Journal of Alloys and Compounds, 194 (1993) 53–57
JALCOM 574

Morphological study of nitrides of NbTi (50:50, by weight) alloy

Silvio Rainho Teixeira
Universidade Estadual Paulista, Faculdade de Ciências e Tecnologia, Cx. Postal 957, 19060-Presidente Prudente-SP (Brazil)

Jose de Anchieta Rodrigues
Universidade Federal de São Carlos, Departamento de Engenharia de Materials, Cx. Postal 676, 13560-São Carlos-SP (Brazil)

Yvonne Primerano Mascarenhas
Universidade de São Paulo, Instituto de Física e Quimíca de São Carlos, Cx. Postal 369, 13560-São Carlos-SP (Brazil)

(Received August 24, 1992; in final form September 17, 1992)

Abstract

Plates of NbTi (50:50, by weight) were nitrided in a nitrogen atmosphere in the temperature range 800–1000 °C for 15, 30, 60, 120 and 180 min. X-Ray diffraction and optical and electronic microscopy were used to characterize the samples. Two nitride layers were identified on the substrate: an external and continuous phase of TiN, named δ, and a deeper and discontinuous phase of Ti_2N, named ϵ. The electron micrographs reveal the presence of paths rich in Nb which may be responsible for the diffusion of nitrogen into the matrix.

1. Introduction

Although there have been several studies on the nitridation of Nb [1–8] and Ti [5, 9–16], very little has been published on the nitridation of NbTi alloys. Felten [17] claims that until 1969 the ternary system Nb–Ti–N had not been investigated. Felten [17] observed the formation of Nb and Ti nitrides on the surface of alloys containing up to 34 wt.% Ti, which were nitrided at 1000 °C at a pressure of 760 mmHg of N_2 for 72 h. Ternary nitrides were not observed. Prokoshkin *et al.* [18, 19] investigated the process of nitridation of several Nb-based alloys. In alloys of Nb containing 3, 5 and 10 wt.% Ti, nitrided at 800–1000 °C for 0.5–5 h in an N_2 atmosphere, these workers found two layers of hexagonal nitrides: one with lattice parameters very close to the ϵ-NbN phase, to which a substitutional structure (Nb, Ti)N was attributed, and another identified as Nb_2N. X-Ray diffraction of the underlying material revealed the presence of pure Nb. Fedirko and Pogrelyuk [20] studied the nitridation kinetics of Ti alloys at 1173 K in a nitrogen atmosphere. They observed TiN (golden layer) and traces of Ti_2N on all their samples, nitrided for times in the range 25–100 h. No other nitrides were detected by X-ray diffraction.

It is important to extend the phase information to a larger range of NbTi alloy compositions, and this work was undertaken to identify the phases formed in the reaction of NbTi (50:50, by weight) with N_2 and to verify their morphology.

2. Experimental details

2.1. *Preparation of the samples*

The NbTi alloys were prepared by electron beam fusion [21] at the Lorena Technological and Industrial Foundation (FTI) and delivered as bars with an approximate diameter of 12 mm. These were cold worked to strips with an approximate thickness of 1.2 mm, and cut as plates with approximate dimensions of 28 mm × 17 mm × 1.2 mm. One of the faces of the plate was successively polished with 180, 350, 400 and 600 sand paper and finally annealed at 960 °C for 12 h in vacuum (less than 10^{-5} Torr). Figure 1 shows the nitridation system. The temperature of the oven was controlled using a chromel–alumel thermocouple and a proportional controller. Five samples were nitrided in an ultrapure nitrogen (99.999%) atmosphere at 808, 857, 905, 957 and 995 °C for 15, 30, 60, 120 and 180 min. In an attempt to reduce contamination, the samples were wrapped in titanium strip to provide gettering of the oxygen. After each selected time the quartz tube was removed from the oven and the sample was quickly cooled by the nitrogen gas flux.

