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PROCESSING OF A Nb-18Al-24V ALLOY BY MECHANICAL ALLOYING

WYTWARZANIE STOPU Nb-18Al-24V METODĄ MECHANICZNEGO STOPOWANIA

The synthesis of an alloy with the composition of 58% Nb, 24% V i 18% Al (atomic %) has been performed. The mechanical alloying of elemental powders was selected as a method of synthesis. During the course of mechanical alloying the splitting of X-ray peaks on two components was observed. Each component corresponded to the niobium solid solution (Nb_I and Nb_{II}) with different lattice parameters and different chemical composition. The Nb_I solid solution and the pure niobium had alike lattice parameters. The intensity of peaks corresponding to the Nb_I decreased with the time of milling. The peaks disappeared completely after 180 hours of milling. The lattice parameter of the Nb_{II} solid solution decreased with milling time and the intensity of corresponding peaks increased. Two brittle phases: Nb_3Al -base with A15 crystal structure and Nb_2Al -base σ phase were observed in solid (consolidated) material. No phase with B2 crystal structure was observed.

W pracy dokonano mechanicznej syntezy proszków czystych metali, otrzymując stop o składzie 58% Nb, 24% V i 18% Al (procenty atomowe).

Po kolejnych stadiach mechanicznego stopowania, na dyfraktogramach rentgenowskich obserwowano rozszczepienie pików na dwie składowe, z których każda odpowiadała roztworowi stałemu na osnowie niobu (nazwane Nb_I oraz Nb_{II}) o różnym składzie chemicznym i różnych parametrach sieci. Roztwór Nb_I miał parametr sieci zbliżony do parametru czystego niobu, a intensywność jego pików rentgenowskich malała wraz z postępowaniem mechanicznego stopowania aż do całkowitego ich zaniku po 180 godzinach procesu. Wraz z postępowaniem mechanicznego stopniowania parametr sieci roztworu Nb_{II} zmniejszał się, a intensywność pików rentgenowskich pochodzących od tego roztworu wzrastała. W materiale skonsolidowanym dominowały dwie kruche fazy: faza o strukturze A15 na osnowie Nb_3Al oraz faza σ na osnowie Nb_2Al . Nie stwierdzono obecności oczekiwanej fazy o strukturze B2.

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1. Introduction

Though interest in intermetallics as structural materials has ceased in recent years many laboratories still search for an alloy offering higher temperature capabilities than state-of-art superalloys. The niobium aluminides, especially Nb_3Al , seem to be right candidate materials for high temperature applications in connection with their high melting points and moderate density [1, 2]. However, despite good high temperature strength and creep resistance the poor room temperature ductility of these alloys hamper their applications. It was shown that ductility of Nb–Al-base alloys can be improved by reducing the average grain size as well as by incorporation into the microstructure a ductile phase [3]. This ductile phase may be disordered or ordered solution of Al and ternary elements in niobium (A2 or B2 structures). It was shown that the phase with the B2 structure may be stabilized by addition of ternary elements to a Nb–Al alloy [4, 5]. One of ternary addition which is considered for this purpose is vanadium [6, 7]. As was shown by Horspool et al. [6], the alloys Nb-10% Al-20% V and Nb-15% Al-20% V (all compositions in this article are expressed in atomic percent unless mentioned otherwise) in the as-cast condition could be deformed by rolling at room temperature up to 80% reduction.

This research is a continuation of our study on a binary Nb-18% Al alloy [3, 8] processed by mechanical alloying of elemental powders followed by consolidation by hot pressing. In the present study the chemical composition of the examined alloy was modified by addition of vanadium as a ternary element.

2. Material and process selection

The addition of vanadium to the binary Nb–Al alloy was inspired by the recent works of Horspool et al. [6] and Tappin et al. [7] who examined a series of Nb–Al–V alloy with different compositions. They found that all Nb–Al–V alloys consisted of a mixture of two phases with A15 (Nb_3Al) and B2 crystal structure. The volume fraction of a particular phase varied linearly with the ratio of the Al content to the V content in the alloy; alloys with $\text{Al/V} \approx 0.5$ exhibited only B2 phase whereas those with $\text{Al/V} \approx 1$ were almost completely A15. The alloy with the Al/V ratio of 0.75 homogenized at 1773 K contained 55% vol. of B2 phase and 45% vol. of A15 phase.

