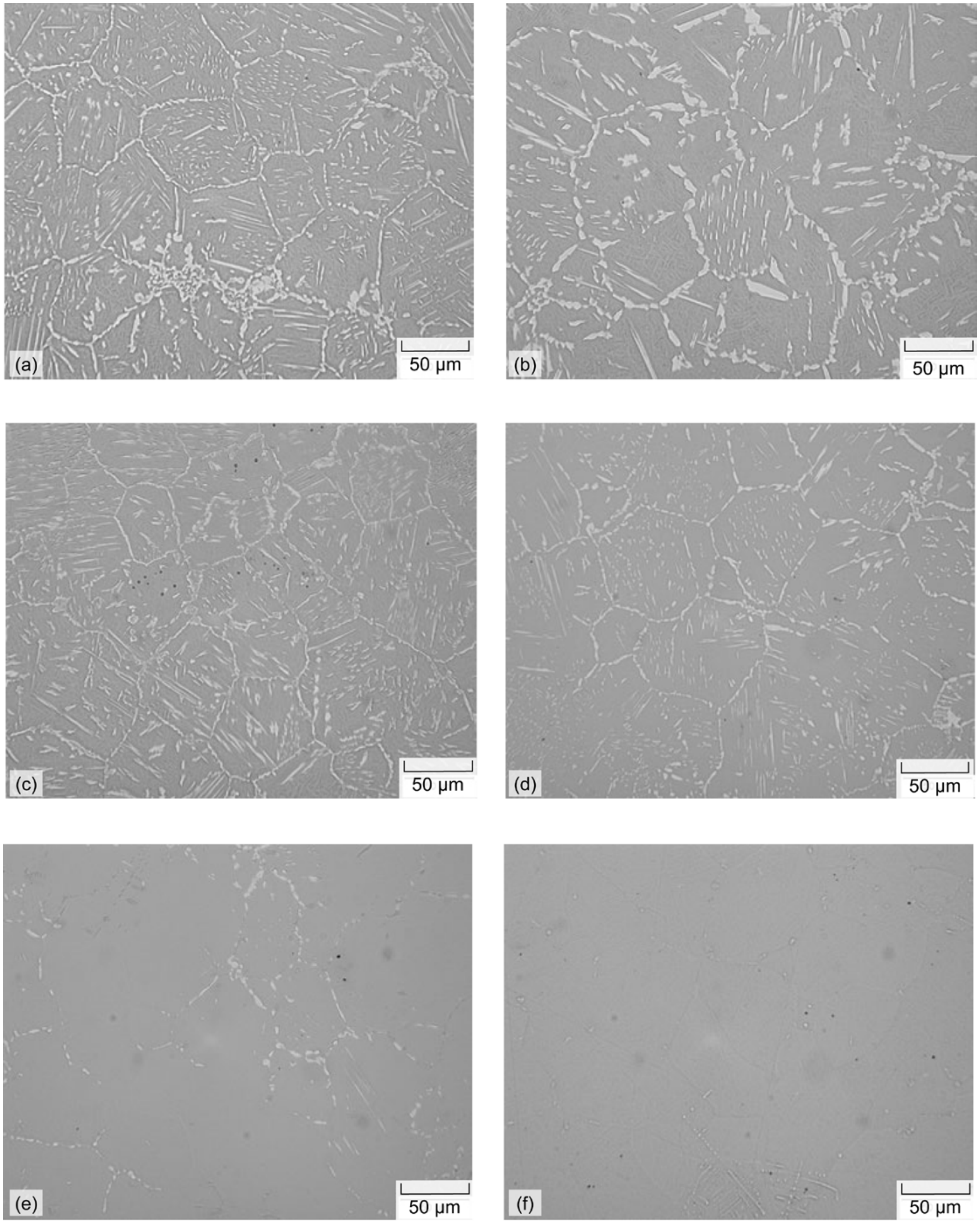

Figure 5.—Optical photomicrographs showing the microstructure of cast 60-NITINOL after furnace-cooling from (a) 900 °C, (b) 1000 °C, and (c) 1050 °C, and after partial solution treatment at (d) 900 °C, (e) 1000 °C and (f) 1050 °C and, similarly, after aging (g) to (i).

