

THE EFFECT OF PREPARATION METHODS ON A MICROSTRUCTURE OF THE Ni₃Al-BASED ALLOYS ALLOYED WITH MOLYBDENUM

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Abstract

A preparation of alloys based on the Ni₃Al intermetallic compound alloyed with molybdenum by classical castings methods, such as an induction melting, is limited by a high melting point of molybdenum (2623 °C). Decreasing of the melting point on the value of 1417 °C was reached by a preparation of the Ni-15Mo (wt.%) master alloy by plasma metallurgy. The master alloy was used as an input material for a preparation of the Ni-7Al-14Mo (wt.%) alloy by an induction melting with a centrifugal casting. Castings of the Ni-7Al-14Mo alloy were directionally solidified in a resistance furnace working on the Bridgman method principle at the rates of 20 and 50 mm/h and the constant thermal gradient of 75 °C/cm. All experimental alloys were examined by a chemical and structural analysis. A matrix of the master alloy was homogeneous without precipitates and formed by the MoNi₈ phase. Matrixes of the casting and directionally solidified rods of the Ni-7Al-14Mo alloy consisted of the Ni₃Al phase and the solid solution of aluminum in nickel, mutually arranged as a mesh. There were small precipitates rich in molybdenum situated along grain boundaries. A structure of the casting and the directionally solidified rods was polycrystalline, but the grains of the directionally solidified rods were oriented in a growth direction of solid-liquid interface.

Keywords: Ni-7Al-14Mo alloy, Ni-15Mo alloy, plasma metallurgy, directional solidification, microstructure

1. INTRODUCTION

The Ni₃Al intermetallic compound has the L₁₂ type of structural lattice, which is a cause of increasing of strength characteristic together with a temperature up to 700 °C [1, 2]. Unfortunately, a polycrystalline Ni₃Al is a very brittle material [3, 4]. Industrial materials for high-temperature applications can be obtained by an appropriate alloying and a preparation of the Ni₃Al intermetallic compound. Molybdenum is used as an alloying element to increase strength of the Ni₃Al-based alloys at room and high temperatures [5, 6]. Controlled conditions of alloy solidification lead to getting of a required microstructure type, eventually in a case of the polycrystalline structure, to grain orienting in a growth direction of solid-liquid interface [7, 8].

The aim of a paper was a preparation of the Ni-15Mo master alloy and the Ni-7Al-14Mo alloy by appropriate metallurgical methods and their chemical and structural examination. The structures of the experimental alloys are compared with each other.

2. EXPERIMENT

The Ni-15Mo (wt.%) master alloy was prepared by a melting of pure components in protective argon atmosphere in a plasma furnace with horizontal crystallizer at VSB - TU Ostrava [9]. Ingots of the master alloy (**Fig. 1a**) were used for a preparation of the Ni-7Al-14Mo (wt.%) alloy by an induction melting in argon atmosphere in the Supercast 13 device. Castings of the alloy (**Fig. 1b**) were directionally solidified in the resistance furnace Clasic, working on principle of the Bridgman method, at the temperature of 1550 °C and the growth rates of solid-liquid interface of 20 and 50 mm/h.



Fig. 1a Ingots of the Ni-15Mo (wt.%) master alloy prepared by a plasma metallurgy



Fig. 1b Castings of the Ni-7Al-14Mo (wt.%) alloy prepared by an induction melting

Metallographic samples were prepared from the experimental alloys. The results of their chemical and structural analysis are published in the next chapter.

3. RESULTS

• Microstructure

Microstructure of the experimental alloys was revealed by etching solution containing H_2SO_4 , HNO_3 and H_3PO_4 in a ratio of 1:1:1. This etching solution preferentially etches the solid solution of aluminum in nickel. Microstructure was observed and photographically documented using the optical light microscope OLYMPUS GX51 equipped with a digital camera OLYMPUS DP12.

Structure of the Ni-15Mo master alloy (**Fig. 2a**) was homogeneous without precipitates and consisted of coarse grains of the $MoNi_8$ phase. There were number of pores along grain boundaries and also inside grain areas. Casting of the Ni-7Al-14Mo alloy was formed by coarse grains with random orientation. A matrix of the casting consisted of two-phase areas formed by the Ni_3Al phase (dendrites) and by the solid solution of aluminum in nickel (interdendritic space). A structure of directionally solidified rods of the Ni-7Al-14Mo alloy was polycrystalline. Coarse grains, oriented in a growth direction of solidus-liquidus interface, were formed by two phases - the Ni_3Al phase and the solid solution of aluminum in nickel - mutually arranged as a mesh. Both rods, directionally solidified at the rates of 20 and 50 mm/h, had a dendritic structure (**Fig. 2b**). There were small precipitates rich in molybdenum along the grain boundaries.