In the present study the amount of vanadium added to the examined alloy was 24%. Thus the Al content was 18% (as in our previous study [3, 8]) and the Al/V ratio was 0.75. According to Ref. [7] the expected volume fraction of the constituent phases (B2 and A15) was approximately equal (50%). The presence of the B2 phase was believed to improve ductility of the alloy.

The processing route was mechanical alloying (MA) of elemental powders (as for Nb-18% Al alloy [3, 8]) followed by consolidation by hot pressing. It was shown previously [3, 9–13] that such technique is a viable route for processing niobium

aluminides. Consolidation of mechanically alloyed powders produces fine grained material with an oxide dispersoid which improves high temperature strength and creep properties.

3. Experimental procedure

Pure elemental powders of constituents (Nb: 99.8 wt.%, Al: 99.9 wt.%, V: 99.5 wt.% pure) were used as starting materials. The powder diameter was less than $45\ \mu\text{m}$ (-325 mesh)¹. The powders were mixed in appropriate amounts to give the nominal composition of 58% Nb, 18% Al and 24% V. Mechanical alloying was carried out in a O1-HD type Szegvari laboratory attritor mill in an argon atmosphere with the controlled oxygen level reduced to less than 10 ppm. This was accomplished by using a positive pressure of 20 kPa in the milling chamber. The pressure was kept constant throughout the entire milling process. The milling was carried out in a sealed stainless steel tank with a 3.63 kg (8 lb) charge of 4.76 mm (3/16") stainless steel balls and a 12:1 ball to powder ratio (by weight). To prevent agglomeration of the relatively ductile powders on the shaft and arms of the mill, the initial 2 hours of milling was carried out at cryogenic temperatures, using liquid nitrogen as the coolant, at a shaft speed of 280 rpm. Following the first two hours of cryogenic milling, the milling was conducted at 450 rpm with water as the coolant. During the course of milling, powder samples were taken out after 5, 10, 20, 40, 80 and 180 hours, allowing for characterization of the powder morphology and the progress of chemical alloying process. The total milling time was 180 hours. The powders collected at the end of milling were sieved through a $45\ \mu\text{m}$ mesh. A small sample of as-milled powder was annealed at 1273 K (1000°C) for 5 hours in vacuum.

The changes in particle morphology and chemical composition during milling were examined using a scanning electron microscope equipped with the X-ray energy dispersive spectrometer (XEDS). The phase analysis was performed in a Philips X-ray diffractometer with $\text{CoK}\alpha$ radiation. The X-ray spectra were also used for evaluation of lattice strains and X-ray crystallite size. As a standard, the initial Nb powder annealed additionally at 1273 K for 5 hours in vacuum was used.

Consolidation was carried out by hot pressing in the argon atmosphere at pressure 25 MPa and temperature 1773 K (1500°C) for 2 hours. The die, die support, plunger and spacers were all made of high strength graphite. The resulting material, in the form of cylinder compact, was fully dense and free from cracks.

The microstructure of the consolidated material was characterized by light and scanning electron microscopy. Back scattering electron images utilizing Z-contrast were used to reveal constituent phases. The component phases were also identified by X-ray diffractometry.

¹ SI metric system was used as a basic one in the present paper. Some traditionally used UK units were additionally used in brackets.

Mechanical testing comprised hardness measurements by Vickers indenter and compression tests. Compression tests, at room temperature, were performed on the 10 mm high by 5 mm diameter cylindrical test pieces electro-discharge machined from the hot pressed compact. An Instron universal testing machine was used for the tests. The compression tests were carried out at a constant cross-head speed of 0.5 mm/min (initial strain rate $\dot{\epsilon} = 8.3 \cdot 10^{-4} \text{ s}^{-1}$). The evaluation of the fracture toughness K_{Ic} was performed on indented specimens (on those with microcracks at indentation corners) following a procedure described by Meyers et al. [14].

