THE MICROSTRUCTURE OF THE Ni-Al-V ALLOYS PREPARED BY LEVITATION, RAPID QUENCHING AND HIGH PRESSURE TORSION

G. Korznikova[1], T. Czeppe[2] and A. Korznikov[1]

[1]Institute of Metals Superplasticity Problems, Russian Academy of Sciences,
Khalturin st. 39, 450001, Ufa, Russia
[2]Institute of Metallurgy and Materials Sciences, Polish Academy of Sciences,
Reymonta 25 St. 30-059 Krakow, Poland

Abstract. Microstructure and mechanical properties of NiAlV alloys of the composition belonging to the pseudo-binary Ni_3Al-Ni_3V cross-section were investigated. The samples were prepared by the cold crucible levitation melting and by re-melting and crystallizing in the small volume copper mould. The phase composition of the samples, which should result from the eutectoidal decomposition was not found. Instead the $Ni_3(Al,V)$ and $Ni(Al,V)$ solid solution or seldom disordered solid solution were retained due to the relatively high cooling rates. In the samples after subsequent high pressure torsion fine lamellar structure was revealed. The lattice parameter in the samples after high pressure torsion was larger than in the samples after rapid quenching.

1. INTRODUCTION

The Ni-based intermetalic phases like Ni_3Al or NiAl, reveal many interesting properties as materials for structural applications [1], however commonly exhibit also high brittleness at room temperature. The NiAlV alloys belonging to the pseudo-binary, Ni_3Al-Ni_3V cross-section through the ternary phase diagram posses at room temperature characteristic microstructure resulting from the eutectoidal decomposition below 1000 °C, which leads to the Ni_3Al–Ni_3V phase composition [2]. The structures of this phases belong to the highly ordered dens packed $L1_2$ and $D0_{22}$ structures, with very high degree of coherence at the interfaces [3-6]. Also, mechanical properties of such alloys investigated in the creep tests are promising [7]. The path of the microstructure formation in eutectoidal decomposition as well as the influence of the prolonged annealing, which leads to the lamellar microstructure [8] remain not completely clear. The paper presents results of comparative investigation of three NiAlV alloys, of composition belonging to the Ni_3Al-Ni_3V pseudo-binary cross-section, prepared with use of:

i) the cold crucible levitation melting (CCLM) and direct cooling in the equipment,

ii) re-melting after CCLM and crystallization in the cooper mould,

iii) by high pressure torsion of the samples after CCLM.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. The composition and preparation of the investigated alloys

The composition of the alloys is presented in Table 1 and, schematically in Fig. 1. In the Table both nominal and experimental compositions of the al-

Corresponding author: G. Korznikova, e-mail: korznikova@anrb.ru

Table 1. The nominal and real compositions of the investigated alloys. Real composition determined with the EDS method.