0925-8388/93/$6.00

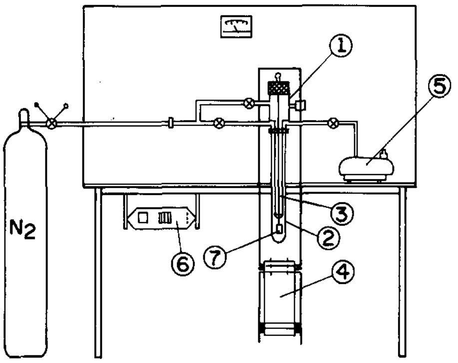

Fig. 1. Nitridation apparatus: 1, vacuum chamber (brass); 2, reaction chamber (quartz); 3, double quartz tube; 4, oven (movable); 5, vacuum system; 6, temperature controller; 7, sample.

2.2. *X-Ray diffraction*

After each treatment the X-ray diffraction pattern of the sample was obtained using an HZG4/B Carl Zeiss Jena diffractometer. Filtered Cu Kα radiation and a simple sample holder were used. The samples were marked before the nitridations and the areas analysed were always the same. The X-ray diffraction patterns of the samples nitrided for 180 min were also obtained using a rotating anode generator.

2.3. *Electron and optical microscopy*

After the total nitridation time and X-ray examination, the samples were cut and polished with 280, 340, 400 and 600 sand paper and with 1 μm and 0.3 μm Al_2O_3 powders. The samples were etched in a mixture of $C_3H_6O_3$, HF and HNO_3 (3:1:1) for about 40 s and analysed by optical and scanning electron microscopy to obtain information about the morphology of the phases formed.

3. Results and discussion

3.1. *Characterization of the alloy*

The annealing of the NbTi plates yielded an annealing texture (secondary recrystallization) characterized by a preferential growth of grains with crystallographic planes (211) parallel to the sample surface and with a lattice parameter of 3.286(4) Å (Fig. 2). This lattice parameter corresponds to the NbTi β phase [22, 23]. The average size of the grains, calculated by the linear intercept method, was determined as 100 ± 40 μm. After 180 min of nitridation all samples presented a golden surface with an increase in colour intensity corresponding to an increase in nitridation temperature (from 808 to 995 °C).

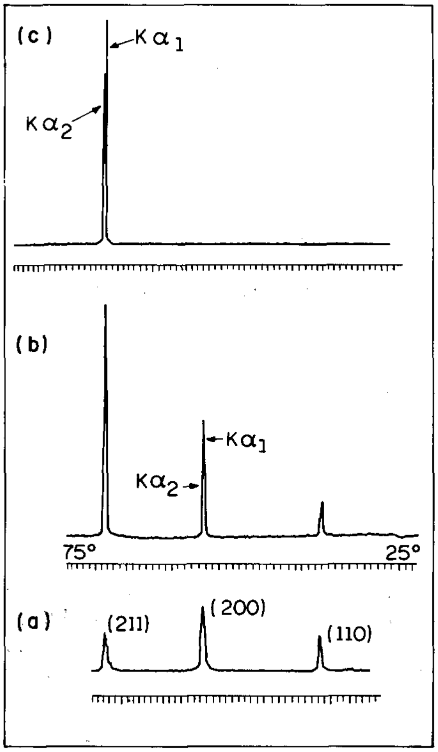

Fig. 2. Annealing texture of the NbTi plates.

TABLE 1. Cell parameters (Å) of the observed phases TiN and Ti_2N

Nitridation temperature (°C)	TiN (f.c.c.) *a*	Ti_2N (tetragonal)	
		a	*c*
808	–	4.9583 ± 0.0007	3.0442 ± 0.0004
857	4.231 ± 0.002	4.956 ± 0.001	3.0363 ± 0.0009
907	4.234 ± 0.002	4.9538 ± 0.0008	3.0375 ± 0.0006
957	4.243 ± 0.001	4.955 ± 0.002	3.040 ± 0.001
995	4.242 ± 0.003	4.9512 ± 0.0005	3.0359 ± 0.0003

