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INFLUENCE OF ALLOYING ELEMENTS ON THE MICROSTRUCTURE AND SELECTED HIGH-TEMPERATURE PROPERTIES OF NEW COBALT-BASED $L1_2$-REINFORCED SUPERALLOYS

The study investigated the primary structure of the new generation of superalloys based on Co-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb cobalt. Research on a group of cobalt-based materials was initiated in 2006 by J. Sato [1]. These materials may replace nickel-based superalloys in the future due to their excellent properties at elevated temperatures relative to nickel-based superalloys. The primary microstructure characterisation of the Co-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb alloy are the basic subject of this article. The Co-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb alloy are tungsten free alloys of a new type with the final microstructure based on the Co-based solid solution $L1_2$ phase of the Co_3(Al,Mo,Nb) type as a strengthened structural element. The analysed alloys were investigated in an as-cast state after a vacuum casting process applied on graphite moulds. The primary microstructure of the alloys and the chemical constituent of dendritic and interdendritic areas were analysed using light, scanning electron and transmission microscopy. Currently, nickel-strengthened γ' phase steels are still unrivalled in aerospace applications, however, cobalt based superalloys are a response to their existing limitations, which do not allow maintaining the current rate of development of aircraft engines.

Keywords: Co10Al5Mo2Nb; Co20Ni10Al5Mo2Nb; casting; primary microstructure; segregation; dendrites

1. Introduction

The term "superalloys" is used to describe alloys resistant to high temperatures, i.e. heat resistant alloys based on nickel, cobalt or iron. The combination of high temperature behaviours allows obtaining a material which, at high operating temperature, will have surface resistance to an aggressive environment, as well as high and stable mechanical properties. It is assumed that superalloys may be used at a temperature above 1500 F [2]. Currently, research is being carried out to increase the life and efficiency of aircraft engines. These studies focus on the search for modern materials with the desired mechanical properties at temperatures up to 1200°C [3].

Materials used for very high temperature operation have to withstand considerable stresses at high temperature over a long period of time. The concept of each superalloy is to: demonstrate high strength, i.e. creep strength, yield strength, tensile strength or high temperature fatigue. Table 1 lists some typical physical properties of superalloys based on cobalt and nickel. Nickel-based superalloys are the primary group (generation) of metallic materials used in high temperature applications. The good behaviour of nickel-based alloys under operating conditions at high temperature is due to the γ/γ' microstructure. These superalloys are the most commonly used materials in turbine engines due to their good combination of high strength, long fatigue life and good resistance to high temperature oxidation and corrosion [4].

TABLE 1

List of physical properties of nickel- and cobalt-based superalloys [5]

Properties	Superalloys based on a nickel matrix	Superalloys based on a cobalt matrix
Density	7.6-9.1 g/cm^3	8.3-9.4 g/cm^3
Melting temperature (liquidus)	1310-1450°C	1315-1495°C
Young's modulus	Room temp.: 210 GPa 800°C: 160 GPa	Room temp.: 211 GPa 800°C: 168 GPa
Thermal expansion	8-18 × 10^{-6} / °C	12.1-16 × 10^{-6} / °C
Thermal conductivity	Room temp.: 9-11 W/m·K 800°C: 22-23 W/m·K	Room temp.: 10-13 W/m·K 800°C: 25 W/m·K

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Cobalt-based superalloys as well as nickel-based superalloys exhibit the same RSC structure at high temperatures. Despite the high melting point (1494°C for cobalt to 1455°C for nickel), the potential of nickel superalloys is higher due to the observed specific microstructure. This microstructure is based on the precipitation of an ordered γ' phase in the matrix with an RSC structure. The γ' phase shows an A_3B, stoichiometry, as it is in the $Ni_3(Al,Ti)$ nickel-based superalloys which has the $L1_2$ structure [5].

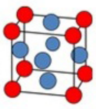
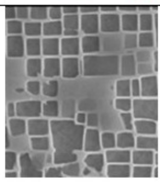
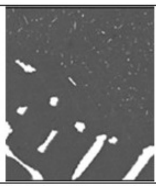
	Nickel	Cobalt
Melting point, °C	1455	1495
Structure	FCC	FCC/HCP (415°C)
Density, g/cm³	8,9	8,9
Strengthen phase	+ Ni_3Al 	✖
Microstructure of alloy		

Fig. 1. List of selected properties of nickel- and cobalt-based materials

The γ′ phase in the new cobalt superalloys is not a direct equivalent of this phase in nickel superalloys, because there is no thermodynamically stable compound of this type in the Co-Al equilibrium system. The phase with the $L1_2$ structure may be found in two-component Co-Ti (Co_3Ti) and Co-Ta (Co_3Ta) systems [6-7]. In the past, studies were carried out on alloys from the Co-Ti system. Unfortunately, the presence of many disadvantages, such as: high degree of crystal lattice mismatch, low volume fraction of the γ′ phase, limited ability to dissolve the components, and insufficient thermal stability resulted in a decline of interest in these materials [8-9].

