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Influence of the Si content on the microstructure and mechanical properties of Ti–Ni–Cu–Si–Sn nanocomposite alloys

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ABSTRACT

$(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ (x = 0, 2, 4 and 6) alloys were prepared by levitation melting mixtures of the high purity elements in an Ar atmosphere. Rods of 3 mm in diameter were obtained from the melt by copper mould casting. The effects of Si addition on the microstructure, elastic and mechanical properties of the $Ti_{48}Ni_{32}Cu_8Si_8Sn_4$ alloy were investigated by scanning electron microscopy, X-ray diffraction, acoustic measurements and nanoindentation. The main phases composing the $Ti_{48}Ni_{32}Cu_8Si_8Sn_4$ alloy are B2 NiTi, B19′ NiTi and tetragonal Ti_2Ni. Additional phases, like Ti_5Si_3 or Ni_2Ti_2Si, become clearly visible in samples with higher Si contents. The microstructure evolution is correlated with the obtained mechanical and elastic properties. These alloys exhibit very high hardness values, which increase with the Si content, from 9 GPa (for x = 0) to around 10.5 GPa (for x = 6). The Young's modulus of $Ti_{48}Ni_{32}Cu_8Si_8Sn_4$ (around 115 GPa) also increases significantly with Si addition, up to 160 GPa for x = 6.

1. Introduction

Owing to their high specific strength, metallic alloys based on low-density elements (like Ti, Mg or Al) are attractive materials for lightweight engineering applications. In particular, Ti-based alloys are currently employed in the aerospace and automotive industries due to their relatively low-cost, good corrosion and wear resistance, large compressive strength and reasonable Young's modulus [1,2]. Some of these alloys, i.e., those not containing toxic or allergic elements, can be also used as biomaterials for orthopaedic implants [3].

Since Ti alloys have been recognized as key materials for structural applications, several studies have been directed toward synthesizing new compositions, either resulting in metallic glasses or nanocomposite microstructures, with improved mechanical properties. Composite materials consisting of micrometer-sized grains surrounded by a glassy or nanostructured matrix have been actually reported to exhibit mechanical properties that are superior to those of conventional polycrystalline alloys, since they combine large values of hardness (provided by the matrix) with enhanced compressive plasticity (due to the presence of the ductile dendritic particles) [4–6]. Alternatively, the strength of composite materials can be increased by introducing second phase reinforcing particles (e.g., ceramic particles, fibres, intermetallic or martensitic phases [7]) to the alloy microstructure. Several routes have been developed to prepare nanocomposite materials. Among them are: (i) rapid solidification techniques (e.g., suction casting), where phase precipitation can occur during the casting or, alternatively, reinforcing particles can be directly added to the melt, (ii) mechanical alloying followed by powder consolidation methods, (iii) electrodeposition or (iv) nanocrystallization of the as-prepared metallic glass induced either by thermal or mechanical treatments.

New types of Ti-based nanocomposite materials are often designed from glass-forming alloy systems. The first Ti-based metallic glass (with composition $Ti_{50}Be_{40}Zr_{10}$) was reported in 1977 [8], although during a long time Ti-based metallic glasses could only be fabricated in the form of ribbons. In 1994 the first Ti-based bulk metallic glass, composed of Ti–Zr–Ni–Be [9], was obtained. Since then, a number of multi-component Ti-based alloys showing glassy or nanocrystalline structures and not containing the highly-toxic Be element, such as Ti–Cu–Ni–Sn [4,10], Ti–Cu–Ni–Si–B [11], Ti–Zr–Ni–Cu–Sn [12], Ti–Cu–Ni–Zr–Hf–Sn–Si [13], Ti–Cu–Ni–Sn–Ta [4] or Ti–Fe–Sn [14], have been synthesized. It is remarkable that some of the properties of Ti-based nanocomposite materials are superior to those of Ti-based metallic glasses. For example, the $Ti_{60}Cu_{14}Ni_{22}Sn_4Nb_{10}$ alloy reaches fracture strength of 2400 MPa and plastic strain beyond 14% [4], while even higher fracture strength (around 2650 MPa) and similar plasticity has been reported for the $Ti_{63.375}Fe_{34.125}Sn_{2.5}$ system [15]. These values of plasticity are larger than for most Ti-based