4. Results and discussion

4.1. Structural evaluation of MA powders

In the initial powder blend (Fig. 1), large, $\sim 40 \mu\text{m}$ niobium particles were observed. The flat angular surfaces of these particles are characteristic of powder crushed from larger pieces during manufacturing. Evenly dispersed around the niobium particles were smaller, $\sim 5\text{--}10 \mu\text{m}$ aluminium and vanadium particles, with a smooth, spherical morphology. Different particles were distinguished by the XEDS analysis. After 5 hours of milling (Fig. 2a), two hours of which was at cryogenic temperatures, particles had a smoother and more rounded surface characteristic for milled powders. Most particles were round and flat with particle diameters between 100 and 200 μm , and particle thickness close to one quarter of the diameter. The increase in particle size from the initial starting blend was due to the predominance of welding over fracturing occurring in the relatively soft particles. Up to 10 hours of milling (Fig. 2b), both particle fracture and welding occurred, however, bigger particles indicate that welding occurred more often than fracture. The large particles

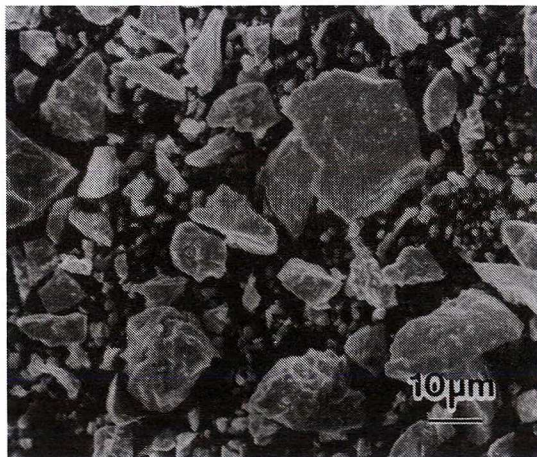


Fig. 1. SEM micrograph of the initial blend of powders

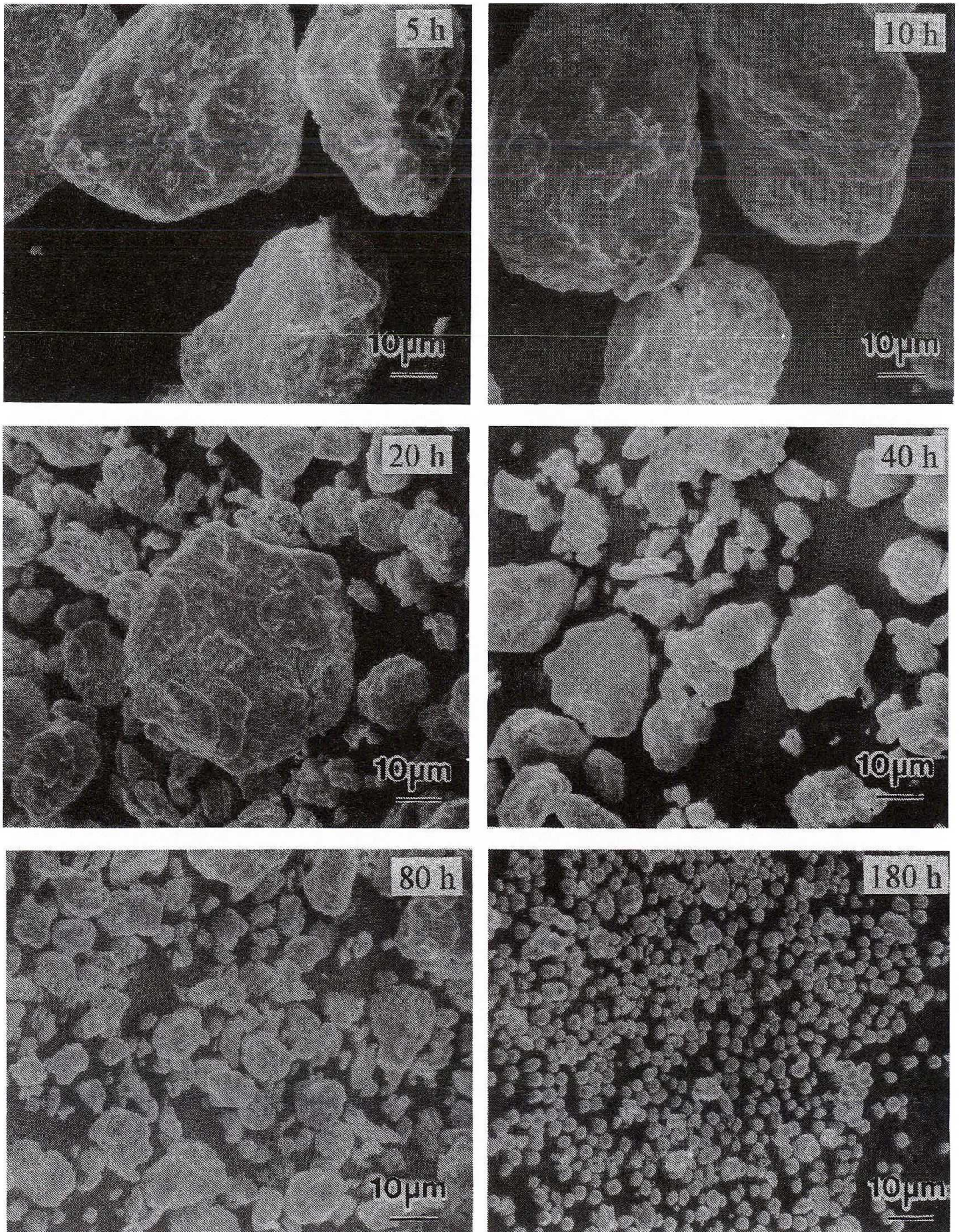


Fig. 2. Characteristic SEM images of milled powders after 5 hours, 10 hours, 20 hours, 40 hours, 80 hours and 180 hours

looked like those found after 5 hours of milling, but in addition to them smaller, 100 μm particles were produced as well. There was a significant scatter in particle size. After 20 and 40 hours of milling the particle morphologies were similar (Fig. 2c, d). A wide distribution in particle size was observed as well, but the shape of particles changed to more spheroidal. However, flat particles were also observed indicating that welding still was at work. After 80 hours of milling particles got much finer (Fig. 2e) indicating predominance of fracturing but the nonuniform particle surface shows that welding still operates. The 180 hours of milling produces uniform powder with almost perfectly spherical particles with smooth surfaces (Fig. 2f). The average size of powder particle (after sieving through a 45 μm mesh) was about 5 μm . The sieved powder was used for consolidation.

The examination of powders after 40 and 180 hours of milling was supplemented by XEDS analysis of powder particles. The mutual ratios of intensities of the strongest peaks (heights) from Nb, Al and V were used as a measure of the alloying progress. The ratios of Nb to Al as well as Nb to V for small particles after 40 hours of milling were close to those after 180 hours of milling. For larger particles, examined after 40 hours of milling, the ratios differed notably even within the same particle. In general, the vanadium content in large particles was smaller than that in the final powder while the aluminium content was almost the same. This shows that Al easier dissolves in niobium than the V does.

