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X-ray diffraction study of low-temperature phase transformations in nickel–titanium orthodontic wires

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ABSTRACT

Objectives. Employ conventional X-ray diffraction (XRD) to analyze three clinically important nickel–titanium orthodontic wire alloys over a range of temperatures between 25 and −110 °C, for comparison with previous results from temperature-modulated differential scanning calorimetry (TMDSC) studies.

Methods. The archwires selected were 35 °C Copper Ni–Ti (Ormco), Neo Sentalloy (GAC International), and Nitinol SE (3M Unitek). Neo Sentalloy, which exhibits superelastic behavior, is marketed as having shape memory in the oral environment, and Nitinol SE and 35 °C Copper Ni–Ti also exhibit superelastic behavior. All archwires had dimensions of 0.016 in. × 0.022 in. (0.41 mm × 0.56 mm). Straight segments cut with a water-cooled diamond saw were placed side-by-side to yield a 1 cm × 1 cm test sample of each wire product for XRD analysis (Rint-Ultima+, Rigaku) over a 2θ range from 30° to 130° and at successive temperatures of 25, −110, −60, −20, 0 and 25 °C.

Results. The phases revealed by XRD at the different analysis temperatures were in good agreement with those found in previous TMDSC studies of transformations in these alloys, in particular verifying the presence of R-phase at 25 °C. Precise comparisons are not possible because of the approximate nature of the transformation temperatures determined by TMDSC and the preferred crystallographic orientation present in the wires. New XRD peaks appear to result from low-temperature transformation in martensite, which a recent transmission electron microscopy (TEM) study has shown to arise from twinning.

Significance. While XRD is a useful technique to study phases in nickel–titanium orthodontic wires and their transformations as a function of temperature, optimum insight is obtained when XRD analyses are combined with complementary TMDSC and TEM study of the wires.

1. Introduction

Nickel–titanium wires, based upon the equiatomic intermetallic compound NiTi, have widespread use in clinical orthodontics, since their very low values of elastic modulus and wide elastic range provide optimal light and continuous orthodontic force [1]. NiTi wires are available as nonsuperelastic and superelastic products [2–6], as well as products

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having true shape memory in the oral environment [7,8]. The mechanical behavior referred to as superelasticity in the orthodontic materials literature [4–6] is termed *pseudoelasticity* in the engineering materials literature [9]. The properties of the nickel–titanium orthodontic wires depend upon the proportion and characteristics of the three-microstructural phases [1,9]: austenitic NiTi (austenite), martensitic NiTi (martensite), and the intermediate R-phase.

Conventional X-ray diffraction (XRD) [1,10] and micro-X-ray diffraction [11,12] have been used advantageously to study phases in nickel–titanium orthodontic wires at room temperature. However, XRD analyses of metallic materials provide information for regions within less than approximately 50 μm from the surface [13], whereas differential scanning calorimetry (DSC) analyses [6–8] provide information about bulk specimens as well as enthalpy changes for phase transformations. Moreover, there has been some disagreement in reported information for phases in nickel–titanium wires obtained by DSC [8] and XRD [10].

New insights into the phases in NiTi orthodontic wires [14,15] have been obtained from the more recently developed technique of temperature-modulated DSC (TMDSC) [16,17], which enables separation of the total heat flow measured by conventional DSC into reversing and nonreversing components. Transformations involving the R-phase, not previously detected by conventional DSC for some orthodontic nickel–titanium wires, are evident on nonreversing heat flow curves. In addition, a low-temperature exothermic peak on the heating and cooling nonreversing TMDSC heat flow curves was not detected by DSC [8]. Such low-temperature transformations within martensite were originally reported from electrical resistivity measurements of NiTi orthodontic wires [18]. A recent transmission electron microscopy (TEM) study [19] has shown that the low-temperature peak arises from twinning in martensite.