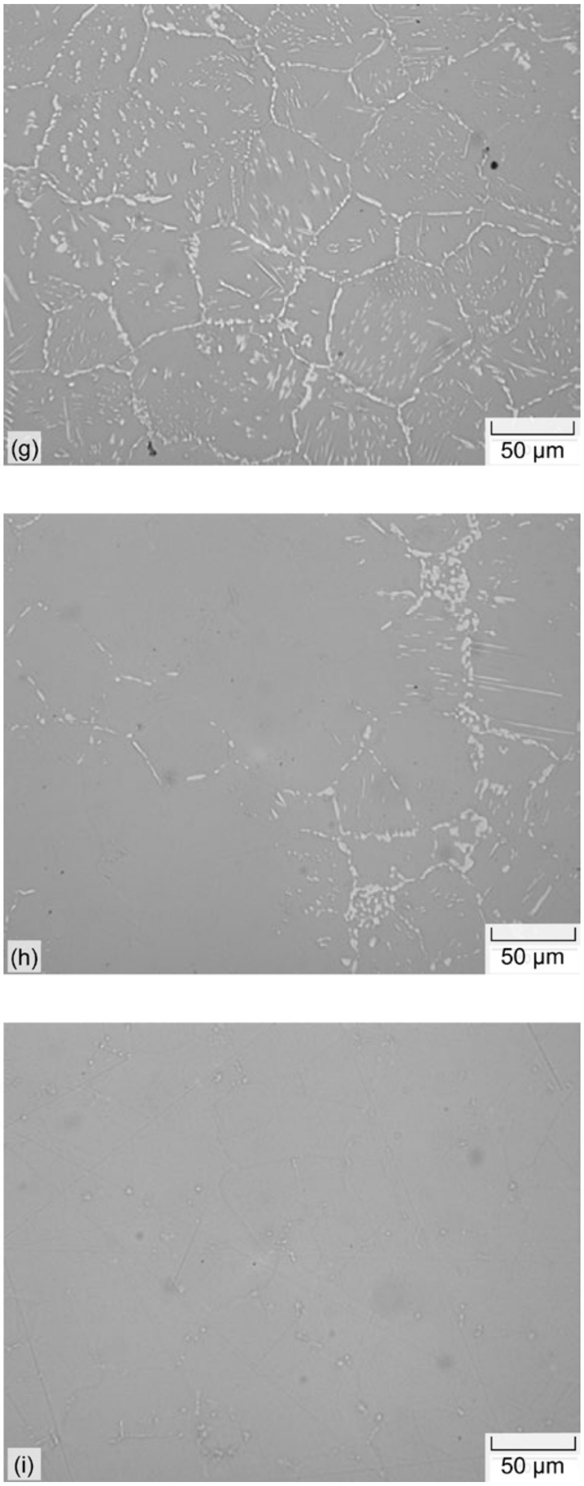

Figure 5.—Concluded.

the fracture mechanisms between the furnace-cooled and the specimens. For furnace-cooled specimens, the fracture surface was dull and non-reflective to the naked eye. Examination by SEM revealed a blocky fracture surface with flat cleavage planes at 1000× magnification possibly indicating brittle, intergranular fracture (see Figure 8).

