Electrolytic phase extraction: a useful technique to evaluate precipitates in nitinol

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Nitinol is a shape memory alloy based on the inter-atomic compound having a composition of 50 at% each of Ni and Ti, NiTi. The shape memory effect results from a reversible martensitic phase transformation. An increasing solubility range with temperature on the Ni-rich side can produce a precipitation reaction resulting in a slight matrix composition adjustment with appropriate heat treatment. Electrolytic phase extraction (Andrews and Hughes, 1957) is used to evaluate the secondary phases in the alloy and Ti_2Ni and TiC are positively identified using powder wide-angle X-ray diffraction procedures. Two samples of an Ni-rich alloy at 57 and 60 at% are also analyzed. These Ni-rich samples show Ti_2Ni and an additional phase, Ni_3Ti. © *International Centre for Diffraction Data* [doi:10.1017/S0885715612000279]

Key words: X-ray diffraction, nitinol, electrolytic phase extraction

I. INTRODUCTION

Metallographic and scanning electron microscopic evaluation (SEM) of NiTi microstructures often reveals a second-phase precipitate whose chemistry is close to the Ti_2Ni phase (Figure 1).

The precipitate size or volume cross-section sampled by an electron beam in the SEM and electron microprobe usually includes part of the matrix which prevents an accurate composition of the precipitate to be determined. One of the goals of this study was to evaluate analytical tools for the investigation of these phases in NiTi. The NiTi chemistry is closely controlled to be slightly Ni-rich and the current phase diagram (Bellen *et al.*, 1996) does not predict Ti_2Ni precipitation in a homogeneous sample cooled from the melt (Figure 2). Carbon is also considered an impurity and specified to be no more than 0.05% in NiTi shape memory alloys.

A standard procedure for extraction of precipitates in Ni base superalloys and their analysis using wide-angle X-ray diffraction (WAXRD) is described in ASTM E 963-95 (2000) Standard Practice for Electrolytic Extraction of Phases from Ni and Ni–Fe Base Superalloys Using a Hydrochloric-Methanol Electrolyte. This technique was used on NiTi and found to be successful in separating and collecting precipitate phases from the parent material.

II. EXPERIMENTAL

Samples of NiTi weighing only a few grams were partially dissolved electrolytically in a 10% HCl–methanol solution containing 1.7 g of tartaric acid per 300 ml. The undissolved residue with electrolyte was collected and vacuum filtered using a 0.4-μm polycarbonate membrane filter. A sample of the filtrate was evaluated for chemistry in the electron microprobe and an image of the material is shown in Figure 3. An energy dispersive spectroscopic (EDS) scan of one of the large particles suggests the precipitate is Ti_2Ni on the basis of the chemical analysis [Figure 4(a)]. A second EDS scan from a group of smaller particles is shown in Figure 4(b). As no other significant elemental species are found in the EDS scan other than titanium and carbon present as impurities, this suggests the fine particles are carbides of titanium. As carbon cannot be determined quantitatively with this method, a complementary technique of X-ray diffraction was used for phase identification.

A few milligrams of material were collected on the filter for analysis. This was attached to a glass slide with petroleum

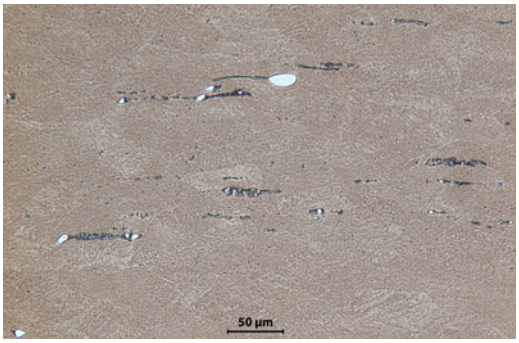


Figure 1. (Color online) Characteristic Ni–Ti microstructure with second-phase particles.

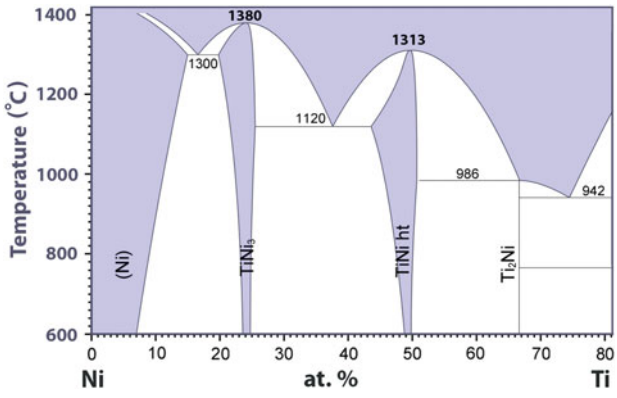


Figure 2. (Color online) Ni–Ti partial phase diagram. (Reprinted with permission from ASM International. All rights reserved.)

