ELECTROLYTIC PHASE EXTRACTION: AN OLD TECHNIQUE TO EVALUATE PRECIPITATES IN NITINOL

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ABSTRACT:

Nitinol is a shape memory alloy based on the inter-atomic compound having a composition of 50 atom percent 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, K.W. et al, 1957) was utilized to evaluate the secondary phases present in the alloy and a positive identification of Ti$_2$Ni and TiC was made using powder wide angle X-ray diffraction procedures (WAXRD). Two samples of a Ni rich alloy identified as 57% and 60% were also analyzed. These Ni rich samples showed Ti$_2$Ni and an additional phase, Ni$_3$Ti.

INTRODUCTION:

Metallographic and scanning electron microscopic evaluation (SEM) of NiTi microstructures often reveals a second phase precipitate whose chemistry is close to the Ti$_2$Ni phase (Figure 1). The precipitate size or volume cross section sampled by an electron beam in the SEM and Electron Microprobe (EMPA) 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 most current phase diagram (Bellen, P. et al, 1996) does not predict Ti$_2$Ni precipitation in a homogenous sample cooled from the melt (Figure 2). The chemical element carbon is also considered an impurity and specified to be no more than 0.05% in NiTi shape memory alloys.

Figure 1. Characteristic Ni-Ti microstructure with 2nd phase particles.
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A standard procedure for extraction of precipitates in Ni base Superalloys and their analysis using WAXRD is described in ASTM E 963-95 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.

EXPERIMENTATION AND RESULTS:

Samples of NiTi weighing only a few grams were partially dissolved electrolytically in a 10% HCl – Methanol solution containing 1.7 g Tartaric acid per 300 ml. The undissolved residue with electrolyte was collected and vacuum filtered using a 0.4 µm Polycarbonate (PC) membrane filter. A sample of the filtrate was evaluated in the electron microprobe for chemistry and an image of the material is shown in Figure 3. An EDS scan from one of the large particles suggests the precipitate is Ti$_2$Ni based on the chemical analysis (Figure 4a). A second EDS scan from a grouping of the smaller particles is shown in Figure 4b. Since there are no other significant elemental species in the EDS scan other than titanium and carbon present as an impurity, this would suggest the fine particles are carbides of Ti. Since carbon cannot be determined quantitatively with this method, a complementary technique of X-ray diffraction was used for phase identification.

A few mg of material was collected on the filter for analysis. This was attached to a glass slide
with petroleum jelly and placed in the sample holder for X-ray analysis. The specimen was

Figure 3. SEM images of extracted particles.

Figure 4. EDS spectra and chemical analysis for two types of particles extracted from NiTi. (a) large particle; (b) cluster of small particles.
scanned over a two theta 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 hour period to improve the data statistics. A positive identification of Ti$_2$Ni (PDF 018-0898) and TiC (PDF 032-1383) phases was made by comparing the diffraction pattern with the ICDD data base for the two compounds (Figure 5).

Figure 5: WAXRD pattern from extracted particles.

Additional samples were acquired and all subsequent electrolytic phase extractions consistently revealed only the two phases: Ti$_2$Ni and TiC. The amount of TiC present in the samples varied depending on supplier and melting practice for NiTi (Fig. 6).

Figure 6. Different melt ‘Heat Lots’ of NiTi showing varying amounts of TiC.
The weight amount of residue remaining after NiTi dissolution was consistently less than 2% and Ti$_2$Ni 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 due to TiC present in the sample which is shown in Figure 8.

The literature suggests the Ti$_2$Ni phase combines with oxygen impurities in the material and is identified as a sub-oxide (Mueller and Knot, 1963). A quantity of Ti$_2$Ni was collected by dissolving several grams of NiTi that exhibited no evidence of TiC and using simultaneous TGA and DSC (SDTA) to analyze the powder. The TGA and DSC data show two significant reactions occurring in the temperature range between 100 °C 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 temperatures of 400 °C, 450 °C, or 900 °C. The weight increase for each of the samples was very close to the amount indicated with 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$_2$Ni when heated in air to 450 °C (Figures 10 and 11).

The changes occurring in Ti$_2$Ni when heated to the higher temperature was to oxidize the phase to TiNiO$_3$ and TiO$_2$ (Rutile). A LECO TCH 600 Analyzer was used to evaluate the oxygen content of Ti$_2$Ni samples before and after exposure at 400 °C for 5 hrs in air. The weight gain, exothermic reaction, and oxygen analysis clearly indicates the Ti$_2$Ni lattice is oxidizing to Ti$_4$Ni$_2$O.

Figure 9. SDTA results for a sample of Ti$_2$Ni without TiC.

Figure 10. Oxidation of Ti$_2$Ni at 400 °C and 450 °C to Ti$_4$Ni$_2$O (PDF 005-0694).
The crystal structure of this oxide is the same as Ti$_2$Ni (Mueller and Knott, 1963) with slightly larger lattice parameter as indicated by the splitting of the diffraction peaks (Figures 10 and 11).

![Splitting of Ti$_2$Ni phase peaks with Ti$_4$Ni$_2$O (PDF 005-0694) formation from exposure in air at 400 °C](image)

Figure 11. Splitting of Ti$_2$Ni phase peaks with Ti$_4$Ni$_2$O (PDF 005-0694) formation from exposure in air at 400 °C.

The average oxygen content for three samples of ‘as extracted’ Ti$_2$Ni was 6.1wt% (17.2 at%) and after heating in air for 5 hrs at 400 °C, the oxygen content measured 19.6 wt% (44.0 at%) but the crystal structure was still consistent with Ti$_4$Ni$_2$O which has 14.29 at% O. There are three other oxides with oxygen atom percents of 53.85 at% (Ni$_5$TiO$_7$), 55.56 at% (Ni$_3$TiO$_5$) and 60 at% (TiNiO$_3$). However, there were no diffraction peaks that could be associated with these phases even though the oxygen level was more than required for the Ti$_4$Ni$_2$O phase that was identified.

Three nickel rich NiTi samples based on 60 at% Ni and one 57 at% Ni were also analyzed using electrolytic dissolution. The dominant phase was still Ti$_2$Ni but Ni$_3$Ti (PDF 051-1169) was also present. A representative XRD scan that was evaluated using the Rietveld procedure is shown in Figure 12.
CONCLUSIONS:

1. Ti$_2$Ni and TiC phases were quantitatively extracted from NiTi using electrolytic dissolution.
2. Ti$_2$Ni and Ni$_3$Ti phases were extracted from Ni rich NiTi using electrolytic dissolution.
3. Ti$_2$Ni oxidizes to Ti$_4$Ni$_2$O at temperatures less than 450 °C with the same crystal structure as Ti$_2$Ni.
4. Ti$_2$Ni oxidizes to NiTiO$_3$ and TiO$_2$ at a temperature of 900 °C.

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