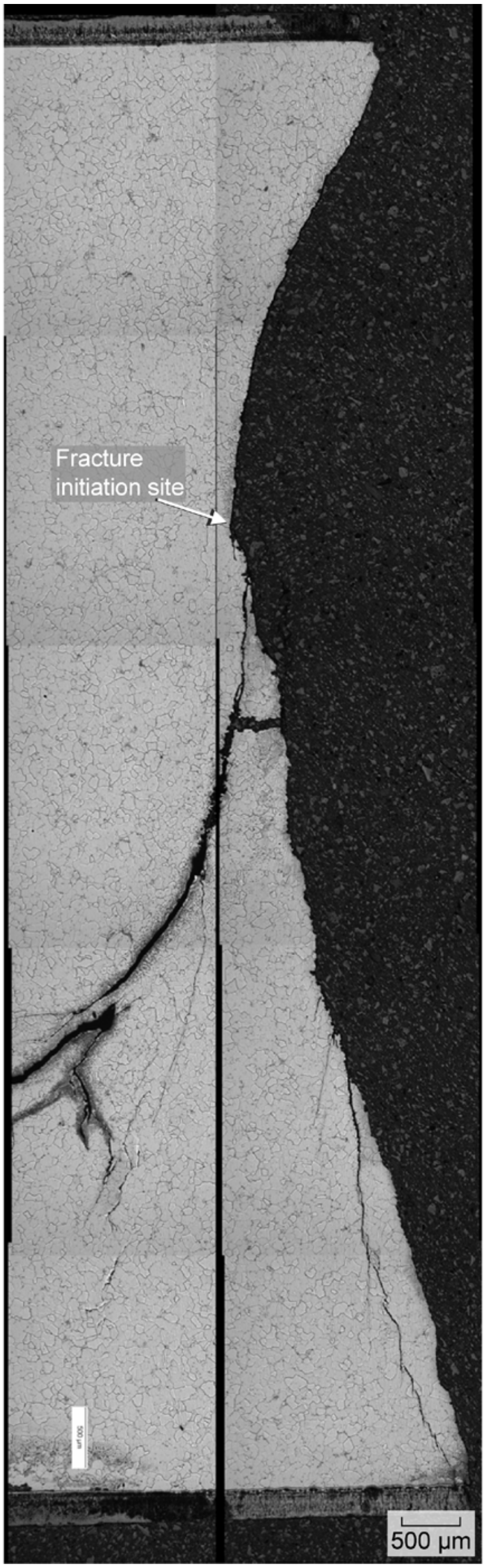

Figure 6.—Montage image of the cross-section of the fracture initiation site. Note the secondary cracks below the primary fracture (the vertical separation at the center of the image is merely an artifact of the software used to compile the montage).

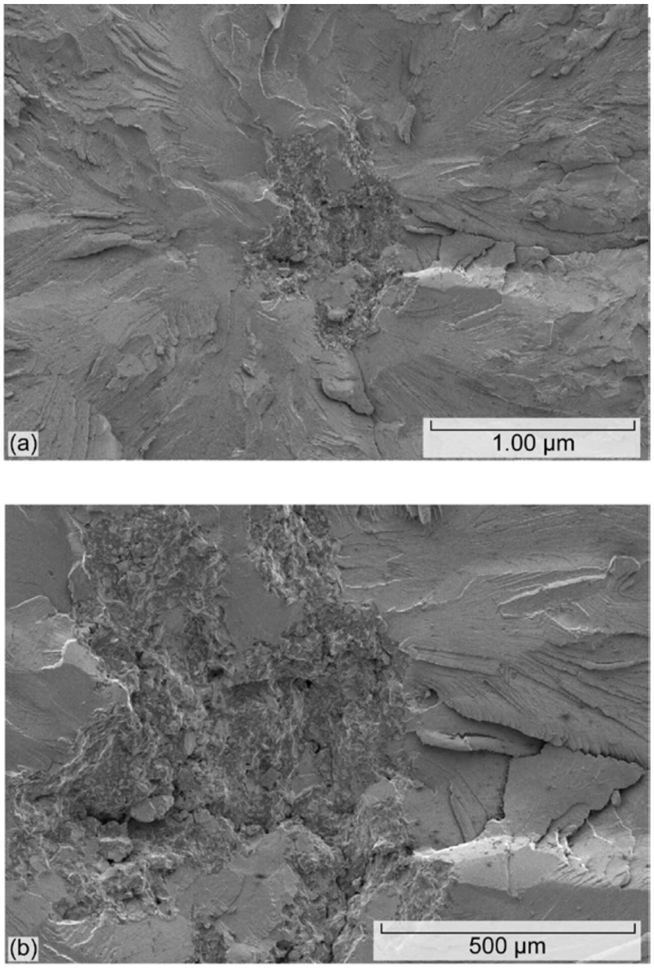

Figure 7.—(a) Quench crack fracture initiation site and (b) higher magnification view of the defect.

TABLE III.—IMPACT TEST RESULTS COMPARED TO OTHER ENGINEERED MATERIALS (REF. 5) AND TO EXTRUDED AND HARDENED 60-NITINOL (REF. 7)

Material	Impact Energy, J
L2 tool steel	26
410 stainless steel	34
Extruded 60-NITINOL	6.8 (notched)
Hardened 60-NITINOL	2.7 (notched)
Cast 60-NITINOL:	
Furnace annealed	1.0 (notched)
Solution treated	0.4 (notched)
Aged	0.5 (notched)
AM100A cast magnesium	0.8