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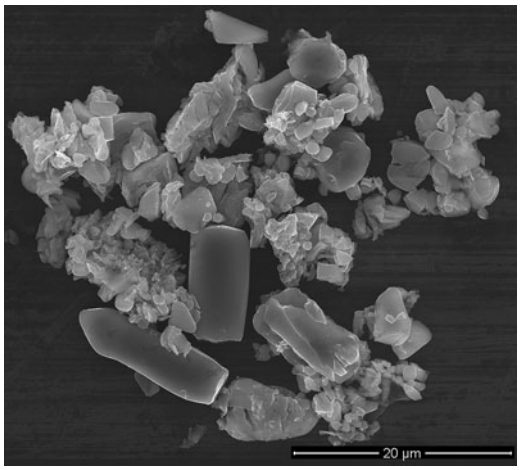


Figure 3. SEM images of extracted particles.

jelly and placed in the sample holder for X-ray analysis. The specimen was scanned over a 2θ angular range from 10° to 145° using a Siemens D5000 diffractometer with a diffracted beam graphite monochromator tuned to Cu$K\alpha$ radiation. The diffracted X-ray intensity is typically collected over a 24-h period to improve the data statistics.

III. RESULTS AND DISCUSSION

Ti_2Ni (PDF018-0898) and TiC (PDF 032-1383) phases were positively identified by comparing the diffraction pattern with the ICDD database for the two compounds (Figure 5).

Additional samples were acquired and all subsequent electrolytic phase extractions consistently revealed only the Ti_2Ni and TiC phases. The amount of TiC present in the samples varied depending on supplier and melting practice for NiTi (Figure 6). The weight amount of residue remaining after NiTi dissolution was consistently <2% and Ti_2Ni made up the largest portion. This is shown in Figure 7, with the amount trending along the 45° line. The symbols represent materials from three suppliers. The deviation from 45° was attributable to the presence of TiC in the sample, as shown in Figure 8.

The literature suggests that the Ti_2Ni phase combines with oxygen impurities in the material and is identified as a sub-oxide (Mueller and Knott, 1963). A quantity of Ti_2Ni was

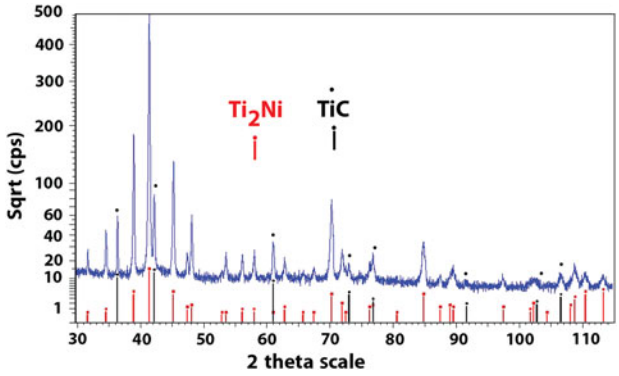


Figure 5. (Color online) WAXRD pattern from extracted particles.

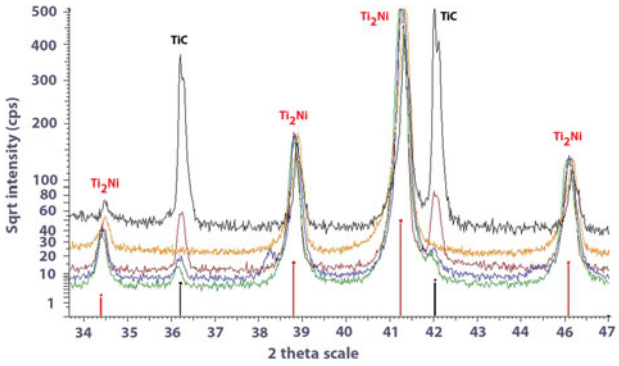


Figure 6. (Color online) Different melt 'heat lots' of NiTi showing varying amounts of TiC.

collected by dissolving several grams of NiTi that exhibited no evidence of TiC and examined using simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (SDTA). The TGA and DSC data show that two significant reactions occur between 100 and 1000 °C (Figure 9). A modest increase in mass occurs at ≈348 °C (~2.5%) and a larger increase at ≈655 °C (~33%). A larger quantity of material was subsequently extracted, apportioned and heated in an alumina crucible at 400, 450, or 900 °C. The increase in weight for each of the samples was very close to the amount indicated in the TGA experiment. These samples were then evaluated to determine changes in the WAXRD pattern. A distinct splitting of the diffraction peaks occurred for Ti_2Ni when heated in air to 450 °C (Figures 10 and 11).

