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

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ABSTRACT

(Ti48Ni32Cu8Si8Sn4)x100−xSi4 (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 Ti48Ni32Cu8Si8Sn4 alloy were investigated by scanning electron microscopy, X-ray diffraction, acoustic measurements and nanoindentation. The main phases composing the Ti48Ni32Cu8Si8Sn4 alloy are B2 NiTi, B19 NiTi and tetragonal Ti3Ni. Additional phases, like Ti3Si, or Ni2Ti2Si, 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 Ti48Ni32Cu8Si8Sn4 (around 115 GPa) also increases significantly with Si addition, up to 160 GPa for x = 6.

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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 Ti50Be40Zr10) 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 Ti0.75Cu0.15Ni2Si0.5Nb0.5 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 Ti63.37Fe34.125Sn2.5 system [15]. These values of plasticity are larger than for most Ti-based
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 (Ti48Ni32Cu8Si8Sn4)100−xSi 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 indentor, 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′, 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.

3. Results and discussion

Shown in Fig. 1 are the XRD patterns of the (Ti48Ni32Cu8Si8Sn4)100−xSi x (x = 0, 2, 4 and 6) as-cast specimens. After a careful matching with known standards, the predominant phase in the Ti48Ni32Cu8Si8Sn4 alloy was determined to be the cubic NiTi B2 phase (space group Pm3m) (code ICSD 105412). Other phases like monoclinic NiTi B19’ (P21/mmc) (code ICSD 105415) and tetragonal Ti3Ni (space group I4/mmm) (code ICSD 15807) are also present in this alloy. When the at.% Si is increased, the hexagonal Ti5Si3 (space group P63/mmc) (code ICSD 44386) and Ni2TiSi (space group P63/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 (Ti48Ni32Cu8Si8Sn4)100−xSi 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
The intermetallic composition (with dissimilar brightness and/or morphologies) were marked (see Fig. 3(a)) and their chemical composition was evaluated by EDX analyses. The obtained results are listed in Table 1.

Taking the compositional analyses and XRD results into account, a phase identification of the different regions shown in Fig. 3(a) was attempted. The darkest areas, A and B, could correspond to Ti2Si3; the dark-grey C area could be assigned to the Ni2Ti2Si phase, while the regions D and E were NiTi phases, with some additional elements in solid solution. Note that a certain amount of Cu is actually detected in region E, evidencing that Ni can be partially substituted by Cu, probably because of their similar atomic size. Also note that there exist some small areas with intermediate grey contrast (indicated with arrows in Fig. 3(a)), whose composition could not be reliably ascertained (because of their small size), but could correspond to Ti2Ni.

The dependences of the elastic constants (Young’s modulus E, bulk modulus K, and shear modulus G), and the Poisson’s ratio ν, as a function of x are presented in Fig. 4. The Young’s modulus of the (Ti48Ni32Cu8Si8Sn4)100−xSi6 alloys gradually increases with Si addition. Measured values of E, ranging from 115 GPa (for x = 0) to 160 GPa (for x = 6) are achieved. The shear modulus also tends to progressively increase with the amount of Si, to above 60 GPa for x = 6. In turn, K remains almost invariable for Si addition up to x = 4, but then it markedly decreases for 6% Si addition.

The variations in elastic constants of composite materials can be rather complex, since they can be influenced by numerous factors, such as: matrix microstructure (i.e., size, shape and composition of the different constituent phases), presence of precipitates (composition, distribution, volume fraction, shape and size of the particles), interface effects (i.e., interactions between dislocations generated in the matrix and the numerous existing interfaces) and metallurgical issues, like texture, porosity and cracks [20,21]. In the particular case of the (Ti48Ni32Cu8Si8Sn4)100−xSi6 alloys, the increase of E with the Si content is likely to be related to the increasing amount of the brittle Ti2Si3 and Ti2Ni2Si phases, which possess higher elastic modulus than the non-containing Si phases. For instance, the Young’s modulus of Ti2Si3 has been reported to be about 225 GPa [22].

Conversely, the Young’s modulus of NiTi phases has been reported to be significantly lower (between 60 and 80 GPa) [23]. A significant decrease in the Poisson’s ratio is also observed when Si is progressively added. This decrease is also ascribed to the increasing amount of Si-containing phases (i.e., Ti2Si3, Ti2Ni2Si) which are known to exhibit low ν values [24,25].