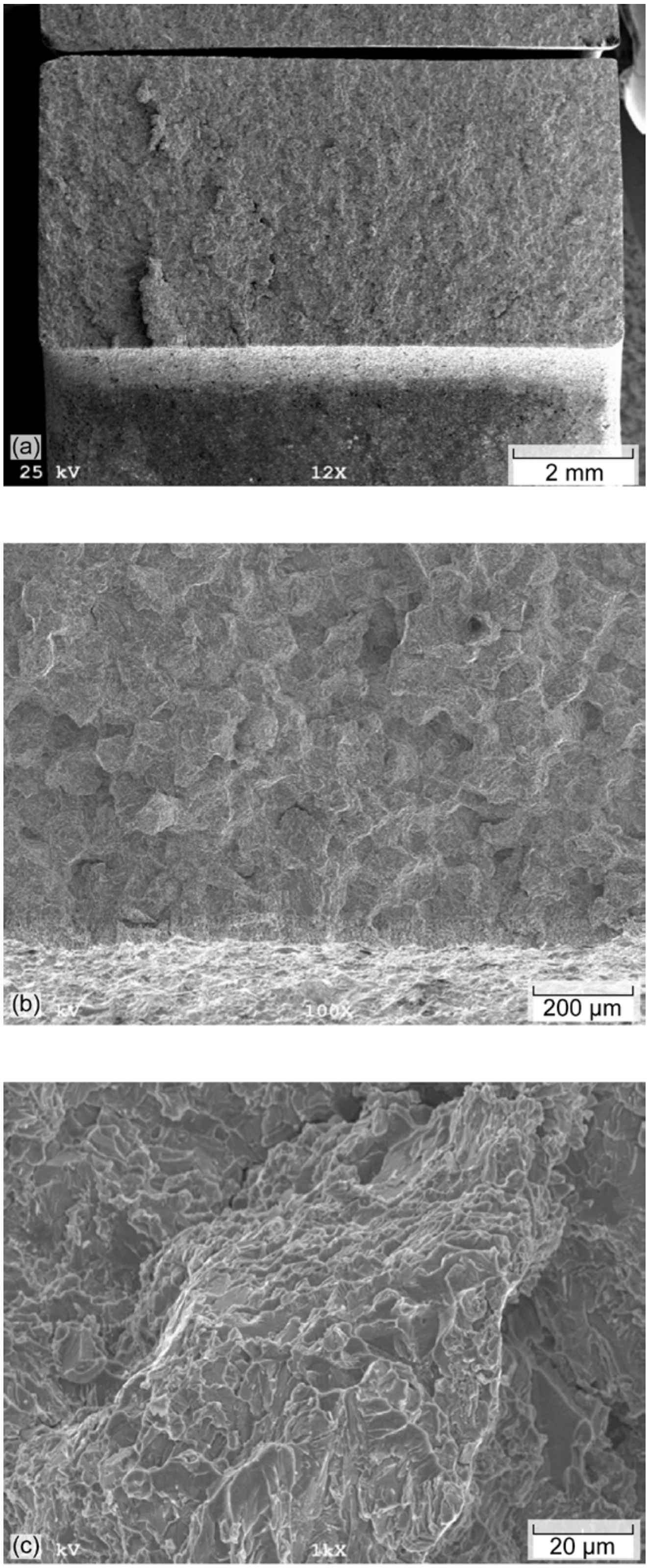

Figure 8.—Overall fracture surface of the furnace-cooled specimen and (b) to (c) higher magnification views of the fracture surface.

Macroscopically, the fracture surfaces of the partially solution treated and the aged impact specimens were more reflective clear indications of beach markings that helped to identify the fracture origin. Closer examination of a partially solution treated specimen by SEM revealed the classical chevron pattern that indicated the direction of crack propagation from the origin (see Figure 9). The fracture initiation sites for both of these specimens had a grainy texture as with the quench-cracked specimens with faceted particles embedded within the fracture initiation site. These locations acquired a static charge from exposure to the electron beam (see Figure 10). Based on the morphology of the contaminant particles, it was thought that the composition of the material was zirconia (ZrO_2). This was confirmed by EDS (see Figure 10 and Figure 11). These faceted particles would tend to act as crack initiators. The maximum tensile stress developed at or near the center of the test specimens. If the angular zirconia particles were present, quench cracking occurred. It is believed that the thermally-induced residual stresses have been magnified because of the added stress concentration of the zirconia particles.