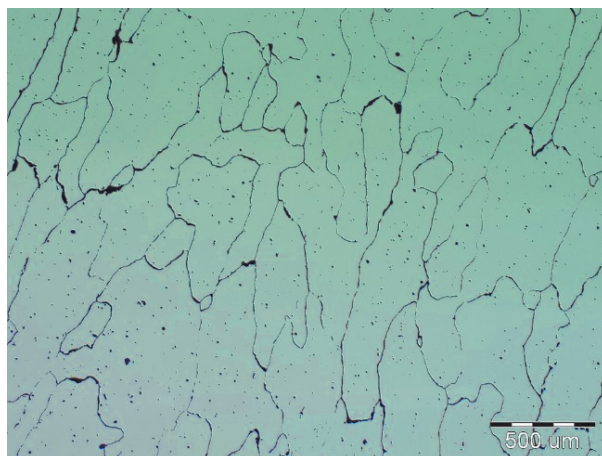


Fig. 2a Microstructure of the Ni-15Mo master alloy (lateral section)

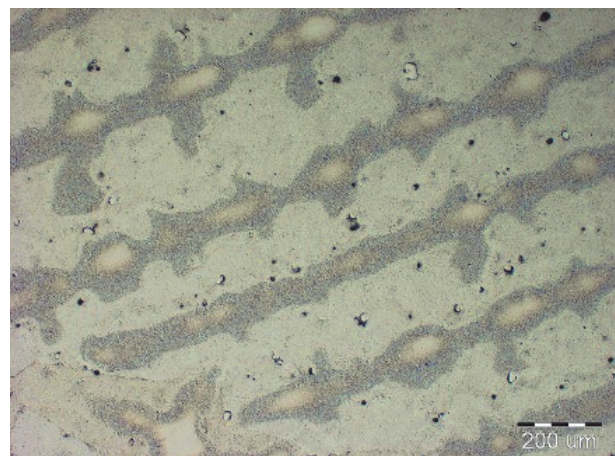


Fig. 2b Microstructure of the Ni-7Al-14Mo alloy after directional solidification (lateral section, 50 mm/h)

• **Chemical composition**

Chemical analysis of the Ni-15Mo master alloy, carried out by the OES method using an optical emission spectrometer of metals SPECTROMAXx, confirmed a significant heterogeneity of composition in the direction of the longitudinal axis of the ingot from the Ni-11.9Mo to the Ni-15Mo (wt.%). The composition heterogeneity is a characteristic feature of materials prepared by plasma metallurgy and it can be removed by additional remelting of the Ni-15Mo ingot in a furnace with induction heating. Inhomogeneous composition of the master alloy is the reason, why the chemical composition of the Ni-7Al-14Mo casting did not correspond to the nominal composition, but it was the Ni-8Al-12.5Mo (wt.%).

The EDS analysis was carried out using a scanning electron microscope QUANTA FEG 450 equipped with an EDAX probe APPOLO X. A chemical composition of the master alloy, determined by a surface EDS analysis, was the Ni-16.3Mo (wt.%) and of the casting was the Ni-8.4Al-13.5Mo (wt.%).

A spot EDS analysis was focused on phase identification in the Ni-7Al-14Mo alloy (A matrix of the Ni-15Mo master alloy did not contain precipitates and a mesh in the Ni-7Al-14Mo casting was so fine (Fig. 3a) that it could not be analyzed for a low resolving power of used electron microscope.) after directional solidification. There were three different phases for the spot EDS analysis - a matrix phase (point 1 in Fig. 3b), a channel of the mesh (point 2 in Fig. 3b) and a precipitate rich in molybdenum (point 3 in Fig. 3b). The results of the spot EDS analysis are summarized in Table 1. A matrix of the directionally solidified samples of the Ni-7Al-14Mo alloy was formed by round areas of the Ni₃Al phase, which were surrounded by the narrow channels of the solid solution of aluminum in nickel. Both of these phases contained dissolved molybdenum.