	Nominal composition [at.%]			Real composition (EDS) [at.%]		
	Ni	Al	V	Ni	Al	V
V-1	75	15	10	75.8	14.5	9.7
V-2	75	10	15	76.8	8.9	14.3
V-3	75	5	20	77.9	4.4	17.7
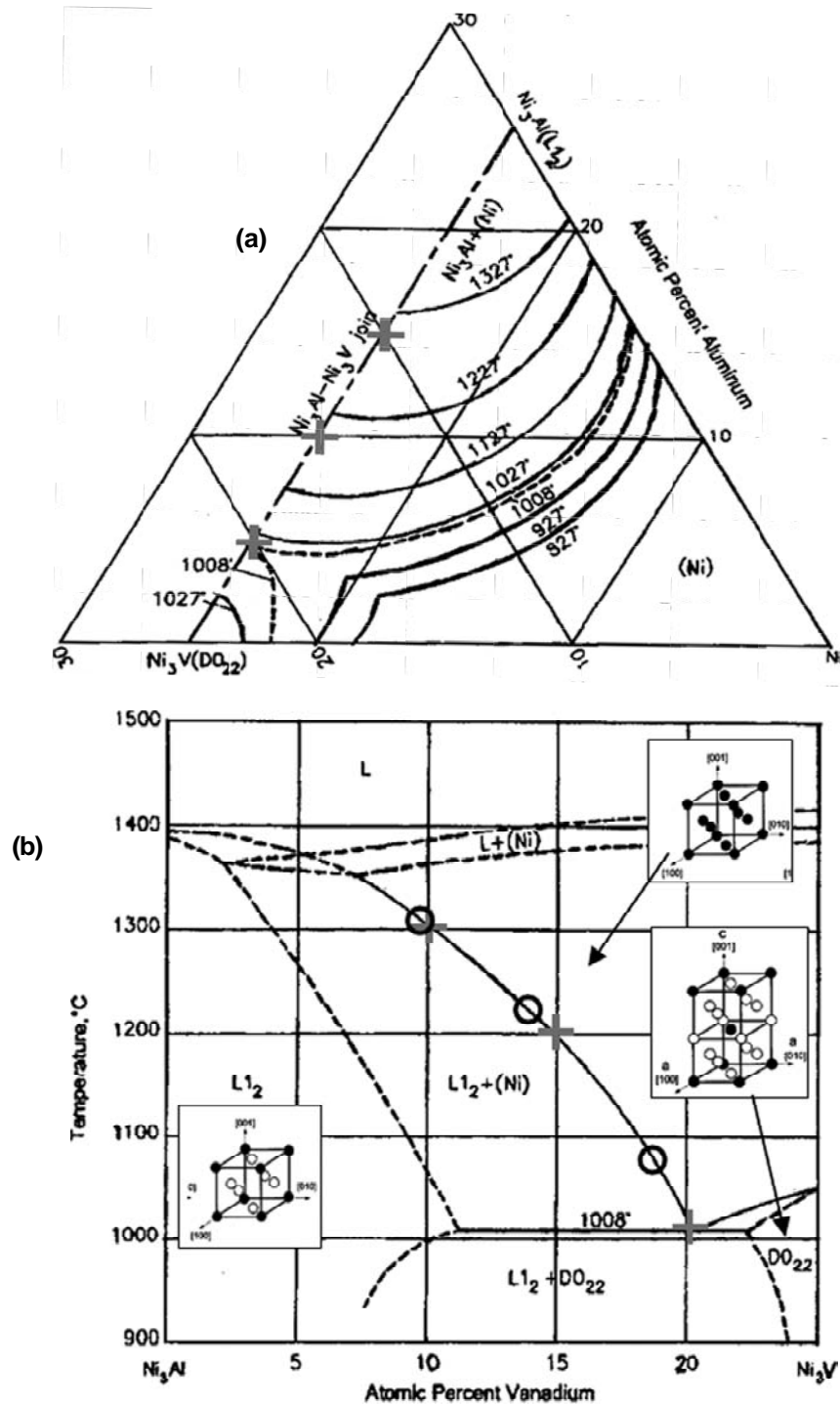
Fig. 1. The nominal composition of the V-1, V-2, V-3 alloys (crosses) and the average experimental composition determined with the EDS (circles): a) In the composition triangle, in respect to the Ni/[Ni+Ni$_3$Al] phase boundary, b) in the pseudo-binary cross-section Ni$_3$Al-Ni$_3$V, reprinted with permission from [2], © 2005 ASM International.
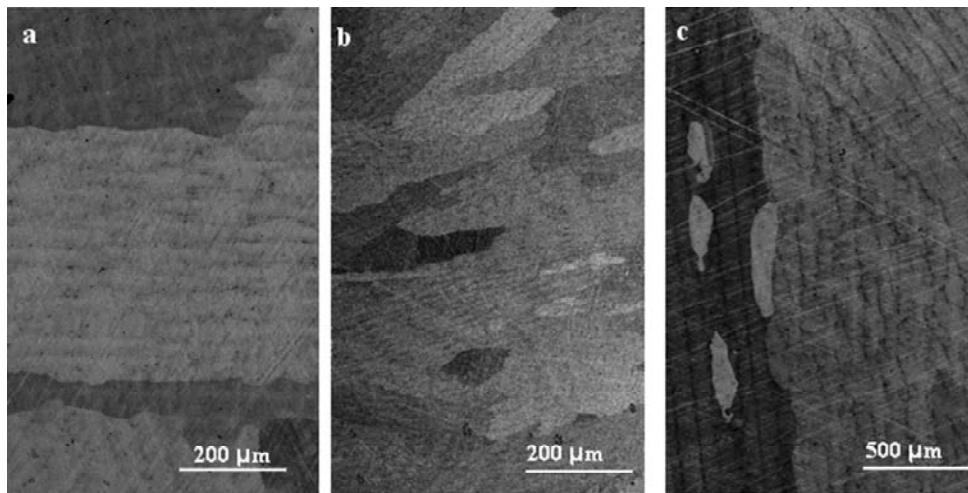
Fig. 2. SEM microstructure on the cross-section of the CCLM samples polished: a) V-1; b) V-2; c) V-3.

