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Journal of Alloys and Compounds 317–318 (2001) 245–249

Journal of ALLOYS AND COMPOUNDS

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High temperature–high pressure nitridation of β-$Ti_{63}Nb_{37}$ by means of the chemical oven technique

M. Ferretti*, A. Martinelli

Istituto Nazionale per la Fisica della Materia and Dipartimento di Chimica e Chimica Industriale, via Dodecaneso 31, I-16146, Genova, Italy

Abstract

High temperature nitridation of a β-$Ti_{63}Nb_{37}$ (47 wt.% Ti) alloy was carried out by means of the *chemical oven* technique at 100 and 400 bar nitrogen pressure. Afterwards nitridation samples showed a golden colour, typical of the δ-(Ti,Nb)N solid solution. Samples were characterized by XRD and EDS analysis, SEM and OM observation and superconductive transition temperature measurements. Microstructure observation reveals that both inward diffusion of nitrogen and long-range Nb–Ti interdiffusion in the β-(Ti,Nb) alloy take place during nitridation. At higher temperature an external δ-(Ti,Nb)N layer grew, while internal nitridation was confined at grain boundaries. At lower temperature internal nitridation lead to the formation of elongated Ti-rich δ-(Ti,Nb)N precipitates that grew beneath the external thin layer constituted by δ-(Ti,Nb)N. Nb enrichment of the δ-(Ti,Nb)N solid solution was detected near the gas/nitride interface.

Keywords: Interstitial alloys; Gas-solid reactions; Nitridation; Microstructure; Superconductivity

1. Introduction

In previous works [1–3] on nitridation of β-(Ti,Nb) alloys characterised by an intermediate composition, the microstructure observation revealed the growth of TiN needles. These structures are generally characterised by an elongated shape, moving from the surface towards the core of the samples.

Buscaglia et al. [1] observed the growth of TiN needles nitriding a β-$Ti_{63}Nb_{37}$ (47 wt.% Ti) alloy at 1300°C under 15 kPa. The external reaction layer was composed of a superconducting solid solution formed by δ-NbN_{1-x} and δ-TiN_{1-x}, whose superconductive transition temperature increased from 15.7 K after 0.5 h reaction up to 17.9 K after 24 h reaction. Moving towards the centre of the sample a two-phase intermediate layer composed of β-Nb_2N_{1-x} and TiN platelets was found, while the core was composed of TiN needles inside the β-(Ti,Nb) alloy. The TiN needles close to the surface appear thinner and closely spaced. Sometimes these needles appear elongated along a direction almost parallel to the sample surface. In other cases when the needles reach the grain boundary they stop growing and other needles grow inside the inner contiguous grain characterised by a different orientation. The growth of these structures was explained invoking a steady-state cooperative-like process taking place during nitridation, leading to the growth of δ-TiN_{1-x} needles characterised by a peculiar cellular microstructure.

Mayr et al. [2] nitrided β-(Ti,Nb) alloys (10, 25, 38, 50, 62, 75, 90 at.% Ti; 5, 15, 24, 34, 46, 61, 82 wt.% Ti) in the temperature range 1300 up to 1650°C under 3 and 30 bar N_2. They observed the formation of the δ-(Ti,Nb)N solid solution at the surface of all nitrided samples whose superconductive transition temperature strongly depends on the [Ti]/[Nb] ratio and on the nitrogen content as well as its lattice parameter and its microhardness; the maximum value of T_c (17.13 K) was detected for equimolar δ-(Ti,Nb)N solid solution. They observed the growth of needles characterised by different length and width, whose sizes were directly proportional to Ti content. Different microstructures were observed for the different composition nitrided alloys.

Nitridation of β-(Ti,Nb) alloys (10, 47, 63, 90 at.% Ti; 5, 31, 47, 82 wt.% Ti) at 1300, 1450 and 1600°C under 0.3, 3 and 30 bar N_2 was studied by Buscaglia et al. [3]: in each case the surface nitride was the δ-(Ti,Nb)N solid solution. In the intermediate composition alloys (63 and 47 at.% Ti alloys) oriented TiN needles were observed, inside

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*Corresponding author. Tel.: +39-010-353-6085; fax: +39-010-362-8252.