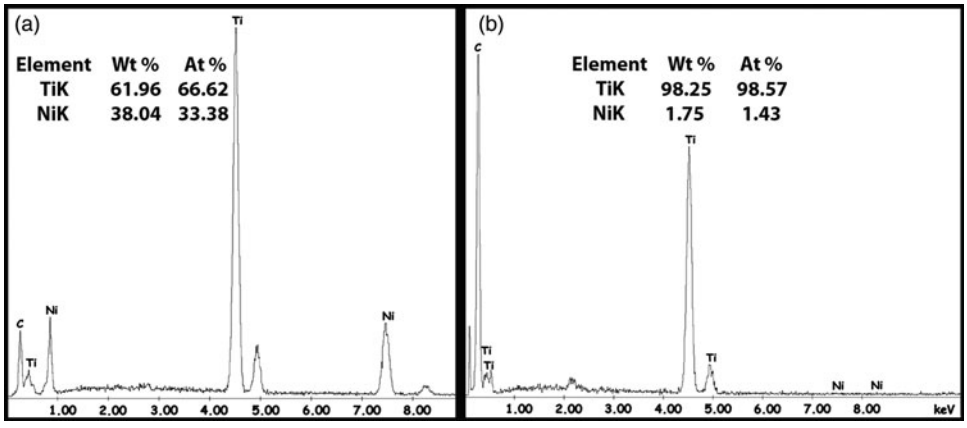


Figure 4. EDS spectra and chemical analysis for (a) large particles and (b) cluster of small particles extracted from NiTi.

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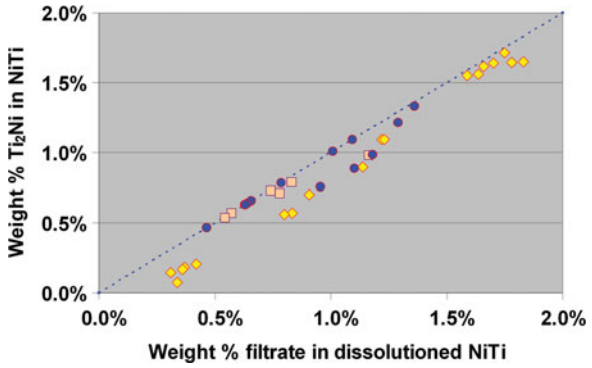


Figure 7. (Color online) Weight percent of Ti_2Ni in NiTi.

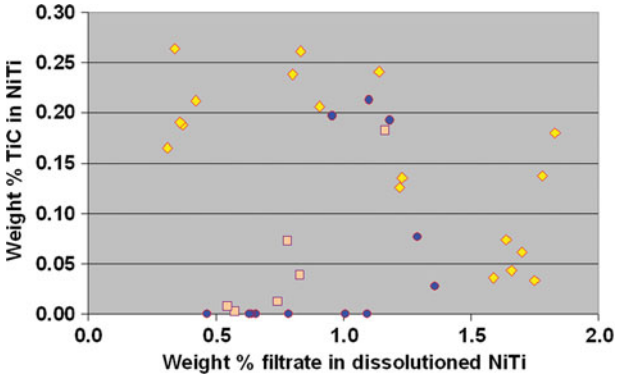


Figure 8. (Color online) Weight percent of TiC in NiTi.

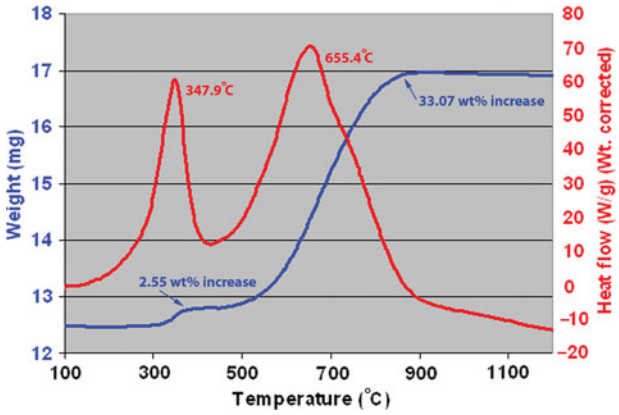


Figure 9. (Color online) SDTA results for a sample of Ti_2Ni without TiC.