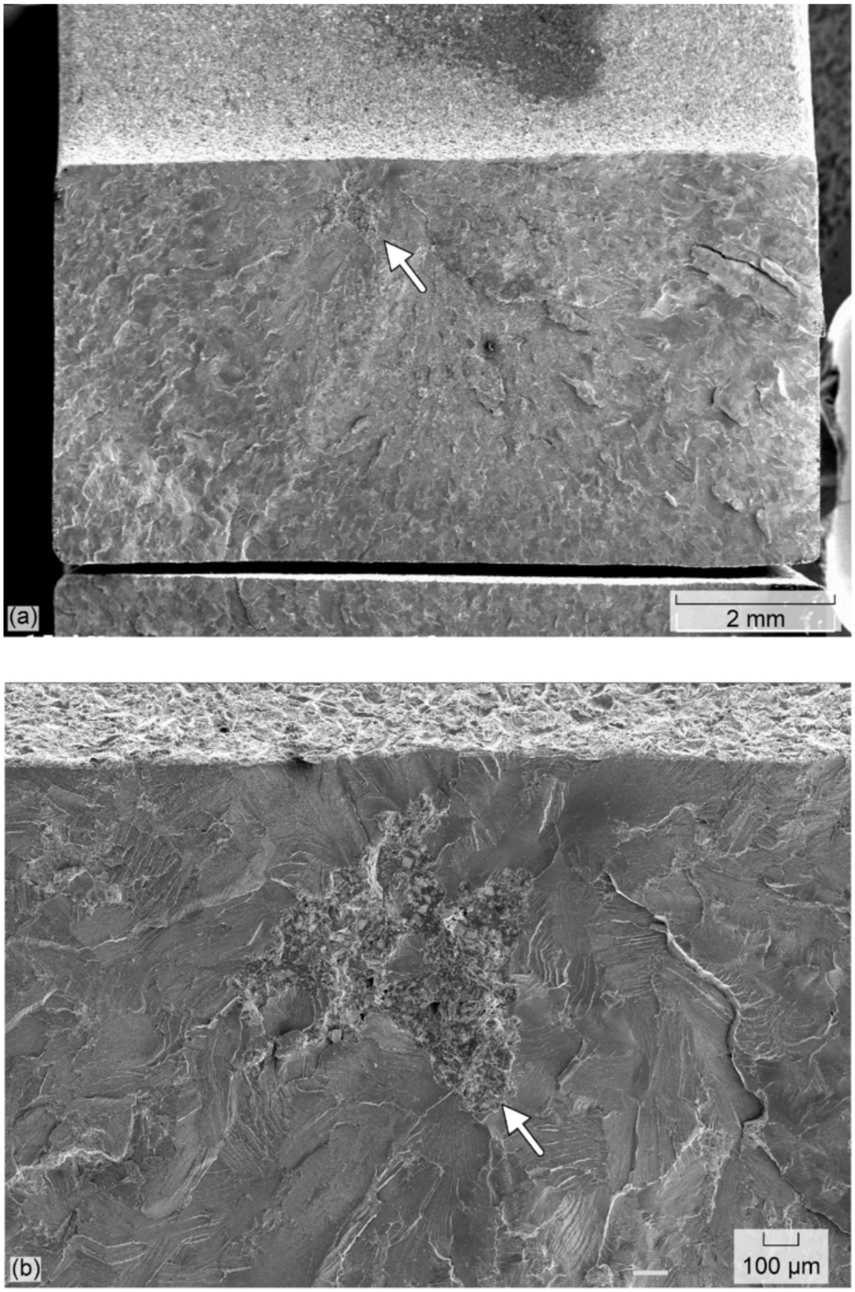

Figure 9.—Partially solution-treated Charpy specimen fracture surface at (a) low and (b) higher magnification with arrows indicating fracture origin.