3.2. *X-Ray diffraction*

The X-ray diffraction patterns of the samples nitrided at different temperatures for 180 min revealed the presence of reflections due to δ-TiN, ϵ-Ti_2N and a solid solution of β-NbTi(N), a few weak reflections that could not be identified and some reflections of pure Nb. Prokoshkin *et al.* [19] also observed niobium reflections below the nitride layer, indicating disaggregation of the NbTi matrix lattice. In Table 1 the cell parameters of the phases TiN and Ti_2N, calculated from diffraction patterns obtained with the rotating anode generator and using a least-squares refinement method, are presented.

The increase in the TiN cell parameter is due to the high solubility of nitrogen in TiN [12, 15]. The TiN cell parameter indicates that mixed nitrides (Nb, Ti)N are not formed. For the sample nitrided at 808 °C only Ti_2N was observed and for the others (857, 907, 957 and 995 °C) two nitrides (TiN and Ti_2N) were observed.

TABLE 2. Thickness (μm) of the nitride layers and the difference between them as a function of the nitridation temperature after 180 min of reaction

	808 °C	857 °C	905 °C	957 °C	995 °C
TiN	–	0.7±0.3	1.4±0.6	2.3±0.7	3±1
Ti_2N	4.0±0.8	8±1	9±1	13±1	18±2
Δx	4.0	6.3	7.6	10.7	15

3.3. *Thickness of the nitride layers*

The thicknesses of the nitride layers were measured in the five plates after 180 min of nitridation using a Zeiss microscope with a grated occular (100 μm per division). Table 2 shows the thicknesses of the nitride layers and the difference Δx between them as a function of the nitridation temperature. Both layers increase monotonically with temperature and the Ti_2N layer grows more rapidly than the TiN layer. Etchessahar *et al.* [16] also observed that the thicknesses of the ϵ and δ phases increased between 800 and 1000 °C.

The photomicrographs (Fig. 3) of the five nitrided plates show the thickness of TiN and Ti_2N, the precipitation of Ti_2N in the grain boundaries and the morphology of the nitride layers after 180 min of nitridation. In Fig. 3(e) the formation of needles in the TiN layer is observed.

Figure 4 shows that the thicknesses of the TiN layers are different inside different grains. This means that the TiN layer grows with different rates depending on the crystallographic orientation of the grain.

3.4. *Morphology of the nitride layers*

Scanning electron microscopy (Fig. 5) shows both diffusion processes: volumetric and by grain boundaries (indicated by nitride precipitation along the boundaries). An analysis of the relative concentrations of Ti and Nb reveals that the concentration of Nb is larger at the centre of the sample (number 5 in Fig. 5(a)) than in the regions where the precipitation of nitrides occurs (numbers 1 and 2). Figure 6 shows a microanalysis of both regions (NbTi and nitride) of a sample nitrided at 1500 °C for 160 s. Figure 7 shows a secondary electron image (a) and X-ray images emitted by Ti (b) and Nb (c) of a nitrided NbTi (50:50, by weight) plate. In the nitride the Ti concentration is higher than the Nb concentration.

If we take into account the fact that Nb is expelled from the regions in which TiN is formed, Nb in the region rich in TiN should be accumulated in the veins observed in the photomicrographs (Fig. 5(b)) and the diffusion of nitrogen in Nb is faster than in TiN and the alloy NbTi [4, 18, 19], and consider the Stratford and Towell [10] postulate (there is a path in the nitride that allows the fast transport of nitrogen through the

Fig. 3. Photomicrographs of the five nitrided plates after 180 min of nitridation: (a) 808 °C; (b) 857 °C; (c) 905 °C; (d) 957 °C; (e) 995 °C.