loys are presented, the last one determined with the EDX method, with use of the scanning electron microscope (SEM). As is shown, real total content of the Al plus V was decreased by the 0.8 to 2.9 at.% simultaneously with the increase of the V content. Three investigated ternary alloys: V-1, V-2 and V-3 belong to the pseudo-binary cross section Ni_3Al-Ni_3V through the equilibrium ternary phase diagram (Table 1, Figs. 1a and 1b), along the line of increasing V content. As is shown in Figs. 1a and 1b this leads to the decrease of the temperature of transformation of the disordered fcc Ni(Al,V) solid solution into the highly ordered Ni_3Al phase with the $L1_2$ structure.

At temperature 1008 °C the eutectoidal decomposition takes place leading to the further precipitation of the Ni_3V phase, owning $D0_{22}$ highly ordered structure. The alloys were prepared by melting of the components with use of the cold crucible levitation and direct cooling in the copper concentrator in argon gas atmosphere. The samples of the 9 g weight were achieved. The alloys were also remelted by the levitation and crystallized in the small volume copper mould, filled with use of the suction, directly from the liquid state. The construction of the equipment let to use the mould of the small mass only. In this case small bars of the 3 mm diameter were achieved.

The method of high pressure torsion (HPT) was invented for fabricating the bulk nanostructured materials, quite often revealing extraordinary phase composition, mechanical and magnetic properties [9]. The microstructure produced by HPT is generally metastable, and may relax in a much lower temperatures than in the coarse-grained samples [9]. The HPT method was also successfully applied for consolidation of the Ni-Al based amorphous ribbons [10]. In this study samples for deformation 9 mm in diameter and 0.25 mm thick were prepared by spark-cutting and mechanical polishing of CCLM samples. They were subjected to high pressure torsion at room temperature under the pressure 5 GPa in a Bridgman anvil-type unit. The processed samples have thickness about 120 μm.

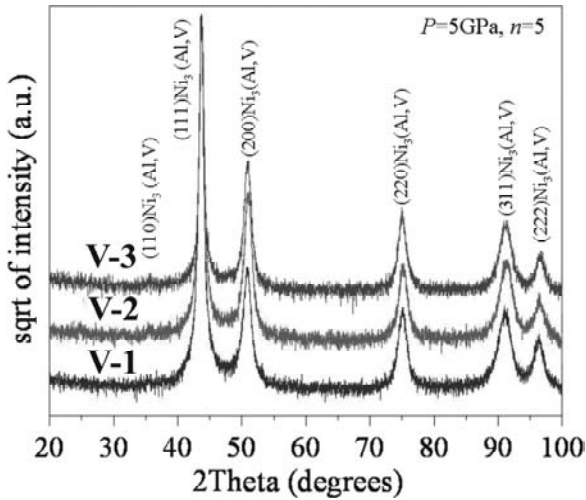## 2.2. Microstructure and phase composition of the alloys