4.2. X-ray diffraction analysis of MA powders

The X-ray diffractograms exhibited dependence on the milling time. The composed figure of diffractograms after 0, 5, 10, 20, 40, 80 and 180 hours is shown in Fig. 3. Peaks from Al, though much weaker than in the starting powder (0 hours), were still present till 20 hours of milling and disappeared after 40 hours indicating dissolution of Al in Nb. Peaks from V, on the other hand, become weaker and weaker with the milling time but were still present after 80 hours of milling. In general, with the milling time peaks became broader and their intensities decreased. The peak broadening was due to refinement of powder and due to strains associated with intense plastic deformation of powder particles. The positions of peaks also change with milling time. All peaks move right toward larger values of θ indicating change in lattice parameter of the alloy with milling time. Such behaviour was also observed for other mechanically alloyed Nb–Al alloys [9–13] and is considered as a typical one for the mechanical alloying process [15]. However, close to the primary Nb peaks, new satellite peaks appeared always on the right side of each primary peak. The intensity of these secondary peaks increased with milling time whereas the intensity of primary ones ceased. Such behaviour is unique and was not reported earlier². This is an evidence that during mechanical alloying two different Nb-base

² In fact, the similar phenomenon was observed by Clark et al. [16] in the Al-50% Mg ball-milled alloy but was not interpreted in detail; it is interesting, however, that double peaks appeared in that study for the Al-50% Mg alloy but did not appear for the Al-30% Mg alloy.

phases with different lattice parameters coexist in the powder mixture. The phases are labeled Nb_I and Nb_{II} . They differ likely in saturation with alloying elements. The values of lattice parameters for both phases and for different milling times are shown in table 1. The volume fractions of Nb_I and Nb_{II} phases were evaluated from the measurements of areas under $\{200\}$ and $\{211\}$ niobium peaks. The results are shown in table 2. For both phases calculation of average X-ray crystallite size and value of lattice strains were performed. The results are shown in table 3. Small differences in lattice parameters for the Nb_I phase and continuous decrease in lattice parameters for the Nb_{II} phase is apparently associated with the presence of vanadium. Since atomic diameters of Nb and Al are almost identical (0.286 nm and 0.2864 nm, respectively), and the atomic diameter of V is much less (0.2621 nm) one can assume that the Nb_{II} phase is enriched with vanadium while the Nb_I phase contains much less vanadium. It appears from crystallite size analysis that progress of alloying in the Nb_I phase is less advanced (larger crystallites) than in the Nb_{II} phase. Also, values of lattice strains demonstrate that the phase Nb_{II} corresponds to smaller, more deformed and more saturated with vanadium, particles. Such behavior may be associated with the different diffusion coefficients of Al and V in niobium. Assuming that the diffusivity of a particular element is proportional to its melting point, Al diffuses faster and deeper into Nb particles than V does. Since V diffuses on smaller distances, the average crystallite size of the phase enriched with V is smaller.

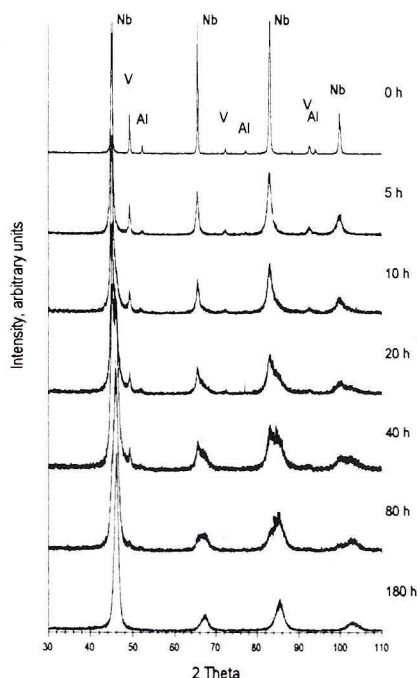


Fig. 3. The compose figure of X-ray spectra after particular milling times

TABLE 1

Change in lattice parameters of Nb_I and Nb_{II} phases with milling time

Time [hours]	Parameter of Nb _I [Å]	Parameter of Nb _{II} [Å]
0	3.305	—
5	3.308	3.303
10	3.308	3.283
20	3.306	3.263
40	3.306	3.245
80	3.306	3.239
180	—	3.235

TABLE 2

Change in volume fractions of Nb_I and Nb_{II} phases with milling time

Time [hours]	Nb _I vol. %	Nb _{II} vol. %
0	100	0
5	73	27
10	54	46
20	31	69
40	31	69
80	16	84
180	0	100