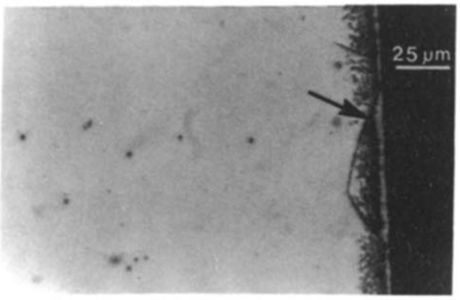

Fig. 4. Different thickness of the TiN layer inside different grains.

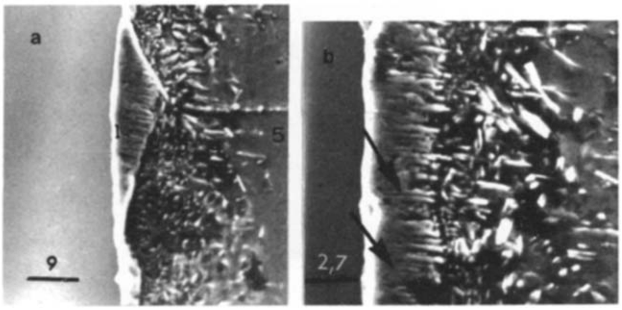

Fig. 5. Scanning electron micrographs: (a) numbers 1–5 show where the Nb and Ti concentrations were measured; (b) arrows indicate the paths by which nitrogen penetrates into the sample.

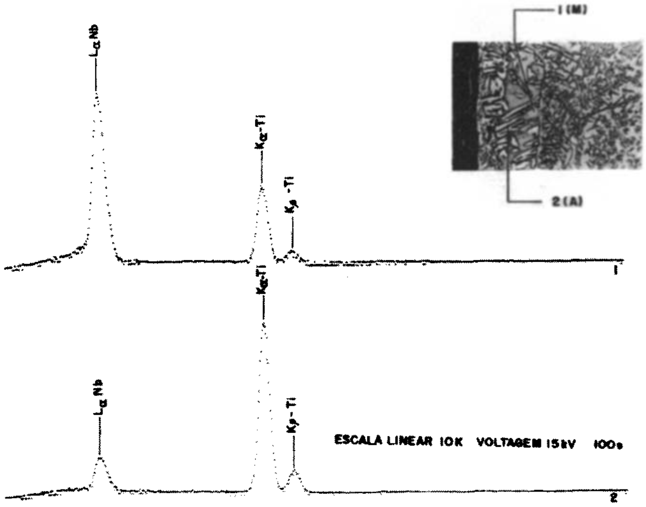

Fig. 6. X-Ray spectrum of the nitrided NbTi plate: 1, in the NbTi region; 2, in the nitride (15 kV, 100 s).

nitride layer), it can be proposed that nitrogen diffuses through the Nb-rich veins until reaching the reaction front where the growth of TiN precipitates and needles is observed (Fig. 5(b)).

4. Conclusions

From this work, the following conclusions can be obtained:

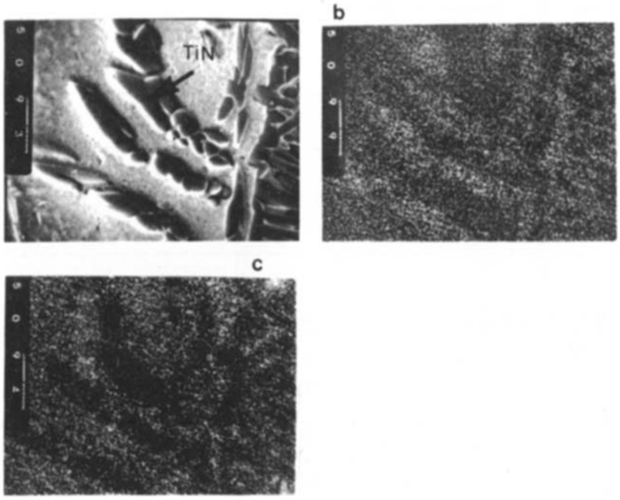

Fig. 7. Secondary electron image (a) and X-ray image emitted by Ti (b) and Nb (c) (3000×).