Images of the microstructure of the samples achieved by the CCLM observed with the scanning electron microscope on the polished cross-sections are showed in Fig. 2. In all cases microstructure consist on the large grains containing cellular structure inside. The composition of the darker and lighter grins was the same in the limits of the precision of the EDX method. At the grain boundaries dark phase or precipitates are visible. In the case of the V-3 alloy larger amount of such precipitates existed (Fig. 2c). To confirmed, if the alloys decomposed into eutectoid structure during cooling below 1008 °C (Fig. 1b), the XRD phase analysis was performed (Fig. 3). As is seen in the case of alloys V-1 and V-2 prepared with CCLM and directly cooled, the regular structure Pm3m, respectful to the Ni_3Al structure, but with the lattice parameter $a = 0.3564$ nm was observed (Figs. 3a and 3b). Fig. 3d presents modeled structure of this type. In case of the alloy V-3 only regular disordered structure Fm3m with the lattice parameter $a = 0.3565$ nm was noticed (Fig. 3c). The results means, that due to the higher temperatures at the solvus line at the phase diagram (Fig. 1b) the CCLM samples V-1 and V-2 transformed
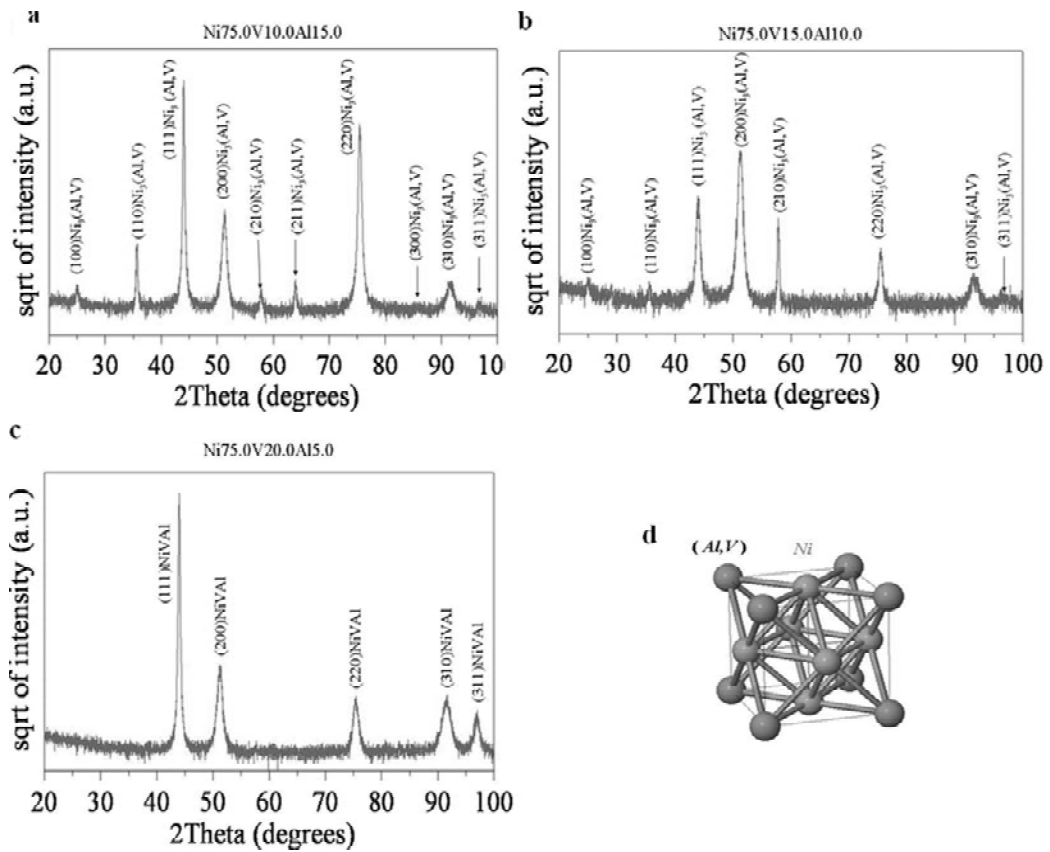
Fig. 3. Phase composition of the alloys prepared with CCLM (XRD): a) V-1, b) V-2,c) V-3 alloys, d) hypothetical atomic order of the alloys V-1 and V-2.
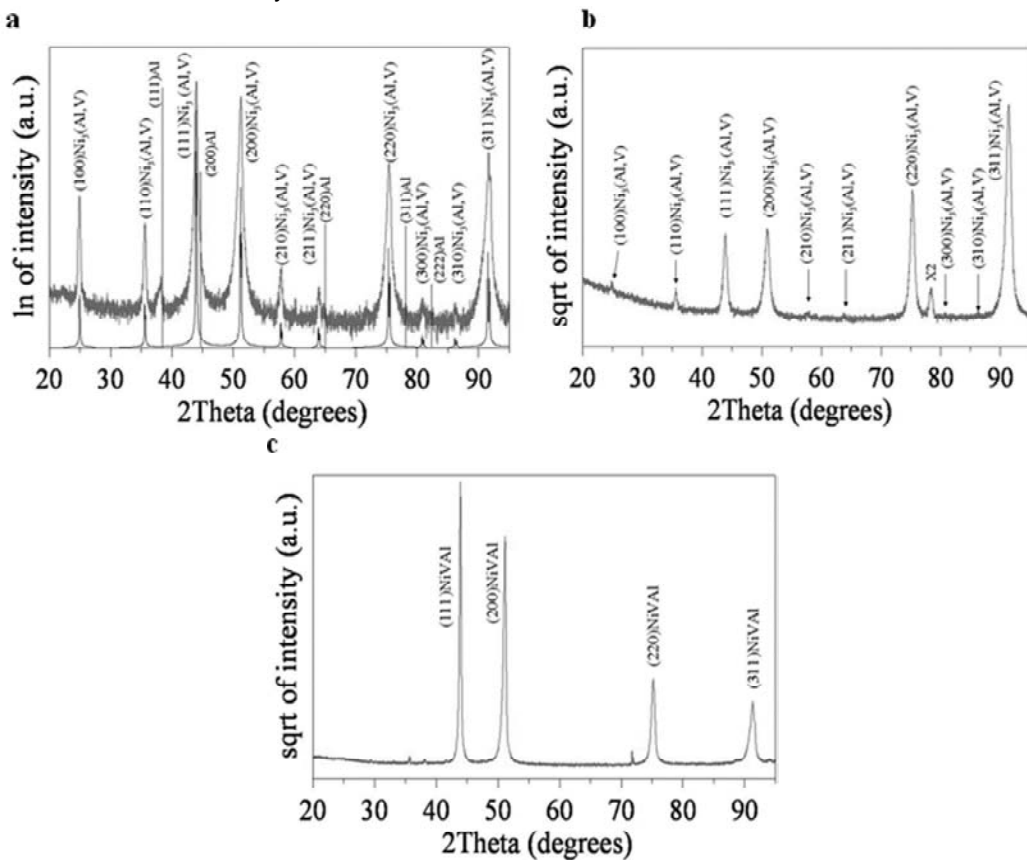
Fig. 4. Phase composition of the alloys prepared by rapid solidification in the copper mould (XRD): a) V-1, b) V-2, c) V-3 alloys. In a) also the simulation of the hypothetical Ni_3Al and A1 structures is presented.