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bulk metallic glasses, where plastic strain does not usually exceed 1% (in Be-free alloys [10,13]) or 5% (in Be-containing ones [16]). Recently, Cheney et al. investigated the glass forming ability and mechanical properties of the Ti–Ni–Cu–Si–Sn system produced by arc-melting followed by copper mould casting [17]. Amorphous and nanocrystalline rods with 3 mm in diameter, fracture strength of 1800 MPa and Vickers hardness around 6.5 GPa were obtained from these alloys. Both the fracture strength and toughness of the Ti–Ni–Cu–Si–Sn system have been later significantly enhanced by adding a certain amount of Mo to obtain a dendritic–nanoeutectic nanocomposite alloy [18].

In this context, our work focuses on the influence of the Si content on the microstructure and mechanical properties of the Ti–Cu–Ni–Si–Sn system. The alloys, which have been prepared by levitation melting followed by copper mould casting, show a composite structure. The increase of the Si content causes a strengthening behaviour resulting from the precipitation of mechanically hard phases during the casting process. The Young's modulus also increases with the addition of Si.

2. Experimental details

Masters alloys with compositions $(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ (x = 0, 2, 4 and 6) (at.%) were prepared from the high-purity metals in a cold crucible levitation melting equipment (with a capacity of 1 kg), under Ar atmosphere, after purging several times with Ar to a base pressure of 6×10^{-6} Pa. The rods (3 mm in diameter) were casted into a copper mould using a smaller levitation melting setup (with a capacity of 200 g and maximum achievable vacuum of 5×10^{-6} Pa).

The samples were structurally characterized using a Zeiss-Evo scanning electron microscopy (SEM), equipped with energy dispersive X-ray detector (EDX), and X-ray diffraction (XRD) using a Philips X'Pert instrument (Cu Kα radiation). The elastic properties were evaluated using ultrasonic measurements (pulse-echo overlap technique) along with density assessment (Archimedes' method). Nanoindentation experiments were carried out at room temperature, in a UMIS indenter, using a Berkovich pyramidal-shaped indenter tip applying a maximum load of 250 mN. A load holding period of 20 s was introduced in all cases before unloading and the thermal drift was always kept below ±0.05 nm s^{-1}. At least 40 indentations for each sample were performed to verify the accuracy of the indentation data. Prior to nanoindentation or SEM observations, the specimens were carefully polished to mirror-like appearance using diamond paste. The hardness, H, and reduced Young's modulus, E_r, values were evaluated at the beginning of the unloading segment using the method of Oliver and Pharr [19], after proper corrections for the contact area, instrument compliance and initial penetration depth; the corrections for the contact area were calculated from a calibration on a fused quartz specimen.

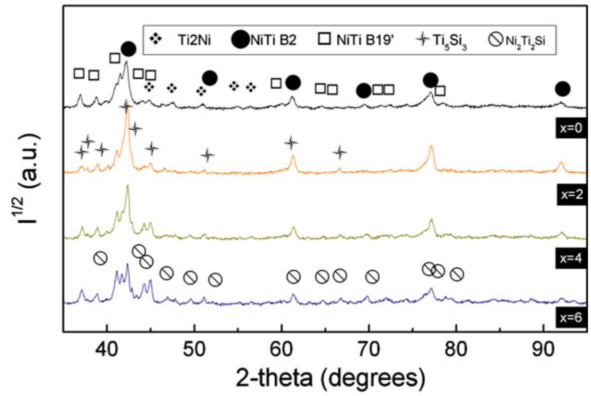

Fig. 1. X-ray diffraction (XRD) pattern of the $(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ alloy with x = 0, 2, 4, 6.