Addition of W and Al with proper proportion in Co stabilizes the γ′ structure with the stoichiometry $Co_3(Al,W)$ that are stable up to 900°C [10]. The addition of Mo as an alloying element should give similar structural effects as in the case of additional reduction of the alloy density. The range of exchange in those between W and Mo is only up to 3 at. %, beyond which the Co_3Mo equilibrium phase appears with the ordered structure $D0_{19}$ [11].

Unfortunately, there are no data confirming the existence of the $Co_3(Al, Mo)$ phase with the $L1_2$ type of structure compared to the confirmed and existing $Co_3(Al, W)$ phase. $L1_2$ ordering does not take place on aging between 600°C and 800°C only takes place at higher temperatures [12]

The development of Co-Al-Mo-Nb alloys started in 2015 year when the first information was presented by Makineni et al. The stabilization of the microstructure of the γ-γ′ type is influenced by even a small addition of Nb [10-12].

This research group was the first to replaced W to Mo because The density of the W-free alloys is decreased to 8,4 gcm-3 when compared to 9,2 gcm-3 for Co-7Al-7W. At the same time, the presence of W makes it difficult to homogenize Co-Al-W cast alloys [12].

The Co-10Al-5Mo-2Nb alloy has a much lower density and shows a high yield strength compared to other cobalt-based superalloys including Co-Al-W [10-12].

The basic goals of presented investigations are characterization of primary microstructure of Co-20Ni-10Al-5Mo-2Nb alloy and, identification of segregation effect of chemical constituent. Another important element is analysis of Ni addition influence on primary microstructure as well as the precipitation volume, chemical composition and its morphology for modified Co-10Al-5Mo-2Nb alloy [13].

2. Material for testing

The testing material consisted of Co-10Al-5Mo-2Nb and Co-20Ni-10Al-5Mo-2Nb alloys. They were the product of the casting process in the form of a 20×100 mm rod (the shape of the castings is shown in Figs. 2 and 3). The chemical composition of the cast alloys is presented in Tables 2 and 3.

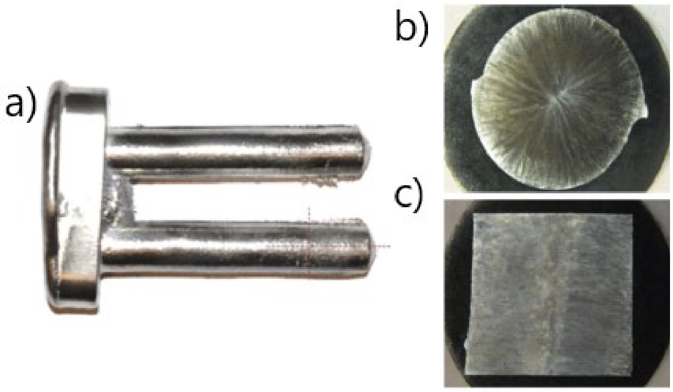


Fig. 2. a) Co-10Al-5Mo-2Nb superalloy cast, b) longitudinal section, and c) cross section through the rod

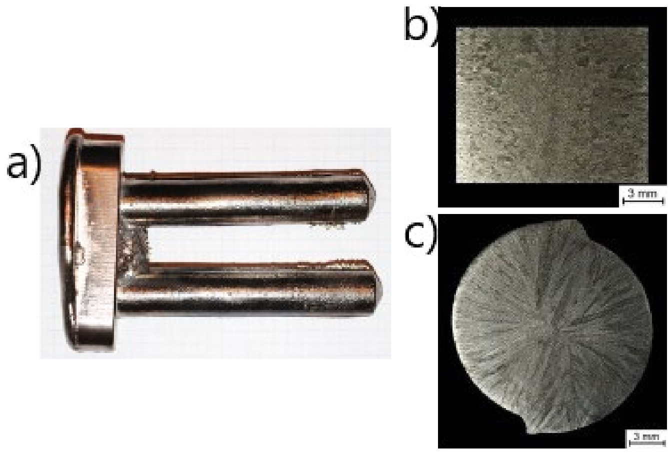


Fig. 3. a) Co-20Ni-10Al-5Mo-2Nb superalloy cast, b) longitudinal section, and c) cross section through the rod