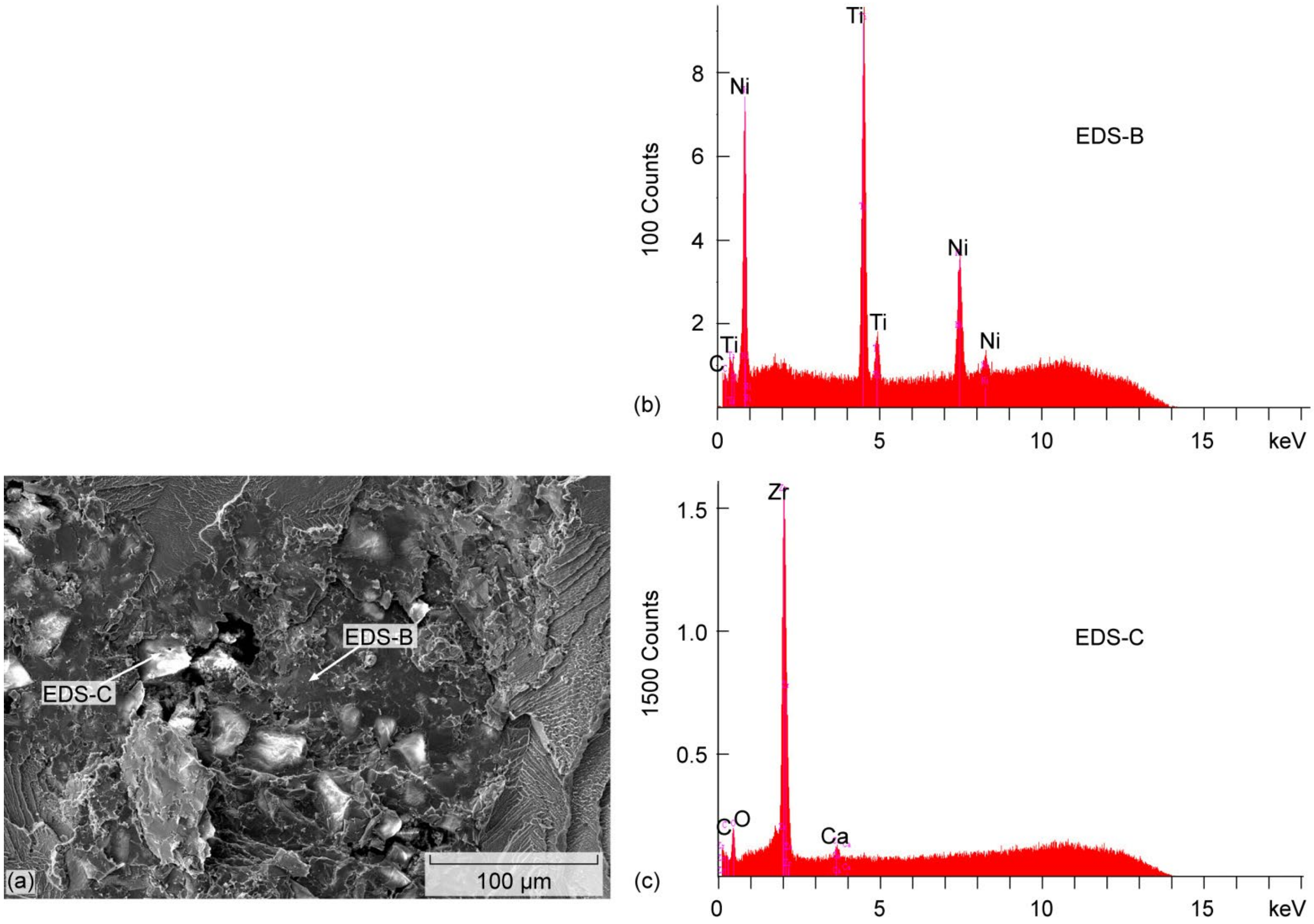

Figure 10.—Scanning electron photomicrograph (a) and energy-dispersive x-ray spectra of fracture origin shown in Figure 9. The area at EDS-B (b) is the Ni-Ti parent material while EDS-C (c) indicates Zr and O (with some Ca).