E-mail address: ferretti@chimica.unige.it (M. Ferretti).

0925-8388/01/$ – see front matter
PII: S0925-8388(00)01341-4

which the Nb content is almost constant (~5 at.%). The external layer composed of the solid solution is very thin; the EDS analysis revealed a depletion of the Ti content compared to the starting composition of the alloy. Below this zone a thin layer composed of β-Nb_2N_{1-x} and TiN needles is present. The internal core composed of β-(Ti,Nb) alloy is characterised by a much higher Nb content than the starting alloy. The morphology of the needles does not depend on temperature and their number is greater beneath the surface; moreover a strong orientation relationship between needles and the matrix was observed. It was supposed that they grew in the early stage of reaction, that is when the inward nitrogen flux is maximum. They concluded that microstructure evolution is mainly determined by inward diffusion of nitrogen and short range Nb–Ti interdiffusion in the β-(Ti,Nb) alloy. The average superconductive transition temperatures of the nitrided β-$Ti_{63}Nb_{37}$ and β-$Ti_{53}Nb_{47}$ alloys [4] are 17.3 and 17.5 K, respectively.

The *chemical oven* technique applied in this work to nitridate the β-$Ti_{63}Nb_{37}$ alloy is derived from the combustion synthesis technique and it was already successfully applied to nitridate Nb at high temperature and under high nitrogen pressure [5].

2. Experimental

Square (10×10×1 mm) and cylindrical (∅~2.2 mm; ~8 mm high) samples of a β-$Ti_{63}Nb_{37}$ alloy were obtained from plane sheets (Teledyne Wah Chang, Albany, USA, Ta 800 ppm, O 600 ppm, Hf <250 ppm, Zr <150 ppm, N, C, Si, W, Sn <60 ppm). Cylindrical samples were used to determine T_c, while square samples were used for the other analysis. After etching in a (1:2:1) mixture of HNO_3, H_3PO_4 and HF, sample plates were embedded in Nb powder (Alpha; 99.8 wt.%; average particle diameter ~55 μm) packed inside quartz crucibles (∅=8 mm; 15 mm high). Combustion was performed in a high temperature–high pressure stainless steel autoclave [6] (for the experimental set-up see Ref. [5]) under nitrogen atmosphere (99.997 at.%; gaseous pressure: 100 and 400 bar). The reaction was ignited by means of an induction copper coil connected to a high power generator; the crucibles were placed on a water cooled copper base. After ignition the reaction temperature instantaneously reached 3000 K and the high power generator was switched off. The temperature decreased very fast and the reactants lasted at $T>$ 1000 K for a few seconds (~5 s). Temperature profiles were recorded by means of an optical pyrometer connected to a PC: as the measurement begins as soon as the reaction is ignited they do not completely describe the thermal profile of the whole reaction. Reaction products were identified by means of XRD analysis in Bragg–Brentano geometry (Philips PW1710, CoK_α, secondary monochromator); diffraction patterns were recorded as a function of depth by stepwise removal of layers on SiC emery paper. After metallographic preparation the cross section microstructures were observed both using a scanning electron microscope (Leo Stereoscan 440) after chemical etching, and metallographic optical microscope after anodization. EDS analysis (Link Gem–Oxford Instruments) was performed to determine the [Nb]/[Ti] ratio inside the different phases. Inductive measurements of the superconducting transition temperatures were performed (Maglab2000–Oxford Instruments) on the nitrided cylindrical samples.

3. Results and discussion

XRD analysis performed as a function of depth (X-ray penetration depth: ~10 μm) shows the presence of the δ-(Ti,Nb)N solid solution in the external layer. In particular, as Fig. 1 shows (sample nitrided under 400 bar), three different fcc structures (indicated by: (p) δ-NbN; (n) Nb-rich δ-(Ti,Nb)N; (t) Ti-rich δ-(Ti,Nb)N) can be distinguished, characterised by different [Nb]/[Ti] ratios. The peaks indicated by (p) were probably generated by nitrided Nb powders bounded to the sample surface. Weak peaks of the β-Nb_2N_{1-x} phase (h) and of the β-(Ti,Nb) alloy (a) are also present. Progressively removing the external layer by SiC emery paper the peaks of the β-Nb_2N_{1-x} phase disappear as well as the peaks of the δ-NbN phase (p). The ratio between the intensity of the peaks generated by the Nb rich δ-(Ti,Nb)N solid solution (n) and the Ti rich δ-(Ti,Nb)N (t) decreases with depth. The inner region of the nitrided zone is composed of Ti-rich δ-(Ti,Nb)N and of the starting β-(Ti,Nb) alloy, inside which some nitrogen is probably dissolved.