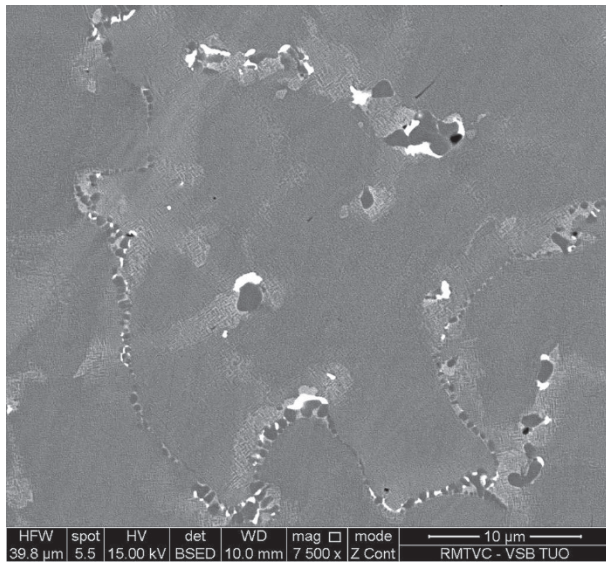


Fig. 3a Microstructure of the Ni-7Al-14Mo casting (lateral section)

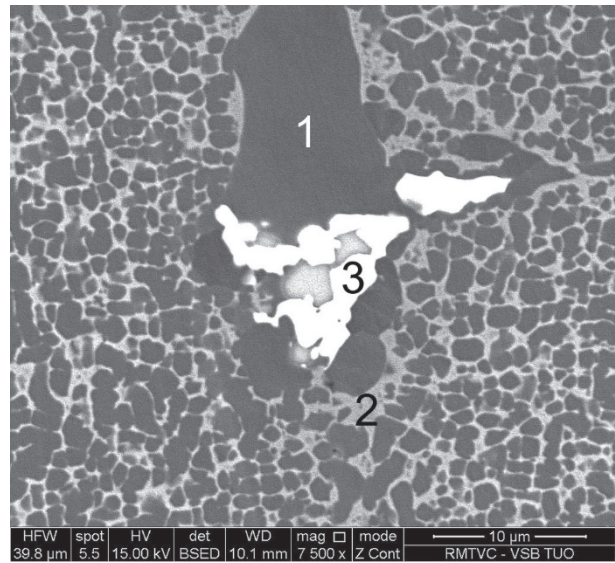


Fig. 3b Microstructure of the Ni-7Al-14Mo alloy after directional solidification (lateral section, 50 mm/h)

Table 1 The spot EDS analysis results of the Ni-7Al-14Mo alloy (wt.%)

Element	Point 1		Point 2		Point 3	
	50 mm/h	20 mm/h	50 mm/h	20 mm/h	50 mm/h	20 mm/h
Al	10.59 ± 0.11	10.13 ± 0.04	3.61 ± 0.23	3.05 ± 0.04	2.62 ± 0.05	1.75 ± 0.04
Mo	7.76 ± 0.38	8.47 ± 0.27	23.58 ± 0.96	23.05 ± 0.44	67.90 ± 0.13	69.28 ± 0.40
Ni	81.65 ± 0.27	81.40 ± 0.23	72.81 ± 0.73	73.90 ± 0.48	29.48 ± 0.17	28.97 ± 0.36

• **Microhardness**

A microhardness measurement was carried out using a microhardness tester FM - 100 equipped with a control unit FM - ARS - 900, working on a principle of Vickers method. A polished surface of every metallographic sample was twenty times subjected by an indenter at the load of 50 g for the time of 7 s. The results of the measurements are listed in **Table 2**.

Table 2 The microhardness measurements results of the Ni-15Mo master alloy and the Ni-7Al-14Mo alloy

Composition (wt. %)	Preparation	Conditions	HV0.05 (-)
Ni-15Mo	plasma melting	-	224.01 ± 15.47
Ni-7Al-14Mo	induction melting	-	422.03 ± 12.58
	directional solidification	50 mm/h	348.65 ± 18.96
		20 mm/h	325.23 ± 16.44

An average value of the HV0.05 microhardness of the Ni₃Al-based alloys unalloyed with molybdenum ranges from 250 to 270 [10]. An obvious hardening can be explained by dissolving of molybdenum in the matrix of the Ni-7Al-14Mo alloy. It was achieved by using of the Ni-15Mo master alloy. Higher microhardness of the Ni-7Al-14Mo casting is given by finer structure of the mesh and smaller grains and their random orientation.