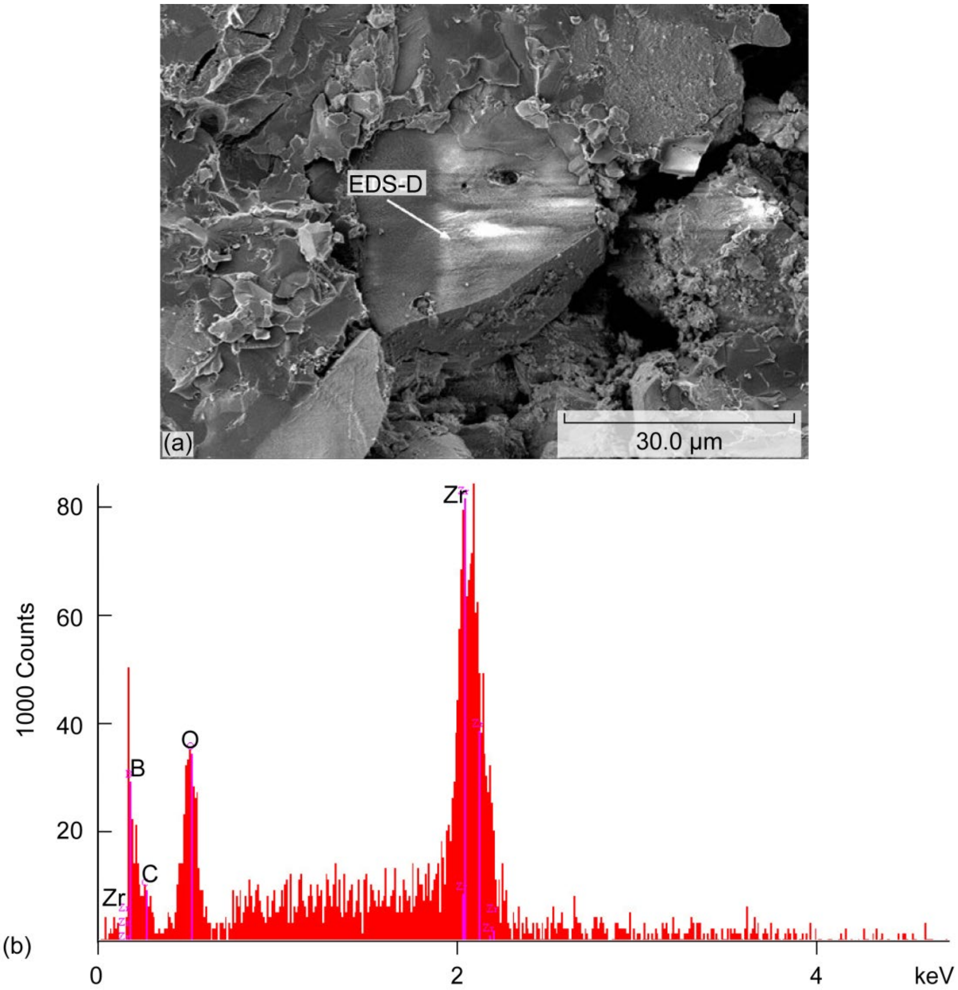

Figure 11.—(a) SEM and (b) EDS of faceted particle within fracture origin shown in Figure 10. With reduced electron beam voltage, it is clear that the primary constituents are Zr and O.

Given the inherent brittleness of this intermetallic material, its cleanliness is extremely important when used under conditions where tensile stresses can be generated. This would include impact loading and thermally-induced strain generation, as well as during basic tensile and flexural loading. A sharp, hard contaminant such as any of those discussed here tends to form a stress concentration that, when encountered by unavoidable tensile stresses, greatly reduces the stress needed for crack propagation. In a material with low ductility such as 60-NITINOL, there is no mechanism for crack blunting, resulting in brittle fracture.

It was determined that the source of the zirconia was an additive in the crucible liner. This lining has been eliminated from the 60-NITINOL casting process and new material is currently being evaluated. However, casting is a processing method that has intrinsic weaknesses. Porosity in cast material tends to be spherical and is thus resistant to elimination, even by hot isostatic pressing. Clearly, casting is not the best processing route for a brittle material that will be exposed to tensile stresses. However, in compression this material performs very well (Refs. 1 and 2). Component designers will need to take the processing route used to produce this material into consideration. Powder metallurgy processing for 60-NITINOL is currently being developed and may provide better performance for applications subjected to multi-directional stresses and fatigue loads (Ref. 8).

Concluding Remarks

The hardness of cast 60-NITINOL after various heat treatments has been investigated. Issues of quench cracking and material contamination were also studied. This investigation has shown that 60-NITINOL can be hardened to approximately 63 HRC with relatively simple heat treatments. Further work will be required to explore heat treatment procedures that can yield a material with an adequate hardness, based on the application envisioned, while avoiding quench cracking. In addition, further testing of the cast material, without the zirconia contaminant, is required to determine the Charpy impact energy. However, the cast form of this material may not be practical for some applications due to the intrinsically low toughness of castings. The results of this study provide guidance for the proper selection of processing routes for 60-NITINOL based on the expected service environments.

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