Fig. 5 shows the variation of the indentation hardness as a function of the added Si content. Indentations were performed at a maximum applied load of 250 mN with the aim of embracing all the existing different phases (as shown in the inset of Fig. 5). However, not all the indents contained all (and the same quantities) of the existing phases. For this reason, there is some scatter in the experimental data. Remarkably, the hardness of all these alloys is rather high, surpassing the values reported for most Ti-based metallic glasses [16,26] and also in some Ti-based nanocomposite alloys, such as Ti80Cu14Ni15Sn4Ta10 [27] or Ti70Fe15Co15 [28]. Furthermore, a slight increase in hardness is observed for larger Si contents (H ∼ 10.5 GPa for x = 6). These results suggest that the large hardness of Ti2Si3 and Ti2Ni2Si phases has a strong influence in the overall strength of the investigated composites. In fact, the Ti2Si3 phase has been used as reinforcement material in iron- and steel-based materials [29] due to its outstanding features including high melting point (2403 K), low density (4.32 g/cm3), high hardness (H ∼ 10.5 GPa for x = 6).
Table 2  
Summary of the values of $H/R_e$ and $H^3/E^2$ (where $H$ and $E$ denote hardness and reduced Young’s modulus, respectively). These ratios are representative of the wear resistance of these alloys.

<table>
<thead>
<tr>
<th>Al % Si (x)</th>
<th>$H/R_e$</th>
<th>$H^3/E^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0876</td>
<td>0.0691</td>
</tr>
<tr>
<td>2</td>
<td>0.0803</td>
<td>0.0636</td>
</tr>
<tr>
<td>4</td>
<td>0.0684</td>
<td>0.0477</td>
</tr>
<tr>
<td>6</td>
<td>0.0708</td>
<td>0.0533</td>
</tr>
</tbody>
</table>

(11.3 GPa), high Young’s modulus (225 GPa), high thermodynamic stability and high oxidation resistance [22,30–32].

Besides hardness and Young’s modulus, nanoindentation is also useful to obtain other important parameters to predict the service life of a component or device. One of these parameters is the so-called wear resistance, which is related to the ratio $H/E_r$ [33,34]. Our results (listed in Table 2) reveal that the ratio $H/E_r$ first decreases when Si is added but then slightly increases for $x = 6$. Another parameter related to the wear characteristics is the ratio $H^3/E^2$, which is indicative of the resistance of the material to plastic deformation in loaded contact, i.e., the so-called yield pressure [35,36]. This ratio follows a similar trend with x as $H/E_r$. However, even if a slight decrease in wear resistance is observed when increasing Si amount, the wear resistance values are analogous or better than for other families of amorphous or nanocrystalline Ti-based alloys [23]. For instance, the ratio $H^3/E^2$ of commercial Ti–6Al–4V alloy is 0.008 [26] and the one of Ni–Cu thin films is around 0.015 [37] (all measured using the same nanoindentation conditions). Thus, our work reveals that the addition of Si in the Ti$_{48}$Ni$_{32}$Cu$_{8}$Si$_{4}$Sn$_{4}$ alloy is an effective way to tune and improve the mechanical properties of this composite material for advanced engineering applications.

4. Conclusions

A correlation between the microstructure and mechanical properties of the (Ti$_{48}$Ni$_{32}$Cu$_{8}$Si$_{4}$Sn$_{4}$)$_{100-x}$Si$_{x}$ alloys, with $x = 0, 2, 4$ and 6, has been established. The largest hardness and Young’s modulus are obtained for the alloy with highest Si percentage ($x = 6$), with a hardness value that surpasses 10 GPa and Young’s modulus beyond 160 GPa. These outstanding mechanical properties are ascribed to the presence of Ti$_3$Si$_3$ and Ni$_2$Ti$_2$Si phases, commonly used as strengthening reinforcements, which increase in percentage for higher the Si contents. In terms of wear characteristics, the investigated alloys exhibit good wear properties. Indeed, even if it is shown that Si addition does not improve the wear resistance, the obtained values are larger than for other Ti-based materials.

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