• **Porosity**

Porosity was evaluated using a program for a quantitative image analysis AnalySIS auto. The measurement procedure of porosity is specified in the article [11]. Porosity of the experimental alloys was investigated in terms of statistics (**Fig. 4a** and **4b**) and morphology (**Fig. 5**).

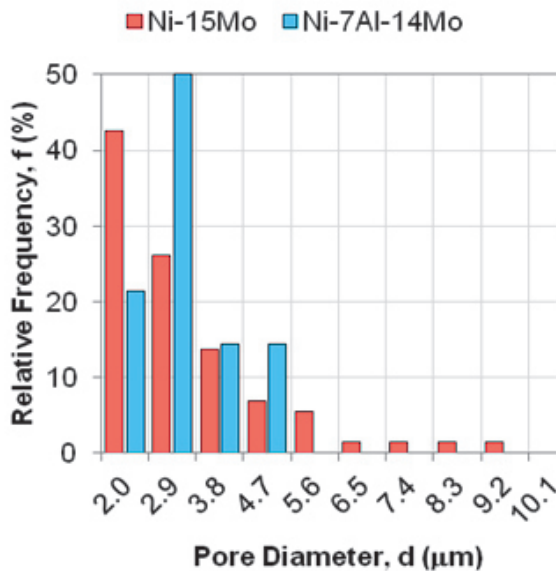


Fig. 4a Distribution of a pore diameter in the Ni-15Mo master alloy and the Ni-7Al-14Mo casting

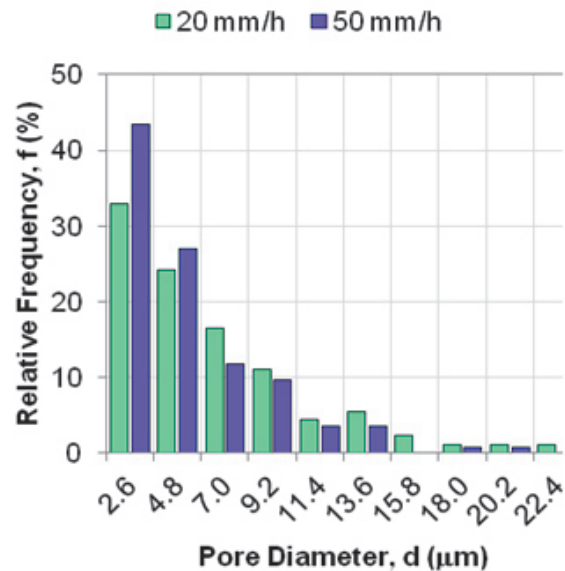


Fig. 4b Distribution of a pore diameter in the Ni-7Al-14Mo alloys after directional solidification

The Ni-15Mo master alloy contained the pores, of which diameter was from 1.5 to 9.6 μm. A distribution of these pores is exponential with a peak in the first class (1.5 - 2.4 μm), which contains 43 % of all identified pores (**Fig. 4a**). The pores, of which diameter was from 1.5 to 5.1 μm, were found in the Ni-7Al-14Mo casting. A pore distribution of the casting is log-normal with a peak in the second class (2.4 - 3.3 μm). There are 50 %

of all identified pores in this class (**Fig. 4a**). An average pore size identified in directionally solidified rods of the Ni-7Al-14Mo alloy was from 1.5 to 23.5 μm . A distribution of pore diameter in these samples was exponential with a peak in the first class (1.5 - 3.7 μm), in which are 33 % of all identified pores in the case of the sample directionally solidified at the rate of 20 mm/h and 44 % of all identified pores in the case of the sample directionally solidified at the rate of 50 mm/h (**Fig. 4b**).

Morphology of the pores identified in the experimental alloys is plotted in **Fig. 5** as a dependence of shape factors [12]. Controlled solidification process positively affects the pore morphology, especially a regular pore shape. During uncontrolled solidification process, different manners of pore formation are occurred (e.g. gas dissolution, shrinkage etc.). Therefore, the pores in the Ni-15Mo master alloy and the Ni-7Al-14Mo casting are morphologically richer and their shape factors have lower value.