TABLE 3

Change of crystallite size and lattice strain in the Nb_I and Nb_{II} phases with milling time

Time [hours]	Nb _I		Nb _{II}	
	size [Å]	strain [%]	size [Å]	strain [%]
0	1433	0.09	—	—
5	122	0.57	66	0.98
10	129	0.56	38	1.67
20	107	0.65	41	1.55
40	87	0.78	48	1.32
80	80	0.83	52	1.23
180	—	—	60	1.06

Comparing the behavior of the present alloy to the alloy Nb-18% Al examined previously [3, 8] significant differences should be pointed out. The alloy Nb-18% Al behaved in a “traditional” manner, i.e., the peaks broaden and their intensities decreased. No satellite peaks were observed. Also, the shifting peaks from their initial positions occurred much later (it was observed after 86 hours of milling) than at the presence of vanadium. Though Al dissolves in Nb relatively fast, the alloy with V has to be milled for longer time in order to completely dissolve V in the Nb-base solid solution.

4.3. Annealed powder

A sample of as-milled powder was subjected to annealing at 1273 K for 5 hours in vacuum. After this the annealed powder was characterized by X-ray diffraction. The result is shown in Fig. 4. During annealing of the supersaturated powder the precipitation of new phases took place. One of them was unequivocally identified as Nb_3Al . The other phase has not been identified yet since peaks from that phase exhibit relatively low intensities. Thus, the annealed powder consisted of three phases: niobium solid solution, Nb_3Al and minor unidentified phase. It is worth to note that peaks from Nb slightly shifted back (leftward) upon annealing but remained still shifted in relation to the pure Nb positions. This may indicate that Nb solid solution contains vanadium. The X-ray diffractogram did not reveal any Nb {100} peaks what means that the niobium solid solution (Nb_{ss}) exhibits b.c.c. crystal structure rather than B2 structure found by Horšpöhl [6] and Tappin [7] in the similar alloys.

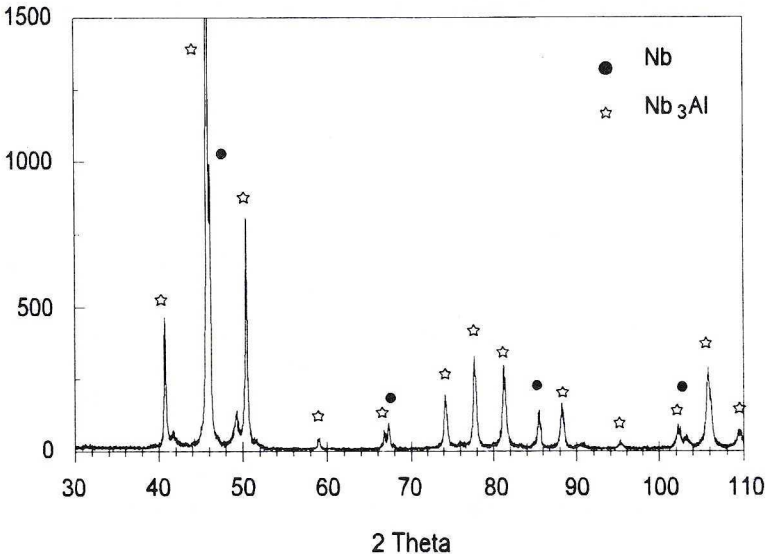


Fig. 4. The X-ray spectrum of as-milled powder annealed at 1273 K for 5 h

4.4. Consolidated material

The optical micrographs revealed little about microstructure. More information provided images formed by backscattered electrons in a scanning electron microscope (Fig. 5). Utilization of Z-contrast allowed for revealing phases with different Nb concentration, i.e. Nb_{ss} and an intermetallic phase. Since back scattered electron yield is higher for higher Z (atomic number) the Nb_{ss} grains are brighter. The darker phase corresponds to an intermetallic phase. The intermetallic phase