(a) Only two nitrides (δ-TiN and ϵ-Ti_2N) are observed in the nitridation of NbTi (50:50, by weight) in the temperature range 800–1000 °C.

(b) Both nitride layers grow monotonically with temperature and the average front of the Ti_2N layer grows faster than that of TiN.

(c) Nitrogen diffusion through TiN is via the veins rich in Nb, where it is more rapid than via NbTi and TiN.

Acknowledgments

The authors are grateful to Coordenadoria de Aperfeiçoamento de Pessoal de Nível Superior, Conselho Nacional de Desenvolvimento Científico e Tecnológico, Fundação para o Desenvolvimento da UNESP and PRONUCLEAR for financial support, to FTI, Lorena for the NbTi alloys and to Usina Siderúrgica de Minas Gerais for the microanalysis.

References

1 G. Brauer and R. Z. Esselborn, *Z. Anorg. Allg. Chem., 309* (1961) 151.
2 N. Terao, *Jpn. J. Appl. Phys., 1* (1965) 353.
3 International Atomic Energy Agency (IAEA), *Niobium: Physico-Chemical Properties of Its Compounds and Alloys,* Atomic Energy Review, Special Issue 2, IAEA, Vienna, 1968.
4 D. A. Prokoshkin, E. V. Vasil'yeva, V. L. Tret'yakov and T. A. Voronova, *Izv. Akad. Nauk SSSR Met., 1* (1975) 92.
5 E. Fromm, in E. Fromm and G. Gebhardt (eds.), *Gase und Kohlenstoff in Metallen,* Springer, Berlin, 1976.
6 N. P. Lyakishev, N. A. Tulin and Y. L. Pliner, *Niobium in Steels and Alloys,* Cia. Bras. de Metalurgia e Mineração (CBMM), São Paulo, 1984.

7 G. Brauer and W. Kern, *Z. Anorg. Allg. Chem., 507* (1983) 127.

8 G. Brauer and W. Kern, *Z. Anorg. Allg. Chem., 512* (1984) 7.

9 R. W. Powers and M. V. Doyle, *J. Appl. Phys., 30* (1959) 514.

10 K. N. Stratford and J. M. Towell, *Oxid. Met., 10* (1976) 41.

11 International Atomic Energy Agency (IAEA), *Titanium: Physico-Chemical Properties of Its Compounds and Alloys,* Atomic Energy Review, Special Issue 9, IAEA, Vienna, 1983.

12 L. R. Wolff, G. F. Bastin and H. J. M. Heijligers, *Solid State Ionics, 16* (105) (1985) 13.

13 W. Lengauer and P. Ettmayer, *Mater. Sci. Eng., A105/106* (1988) 257.

14 W. Lengauer, *Acta Metall. Mater., 39* (1991) 2985.

15 H. A. Wriedt and J. L. Murray, *Bull. Alloy Phase Diagrams, 8* (1987) 378.

16 E. Etchessahar, J. P. Bars and J. Debuigne, *J. Less-Common Met., 134* (1987) 123.

17 E. J. Felten, *J. Less-Common Met., 17* (1969) 207.

18 D. A. Prokoshkin, E. V. Vasil'yeva and T. A. Voronova, *Izv. Akad. Nauk SSSR Met., 4* (1979) 170.

19 D. A. Prokoshkin, E. V. Vasil'yeva and T. A. Voronova, *Met. Sci. Heat Treatment, 22* (1980) 172.

20 V. N. Fedirko and I. N. Pogrelyuk, *Sov. Mater. Sci., 19* (1983) 511.

21 D. G. Pinatti, J. A. Pimenta Neto and C. A. Baidan, *J. Less-Common Met., 139* (1988) 29.

22 T. S. Hutchison, G. Ocampo and G. J. C. Carpenter, *Scr. Metall., 19* (1985) 635.

23 J. L. Murray, *Bull. Alloy Phase Diagrams, 2* (1981) 55.