The purpose of this study was to investigate phase transformations in three commercial nickel–titanium orthodontic wires, using conventional X-ray diffraction over the temperature range from −110 to 25 °C, and to compare the results with those obtained from TMDSC [14,15]. This is the first study that has compared the results from these two techniques for the same NiTi orthodontic wires, and it was hypothesized that XRD would verify the transformations that were reported from the previous TMDSC investigations. Because of the dynamic nature of TMDSC in which temperature is varied slowly during thermal scanning, along with the relatively narrow temperature range for transformation between austenite and martensite in some orthodontic wire alloys [14,15], it is important to confirm the NiTi phases that occur at fixed temperatures by XRD. This is particularly necessary for the intermediate R-phase [9], which is not resolved by conventional DSC plots [8] or by the TMDSC reversing heat flow curve for some wires, and is inferred from the TMDSC nonreversing heat flow curve [14,15]. Moreover, the reported use of subambient cooling for Copper Ni–Ti orthodontic wire to yield improved ligation for treatment of severe rotations [20] suggests the need to study low-temperature transformations in NiTi wires.

2. Materials and methods

Three clinically popular nickel–titanium orthodontic archwire products, having cross-section dimensions of 0.016 in. × 0.022 in. (0.41 mm × 0.56 mm), were selected: Neo Sentalloy (GAC International, Islandia, NY, USA), Nitinol SE (3M Unitek, Monrovia, CA, USA), and 35 °C Copper Ni–Ti (Ormco, Glendora, CA, USA). Neo Sentalloy and Nitinol SE are near-equiatomic nickel–titanium alloys, while 35 °C Copper Ni–Ti contains slightly less than 5% copper in place of nickel [21], with a small amount of chromium to compensate for copper raising the austenite-finish (A_f) temperature [1,22]. The 35 °C Copper Ni–Ti product has previously been studied by TMDSC [15] and TEM [19]. Both Nitinol SE and Neo Sentalloy have been studied by conventional DSC [8], and Neo Sentalloy has been investigated in two TMDSC studies [14,15].

Approximate phase transformation temperatures for these three wire products that were determined from the heating cycles of the TMDSC curves in a previous study [15] are shown in Table 1. Use of the TMDSC heating cycle to determine transformation temperatures results in the M'_s temperature for the low-temperature martensite transformation, which is designated as $M' \rightarrow M$ in [15], being lower than the M'_f temperature. The prime symbols have been employed with this low-temperature transformation to designate that it occurs within the martensite structure, before the subsequent heating transformation from martensite to R-phase. The M'_s and A_f temperatures in Table 1 were determined from intersections of tangent lines on the TMDSC plots [15] with the adjacent baselines. The M'_f and R_s temperatures in Table 1 were determined from points marked with the computer on the TMDSC plots [15] that were used to obtain the enthalpy changes (ΔH) from peak areas. Values of the R_f and A_s temperatures could not be determined from TMDSC heating curves [14,15] because of overlapping peaks for the martensite to R-phase and the R-phase to austenite transformations.

Segments from the straight portions of as-received blanks of each archwire product were cut into approximately 1-cm lengths, using a low-speed, water-cooled diamond saw (Isomet, Buehler, Lake Bluff, IL, USA). Multiple segments yielding an approximately 1 cm × 1 cm test sample were placed side-by-side on the approximately 2 cm × 2 cm base of the copper sample holder, with the wire surfaces and sample

Table 1 – Approximate transformation temperatures for wire products [15]

Wire Product	M'_s	M'_f	R_s	A_f
35 °C Copper Ni–Ti	−103	−15	−8	35
Nitinol SE	−107	−9	−5	62
Neo Sentalloy	−102	−11	−5	29

Values determined from TMDSC heating curves. M'_s and M'_f are the starting and ending temperatures for low-temperature transformation in martensite. R_s is the starting temperature for transformation from martensite to R-phase, and A_f is the ending temperature for transformation from R-phase to austenite. Other transformation temperatures could not be determined from the TMDSC heating curves (see text).