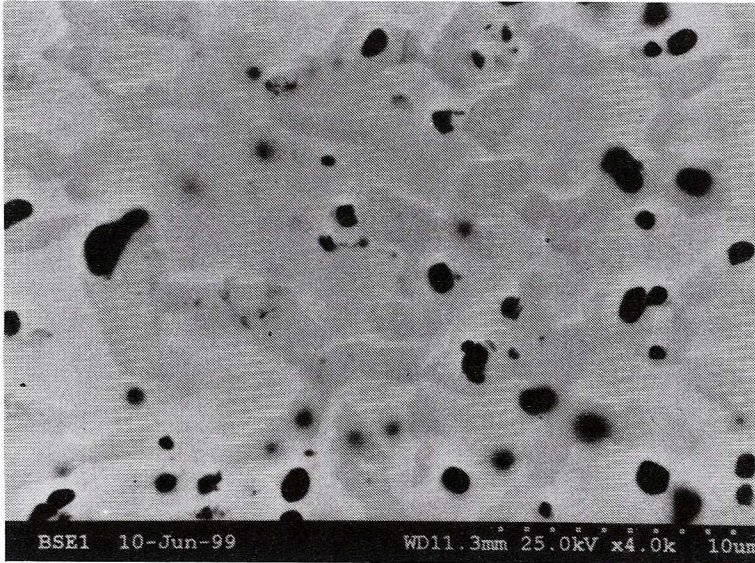


Fig. 5. Backscattered electron image of the consolidated material

surrounded areas of Nb_{ss} forming precipitates on primary powder particle boundaries (Fig. 5).

The X-ray phase analysis showed that the consolidated material consists mainly of Nb_{ss} and Nb_2Al (σ) phases (Fig. 6). Also, weaker peaks coming from Nb_3Al could be recognized (the overlapping of peaks from the Nb_3Al and Nb_2Al phases makes detection of the Nb_3Al phases perplexed). Since the ternary Nb–Al–V phase diagram is known only for 1273K [17], the present study shows that occurrence of the Nb_2Al phase is shifted to higher Nb content at higher temperature. It is worth noting, however, that this phase was also found in the binary Nb–18% Al alloy [3]. This finding is inconsistent with work of Tappin et al. [7] who found, in the alloy Nb–15% Al–20% V (i.e. in alloy with the same Al/V ratio) subjected to annealing at 1773 K, only two phases with A15 and B2 crystal structures. Since no $\{100\}$ peaks were observed in this research it appears that niobium solid solution remain in a disordered state. As in powder annealed at 1273 K peaks from Nb were moved slightly leftward but still were shifted in relation to the pure Nb position. This shows that alloying elements, especially vanadium, remain dissolved in niobium.

The consolidated material was characterized by compression test and hardness measurements. The average Vickers hardness number was 616 HV with relatively low scatter of results. The scatter of results remained low for different applied loads. For loads lower than 2 kG the indentations were free from cracks while indentations at 5 and 10 kG loads had well developed cracks (Fig. 7). These cracks were used for fracture toughness evaluation followed by the formula given by Meyers and Chawla [14]