SEM and OM observation, performed on the samples nitrided both under 100 and 400 bar, reveals that the

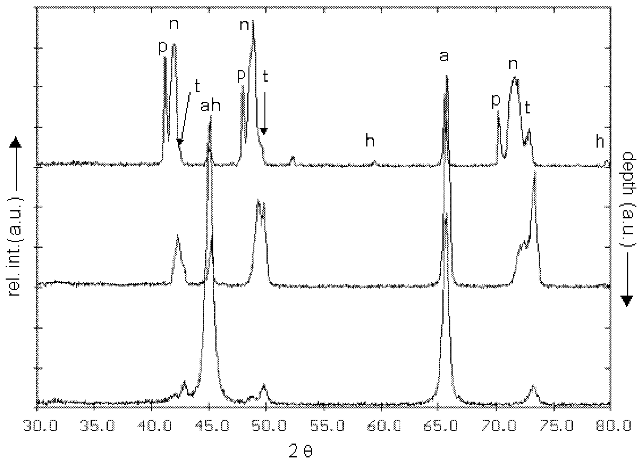

Fig. 1. X-ray diffraction patterns obtained as a function of the depth on a sample nitrided under 400 bar: (a) alloy β-(Ti,Nb); (h) hexagonal β-$(Ti,Nb)_2N_{1-x}$; (n) Nb-rich δ-(Ti,Nb)N; (p) fcc δ-NbN_{1-x}; (t) Ti-rich δ-(Ti,Nb)N.

external nitrided layer shows a variation of appearance moving along the sample. Three different kinds of microstructures can be distinguished, which may be due to the different experimental factors affecting the various regions of the same sample: different reaction rates on account of different temperatures experienced during reaction and not homogeneous nitrogen permeation inside the Nb powders and different cooling rates.

3.1. Region of type 1

Fig. 2a shows a thick δ-(Ti,Nb)N solid solution layer growth in the sample synthesised under 100 bar: its appearance is not homogeneous, lighter in the external side and darker near the alloy. As expected by thermodynamic, EDS analysis, reported in Table 1, confirmed that the Nb content is very high near the nitride/gas interface and decreases moving towards the centre of the sample. This can be explained by the higher dissociation pressure of δ-NbN_{1-x} compared to δ-TiN_{1-x}. The [Ti]/[Nb] ratio in the inner zone is almost the same as the starting β-$Ti_{63}Nb_{37}$ alloy. Darker structures are present inside the nitrided layer, probably characterised by a high Ti content. The δ-(Ti,Nb)N layer is approximately 9 μm thick. Ti-rich δ-(Ti,Nb)N precipitates are present along the nitrided grain boundaries of the β-(Ti,Nb) alloy. An extremely fine structure is present inside the nitrided alloy: these precipitates probably grew during cooling on account of the supersaturation of the alloy in nitrogen. In this region the microstructure is dominated by the growth of an external layer, while internal nitridation is confined to grain boundaries. This kind of microstructure has never been reported in previous studies on nitridation of β-(Ti,Nb) alloys, in every case performed at temperature lower than 2000 K; it may be argued that this kind of region experienced the highest reaction temperature during combustion.