Fig. 5. Phase composition of the samples subjected to HPT.

partially to the L1$_2$ structure while alloy V-3 preserved high temperature solid solution. The cooling rate however was too high to let the samples further decomposed into Ni$_3$Al (L1$_2$) and Ni$_3$V (D0$_{22}$) structures.

The XRD phase analysis performed for the same alloys prepared with the higher cooling rate by cooling from the liquid state in the copper mould gave somehow similar results (Fig. 4). In case of all alloys, except dominant phases, previously mentioned, some hard to identify, probably meta-stable phases exist. In case of V-1 alloy the additional peaks could be fitted to the Al structure, possibly Al solid solution (Fig. 4a), in case of V-2 alloy additional peak marked X2 (Fig. 4b) could not be identified, similarly small peaks at XRD plot of V-3 alloy (Fig. 4c). Some differences in the lattice parameters of the Ni$_3$(Al,V) and Ni(Al,V) solid solution were noticed after rapid crystallization. In case of V-1 alloy the a = 0.3563 nm remained nearly the same like for sample prepared by the CCLM but for the alloy

V-2 a= 0.3571 and V-3 alloy a= 0.3572 nm remarkably increased. This may result from the larger amount of the vanadium atoms retained in the lattices due to the higher cooling rate achieved in the copper mould.

In the case of all alloys subjected to HPT the XRD phase analysis revealed only Ni$_3$(Al,V) phase (Fig.5). The lattice parameters increased still more after HPT and varied from a = 0.3577 nm in V-1 alloy to a = 0.3583 nm in V-3 alloy.

The structure of the samples prepared by rapid crystallization was also studied with the transmission microscopy (Figs. 6 and 7). The microstructure of the alloys V-1 and V-2 were similar consisting on cubical particles of Ni$_3$(Al,V) phase (Figs. 6a and 6c). At the selected area diffraction pattern (SADP) the lattice and superlattice spots of L1$_2$ structure are visible but, in agreement with the XRD results, D0$_{22}$ spots are not present (Fig. 6b).