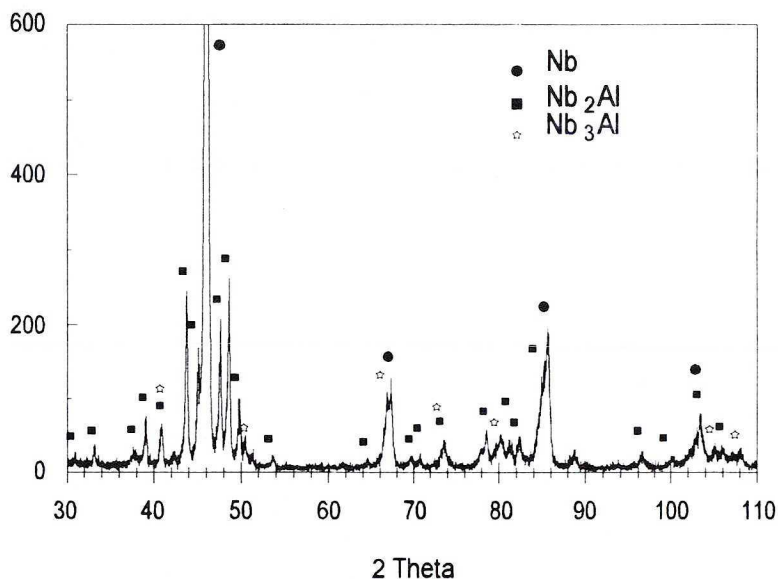


Fig. 6. The X-ray spectrum of the consolidated material

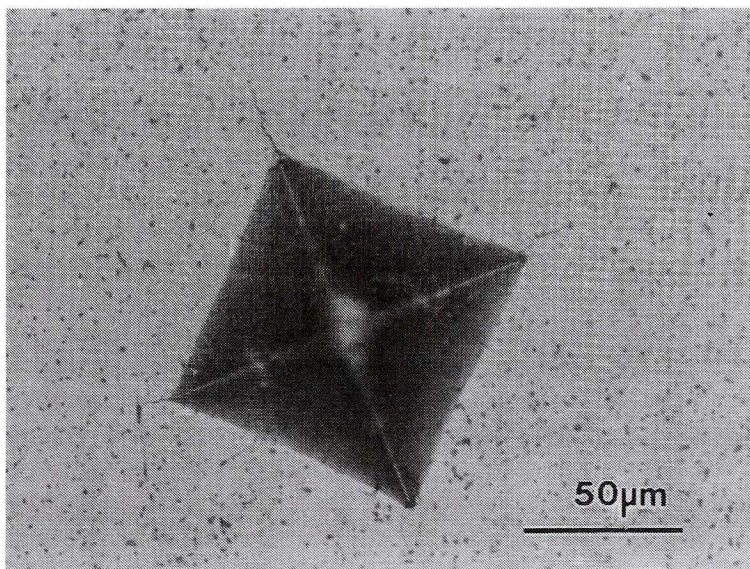


Fig. 7. Optical micrograph of the indented specimen

$$K_{Ic} = \delta \left(\frac{E}{H} \right)^{1/2} \cdot \frac{P}{a^{3/2}},$$

where E is Young modulus determined from the compression test ($E = 40$ GPa), H is hardness in GPa ($H = 6,04$ GPa), P is load in kG ($P = 9.81$ N), a is the length of the crack ($a = 0.12 \cdot 10^{-3}$ m) and δ is a coefficient equal to 0.0016.

The K_{Ic} calculated from the above formula was about $3 \text{ MPa} \cdot \text{m}^{1/2}$. Such low value is typical for ceramic materials like Al_2O_3 ($2.1 \text{ MPa} \cdot \text{m}^{1/2}$), Si_3N_4 ($5 \text{ MPa} \cdot \text{m}^{1/2}$) or SiC ($4 \text{ MPa} \cdot \text{m}^{1/2}$) [14].

The strength of the examined alloy was about 1880 MPa and ductility about 2%. The very low fracture toughness as well as relatively high strength of the examined alloy is associated likely with the presence of the Nb_2Al -base σ phase.

5. Summary and conclusions

Mechanical alloying of elemental powders mixture of 58% Nb, 18% Al and 24% V leads to the formation of two niobium solid solution phases (Nb_I and Nb_{II}) differed from each other in lattice parameters. Different lattice parameters are likely due to different saturation with alloying elements (Al and V). The lattice parameter of the Nb_I phase is close to the lattice parameter of pure niobium. The peaks from the Nb_I phase decreased with milling time and ceased completely after 180 hours of milling. The peaks from the Nb_{II} phase behaved in an opposite manner.

After consolidation of powders at 1773 K the dominant phases are: Nb_2Al -based σ phase and niobium solid solution in the disordered form. The consolidated material exhibits high compression strength but very low fracture toughness.

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