3. Results and discussion

Shown in Fig. 1 are the XRD patterns of the $(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ (x = 0, 2, 4 and 6) as-cast specimens. After a careful matching with known standards, the predominant phase in the $Ti_{48}Ni_{32}Cu_8Si_8Sn_4$ alloy was determined to be the cubic NiTi B2 phase (space group Pm3m) (code ICSD 105412). Other phases like monoclinic NiTi B19′ ($P2_1$/m:c) (code ICSD 105415) and tetragonal Ti_2Ni (space group I_4/mmm) (code ICSD 15807) are also present in this alloy. When the at.% Si is increased, the hexagonal Ti_5Si_3 (space group $P6_3$/mmc) (code ICSD 44386) and Ni_2Ti_2Si (space group $P6_3$/mmc) (code ICSD 194778) phases become clearly observable, although some traces of these phases could be also envisaged in the samples with lower Si content.

Fig. 2 shows the SEM images (obtained using backscattered electrons) corresponding to the $(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ (x = 0, 2, 4 and 6) alloys. These materials exhibit a composite-like microstructure, with the presence of at least four different regions that display different brightness. Energy dispersive X-ray (EDX) analyses indicate that the darkest (almost black) precipitates are enriched in Ti and Si, whereas the other phases are overall rich in Ni and Ti. After a close inspection of the sample with x = 6, five different regions

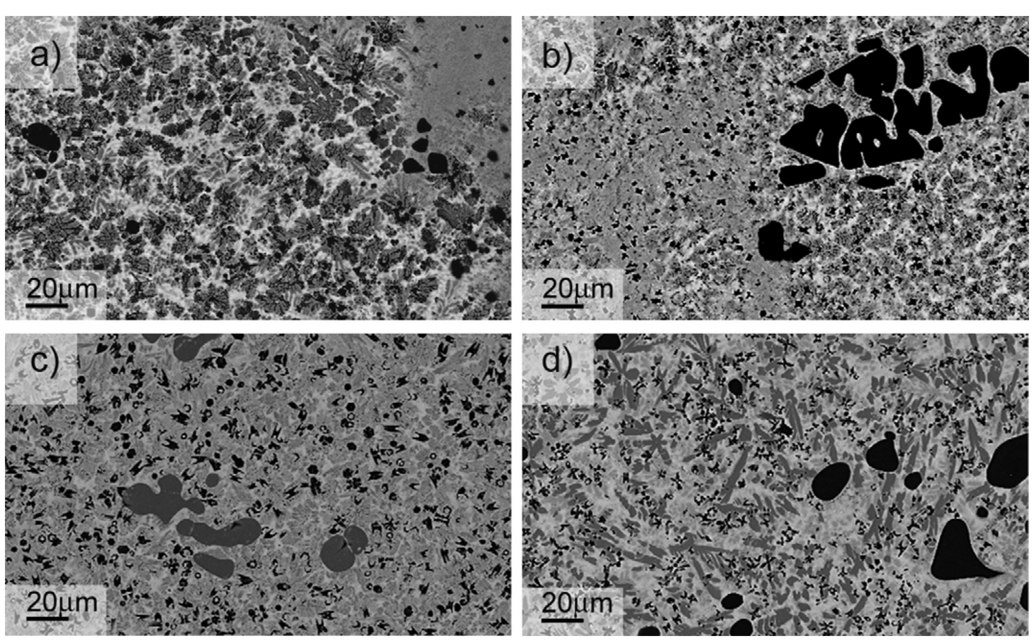

Fig. 2. Scanning electron microscopy (SEM) images (backscattered electrons) of the $(Ti_{48}Ni_{32}Cu_8Si_8Sn_4)_{100-x}Si_x$ alloy with: (a) x = 0, (b) x = 2, (c) x = 4 and (d) x = 6.