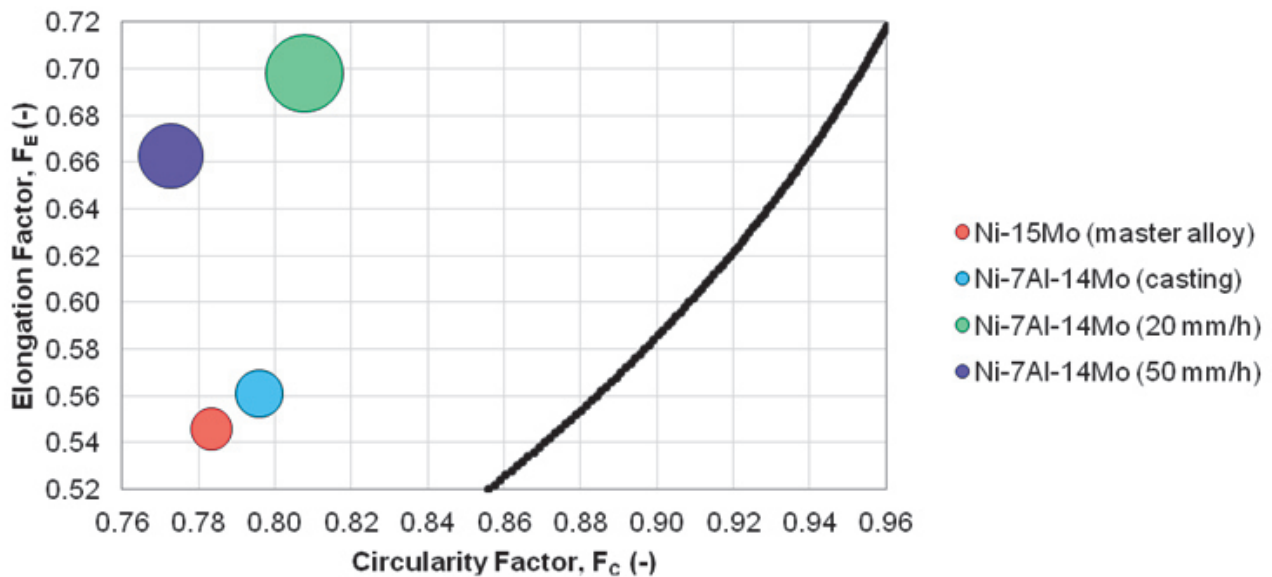


Fig. 5 Pore morphology in the Ni-15Mo master alloy and the Ni-7Al-14Mo alloys

Porosity related to the area of 382,389.84 μm^2 is listed in **Table 3** together with an average pore size. A minimum porosity was achieved in the alloys prepared by induction and plasma melting. Conversely, the porosity of the Ni-7Al-14Mo alloys after directional solidification is maximal and pores in these alloys are almost three times greater than in the Ni-7Al-14Mo casting.

Table 3 The porosity measurement results of the Ni-15Mo master alloy and the Ni-7Al-14Mo alloys

Composition (wt.%)	Preparation	Conditions	P (%)	d (μm)
Ni-15Mo	plasma melting	-	0.0385 ± 0.0139	4.53
Ni-7Al-14Mo	induction melting	-	0.0065 ± 0.0034	4.69
	directional solidification	50 mm/h	0.1193 ± 0.0464	13.37
		20 mm/h	0.1334 ± 0.0395	12.73

4. CONCLUSIONS

The Ni-15Mo (wt.%) master alloy was prepared by plasma metallurgy process. A structure of the master alloy was homogeneous and formed by the MoNi_8 phase. The master alloy was used for a preparation of the Ni-7Al-14Mo (wt.%) alloy by an induction melting process. The positives of this progress are:

(a) a dissolution of molybdenum charge,

- (b) a decreasing of operating temperature,
- (c) a reduction of aluminum vaporization.

After directional solidification of the Ni-7Al-14Mo castings, the final structure consisted of coarse grains oriented in a growth direction of solid-liquid interface. A matrix of directionally solidified samples was formed by small grains of the Ni₃Al phase surrounded by channels of the solid solution of aluminum in nickel. There was dissolved molybdenum in the both phases. In addition, phases rich in molybdenum were situated along grain boundaries.

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