Two different techniques of the foil preparation were used in the case of V-3 sample. The foils were prepared by electrolytic polishing in perchloric acid, at -150 °C, and by the Focused Ion Beam (FIB) technique enabling precise choose of the polished area. In both foils two different polycrystalline areas were found, of coarse and of nanograined structure (Figs. 7a and 7c). In all cases however disordered solid solution existed (Figs. 7b and 7d). All above results proves that the eutectoidal decomposition did not proceed in the alloys due to the rapid cooling of the high temperature solid solution. In case of alloys V-1 and V-2 ordering process took place due to the high enough transformation temperatures, giving as a result L1$_2$ structure observed both in XRD and electron diffraction.

The structure of the samples subjected to HPT is rather different and consists of fine lamellas with a thickness less than 10 nm (Fig. 8a). This result
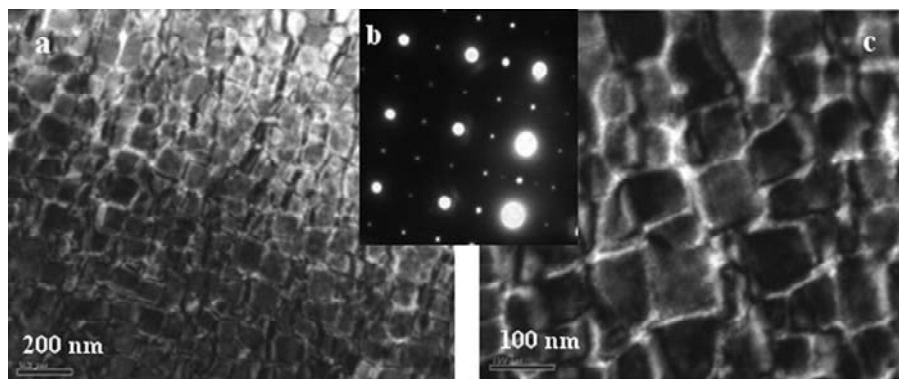
Fig. 6. TEM microstructure of the V-2 alloy after crystallization in the copper mould: a) BF image, b) SADP, [001]L1$_2$ orientation, c) DF image.
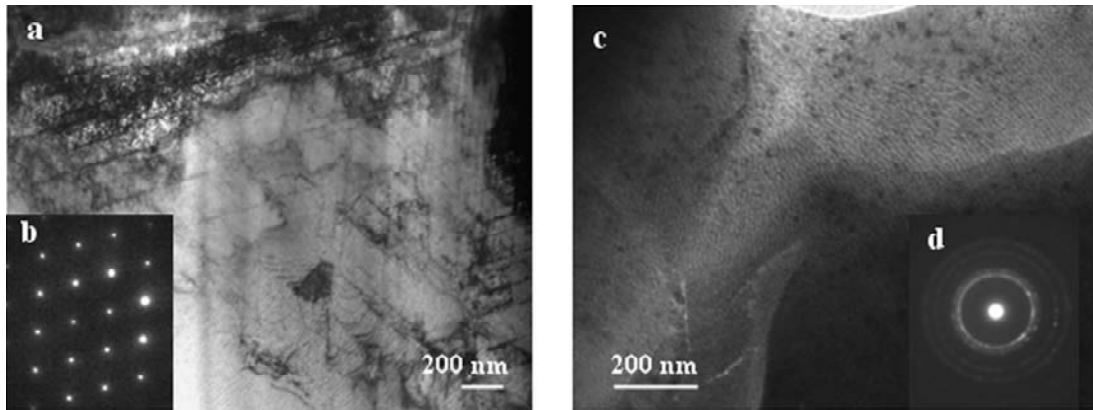
Fig. 7. TEM microstructure of the V-3 alloy after crystallization in the copper mould: a), c) BF image, b), d) SADP, [011] fcc orientation . Foil prepared with FIB technique - a, b) foil prepared with electrolytic polishing- c, d).
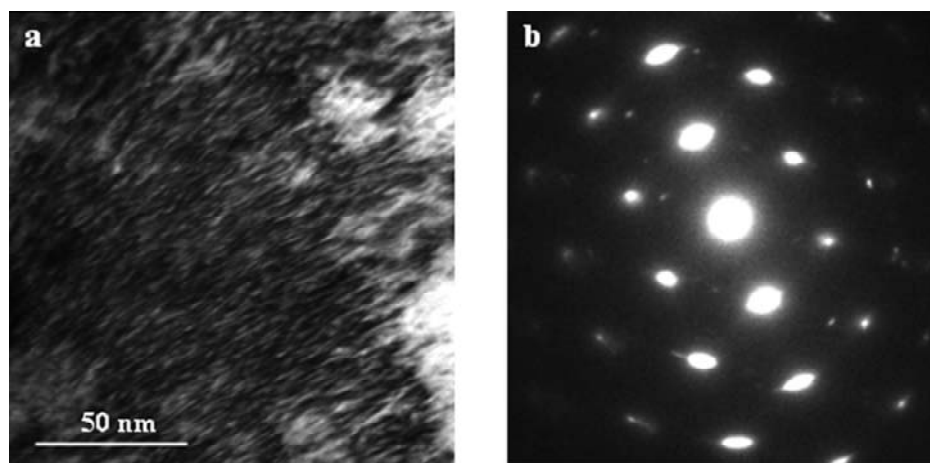
Fig. 8. TEM microstructure of the V-1 alloy after HPT: a) BF image, b) SADP, [011] fcc orientation.