3.2. Region of type 2

Fig. 2b shows a region characterised by the presence of an internal continuous layer composed of Ti-rich δ-(Ti,Nb)N separated from the Nb-rich external δ-(Ti,Nb)N layer by an intermediate duplex region. EDS analysis performed on the external layer reveals a depletion of Nb content moving from the gas/nitride interface towards the external nitride/duplex region interface. Inside the intermediate duplex region Ti-rich δ-(Ti,Nb)N needles ($Ti > 68$ at.%) are observed inside a matrix characterised by a high Nb content ($Nb > 92$ at.%); an orientation relationship holds between the matrix and the needles. This region is divided from the alloy by a dark continuous band composed of Ti-rich δ-(Ti,Nb)N. It can be observed that Ti-rich δ-(Ti,Nb)N needles develop from the nitrided grain boundaries inside the β-(Ti,Nb) alloy. As in the previous case an extremely fine structure formed inside the nitrided

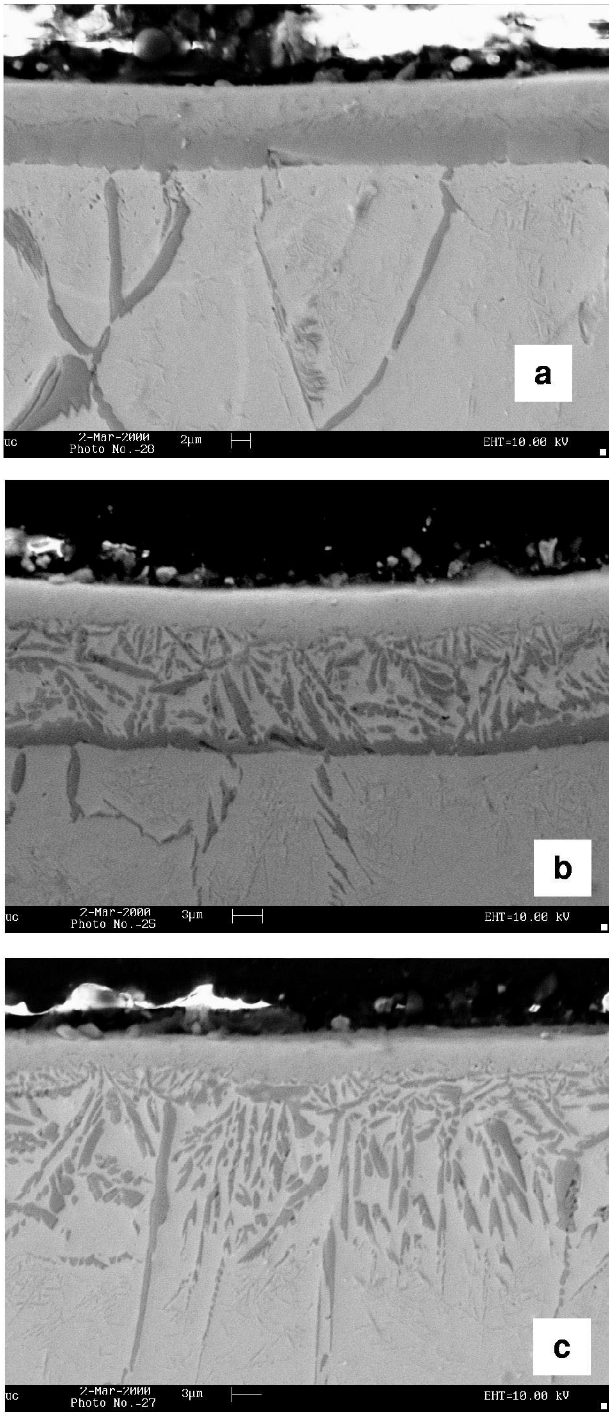

Fig. 2. Microstructures (SEM–SE image) of a sample nitrided under 100 bar: (a) From top to bottom: the external (Nb rich, lighter) and the internal (Ti rich, darker) zone of δ-(Ti,Nb)N solid solution; some dark structures are present between these two zones; the inner zone is composed of the nitrided alloy. (b) From top to bottom: external layer of Nb-rich δ-(Ti,Nb)N, duplex layer with small Ti-rich δ-(Ti,Nb)N needles, thin continuous band of Ti-rich δ-(Ti,Nb)N solid solution, nitrided alloy. (c) From top to bottom: external layer of Nb-rich δ-(Ti,Nb)N and Ti-rich δ-(Ti,Nb)N needles inside the Nb enriched alloy.