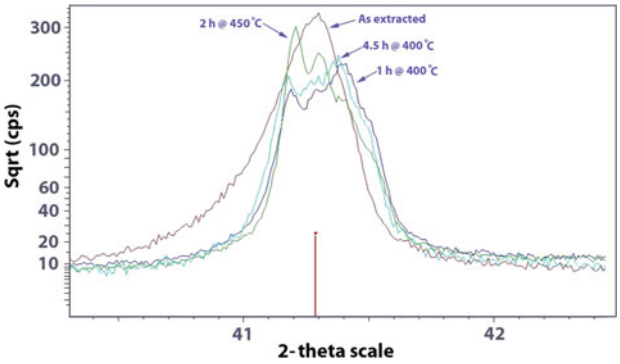


Figure 10. (Color online) Oxidation of Ti_2Ni at 400 and 450 °C to Ti_4Ni_2O (PDF 005-0694).

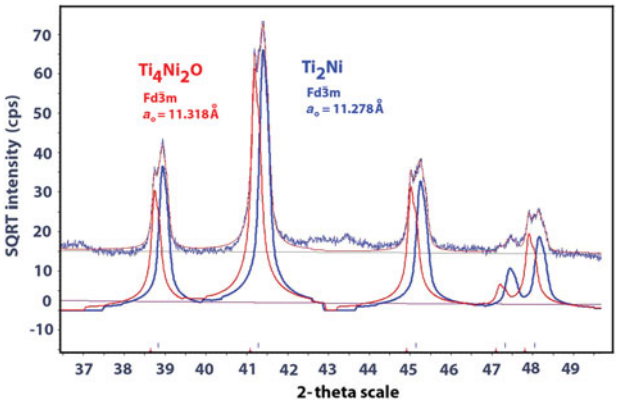


Figure 11. (Color online) Splitting of Ti_2Ni phase peaks with Ti_4Ni_2O (PDF 005-0694) formation from exposure to air at 400 °C.

When heated to higher temperatures, Ti_2Ni was oxidized to $TiNiO_3$ and TiO_2 (Rutile). A LECO TCH 600 Analyzer was used to evaluate the oxygen content of Ti_2Ni samples before and after exposure to air at 400 °C for 5 h. The weight gain, exothermic reaction, and oxygen analysis clearly indicate that the Ti_2Ni lattice oxidizes to Ti_4Ni_2O. The crystal structure of this oxide is the same as Ti_2Ni (Mueller and Knott, 1963) with a slightly larger unit-cell parameter as indicated by the splitting of the diffraction peaks (Figures 10 and 11).

The average oxygen content for three samples of "as extracted" Ti_2Ni was 6.1 wt% (17.2 at%) and after heating in air to 400 °C for 5 h was 19.6 wt% (44.0 at%), but the crystal structure was still consistent with Ti_4Ni_2O, which has an oxygen content of 14.29 at%. Three other oxides have oxygen atom percents of 53.85 (Ni_5TiO_7), 55.56 (Ni_3TiO_5), and 60 at% ($TiNiO_3$). However, no diffraction peaks could be associated with these phases even though the oxygen level was more than required for the Ti_4Ni_2O phase that was identified.

Three Ni-rich NiTi samples with 60 at% Ni and one with 57 at% Ni were also analyzed using electrolytic dissolution. The dominant phase was still Ti_2Ni, but Ni_3Ti (PDF 051-1169) was also present. A representative X-ray diffraction scan was evaluated using the Rietveld procedure and is shown in Figure 12.

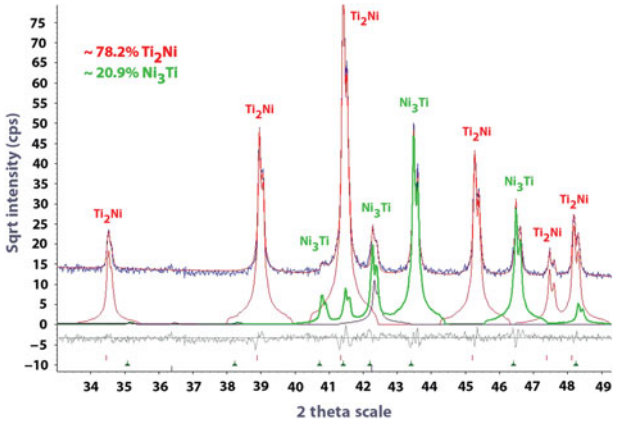


Figure 12. (Color online) Rietveld analysis of X-ray diffraction pattern revealing Ti_2Ni and Ni_3Ti precipitates (PDF 051-1169) in 60% NiTi.

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IV. CONCLUSION

Ti_2Ni and TiC phases were quantitatively extracted from NiTi using electrolytic dissolution and identified using powder X-ray diffraction. When Ni-rich NiTi was evaluated using this technique, Ti_2Ni and Ni_3Ti phases were extracted and identified. Ti_2Ni oxidizes to Ti_4Ni_2O at <450 °C with the same crystal structure as Ti_2Ni and further oxidizes to $NiTiO_3$ and TiO_2 at 900 °C.

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