supports XRD data. According XRD the mean size of coherent-scattering regions is about 9 nm. At the selected area diffraction pattern (SADP) the lattice and some weak superlattice spots of $L1_2$ structure are visible (Fig. 8b). Previously it has been shown [11] that HPT under the pressure of 8 GPa with 10 revolutions of the anvil results in total disordering of pure Ni_3Al and its transformation into nanocrystalline granular type structure. Our result proves that the applied pressure was not enough for total disordering of the structure.

3. SUMMARY

During cooling from the melt the investigated NiAlV alloys should first undergo precipitation of the $Ni_3(Al,V)$ phase from the disordered solid solution and later, at about 1000 °C to eutectoidal decomposition. The relatively large cooling rates achieved by the direct cooling in CCLM method or re-melting and crystallization in the cooper mould led only to the first reaction. The observed phase composition was metastable at room temperature. The V-1 and V-2 alloys revealed typical microstructure of the cubical particles of $L1_2$ structure in the Ni solid solution, while V-3 alloy, of the near to eutectoidal composition, retained only disordered solid solution. Particular differences may be attributed to the coarse grain structure of the alloys after CCLM and much smaller grains size after crystallization in the copper mould as well as to the differences in microstructures of the samples caused by the different phase composition of the alloys. Homogeneous fine lamellar structure was achieved by means of HPT at 5 GPa with 5 revolutions of the anvil. All alloys after HPT revealed only $Ni_3(Al,V)$ phase with an increased lattice parameters as compared with the samples after CCLM.

REFERENCES

[1] D.B. Miracle // *Acta metal. mater.* **41** (1993) 649.

[2] V. Raghaven // *J Phase Equilib.* **26** (2005) 273.

[3] J.H. Van Vucht // *J Less-Common Metals* **11** (1966) 308.

[4] A. K. Sinha // *Trans. Met. Soc. AIME* **245** (1969) 911.

[5] Y. Nunomura, Y. Kaneno, H. Tsuda and T. Takasugi // *Intermetallics* **12** (2004) 389.

[6] Y. Nunomura, Y. Kaneno, H. Tsuda and T. Takasugi // *Acta Mater.* **54** (2006) 851.

[7] S. Shibuya, Y. Kaneno, M. Yoshida and T. Takasugi // *Acta Mater.* **54** (2006) 861.

[8] S. Shibuya, Y. Kaneno, H. Tsuda and T. Takasugi // *Intermetallics* **15** (2007) 338.

[9] R.Z. Valiev, R.K. Islamgaliev and I.V. Alexandrov // *Prog. Mater. Sci.* **45** (2000) 103.

[10] G. Korznikova, T. Czeppe and A. Korznikov // *Reviews on Advanced Materials Science* **25** (2010) 67.

[11] A.V. Korznikov, O. Dimitrov, G.F. Korznikova, J.P. Dallas, S.R. Idrisova, R.Z. Valiev and F.Faudot // *Acta Mater.* **47** (1999) 3301.