Table 1
Average compositions in proximity of the gas/nitride (ext.) and the nitride/alloy (int.) interfaces, cell parameters and superconductive transition temperatures of δ-(Ti,Nb)N as a function of the nitrogen pressure

Pressure (bar)	Average composition (at.%)			Cell parameter (nm)		T_c (K)
		ext.	int.	Nb rich	Ti rich	
100	Nb	7 2.17	45.43	0.433	0.424	14.99±0.01
	Ti	27.83	54.57			
400	Nb	66.90	35.37	0.439	0.424	14.36±0.01
	Ti	33.10	64.63			

alloy, but it is absent inside the duplex region. Also this kind of microstructure has never been reported in previous studies on nitridation of β-(Ti,Nb) alloys; probably this region experienced a temperature lower than that reached in region 1.

3.3. Region of type 3

Fig. 2c shows a region where the external Nb-rich δ-(Ti,Nb)N layer is less than 3 μm; well-developed Ti-rich δ-(Ti,Nb)N needles grew inside the Nb enriched alloy. Moving towards the centre of the sample a fine structure appears inside the β-(Ti,Nb) alloy where the number of Ti-rich δ-(Ti,Nb)N needles decreases; moreover there are no nitrided grain boundaries in this zone. This kind of microstructure is similar to that reported in Refs. [1–3]; for this reason it may be argued that this region probably experienced the lowest combustion temperature of the whole sample.

3.4. Microstructural evaluation and superconductive measurements

The three different types of microstructures observed (Fig. 2a–c) indicate that two different phenomena take place during the nitridation process: inward diffusion of nitrogen and long-range Nb–Ti interdiffusion. Their contribution is strongly dependent on temperature: at lower temperature long-range Nb–Ti interdiffusion plays an important role and an internal nitridation process takes place inside the β-(Ti,Nb) alloy, leading to the formation of Ti-rich δ-(Ti,Nb)N needles (Fig. 2c). Two main conditions must be satisfied in order that internal nitridation occurs in binary alloys: (1) one of the alloying components must have a much greater affinity for nitrogen than the other one; (2) nitrogen diffuses faster inwards than alloying components interdiffuse. Both conditions are satisfied since δ-TiN_{1-x} has a much more negative value [7] of ΔG^0 than δ-NbN_{1-x}, and hence a lower dissociation pressure ($\Delta G^0 = -RT \ln K_p$), and nitrogen diffuses inside transition metals much faster than metals themselves [8]. At higher temperature internal nitridation (Fig. 2a) occurs on grain boundaries and the reaction is mainly controlled by the fast inward diffusion of nitrogen.

Superconductive transition temperature measurements showed that T_c decreases as nitrogen pressure increases. This is probably due to the higher Ti content near the surface at higher pressure (see Table 1).

4. Conclusions

Thin δ-(Ti,Nb)N solid solution layers (3–9 μm) were obtained nitriding a β-$Ti_{63}Nb_{37}$ (46 wt.% Ti) alloy by means of the *chemical oven* technique under high nitrogen pressure (100 and 400 bar) and at high temperature (T_{max} ~3000 K) in a few seconds. The Nb content inside the solid solution decreases as the depth increases: the external region is characterised by an extremely high Nb content, according to the higher dissociation pressure of δ-NbN_{1-x}. Where the sample temperature was higher, the microstructure is dominated by the growth of an external scale, while internal nitridation is confined to grain boundaries. Where the temperature was lower, long-range Nb–Ti interdiffusion lead to the formation of Ti-rich δ-(Ti,Nb)N needles inside the β-(Ti,Nb) alloy. Transition from the external to external plus internal nitridation was observed as the external δ-(Ti,Nb)N layer thickness decreases. The superconductive transition temperature of the solid solution was measured revealing a dependence on nitrogen pressure applied during combustion, as well as its cell parameter.

Further research performed in isothermal conditions are needed in order to establish the contribution of the internal nitridation reaction as a function of temperature also at very high temperature.

Acknowledgements

The authors are grateful to dott. Riccardo Musenich (INFN, Genoa) who supplied the Ti–Nb alloy and to dott. Vincenzo Buscaglia (ICFAM-CNR, Genoa) for his helpful discussion. We also wish to thank dott. Fabio Canepa (INFM and DCCI, Genoa) and dott. Myrta Napoletano (INFM and DCCI, Genoa) who supplied the T_c measurements.

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