TABLE 2

Actual chemical composition of the Co-10Al-5Mo-2Nb superalloy

Item	Al	Mo	Nb	Co
at%	8.5	4.6	2.0	rest
wt%	3.9	7.6	3.2	rest

TABLE 3

Actual chemical composition of the Co-20Ni-10Al-5Mo-2Nb superalloy

Item	Ni	Al	Mo	Nb	Co
at %	20.5	9.8	5.2	2.4	rest
wt %	20.6	4.5	8.5	3.8	rest

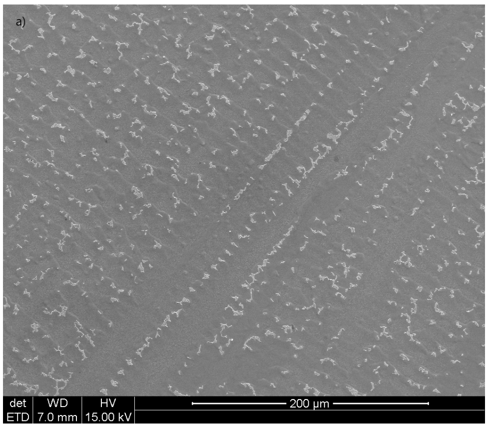
3. Methodology

The observation of the microstructure of the materials was carried out on metallographic microsection. They were made of samples cut from the cross section and longitudinal section of the rod. The microsections were ground, mechanically polished and electrochemically etched (reagent 25 ml H_2O, 50 ml HCl, 15g $FeCl_3$ and 3 g $CuCl_2$ × NH_4Cl × $2H_2O$). The microstructure studies were performed using a Nicon Eclipse 200MA light microscope (LM) at magnification up to 1000× and a Fei Inspect F scanning electron microscope (SEM) at magnification up to 5000×. The structure analysis in greater detail and phase identification were confirmed using a Fei TITAN scanning and transmission electron microscope (S/TEM). The microanalysis of the chemical composition of the precipitates occurring in the microstructure of the material was performed using an EDX detector which analyses chemical composition in micro-areas. The detector in the form of an attachment was part of the scanning and scanning transmission electron microscope.

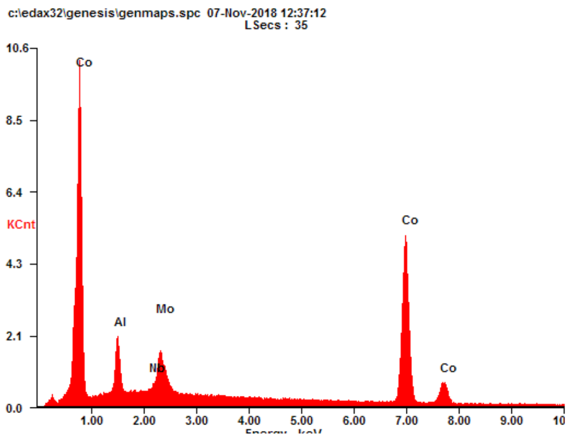
4. Test results

After casting, the Co-10Al-5Mo-2Nb alloy is characterised by a microstructure of a solid cobalt solution (austenitic) with a low content of primary precipitates in interdendritic regions. The microstructure of the alloy as observed using a scanning electron microscope (SEM) is shown in Fig. 4a). The distribution of crystals in the material structure from the surface toward the axis of the sample was observed. The zone of grains "frozen" on the surface of the material, elongated grains and equiaxed grains was also visible. Fig. 4b) shows the microstructure observed using a scanning electron microscope (SEM) as well and analysis of the precipitation area.

Precipitates of complex shape containing a greater amount of niobium and molybdenum relative to the matrix can be observed in the alloy's structure. X-ray studies of the phase composition showed that these precipitates can be composed of Co_3Mo and Co_3Nb phases (Fig. 5).



Element	Wt%	At%
Al	04.18	08.97
Nb	01.36	00.85
Mo	07.14	04.31
Co	87.32	85.87
Matrix	Correction	ZAF



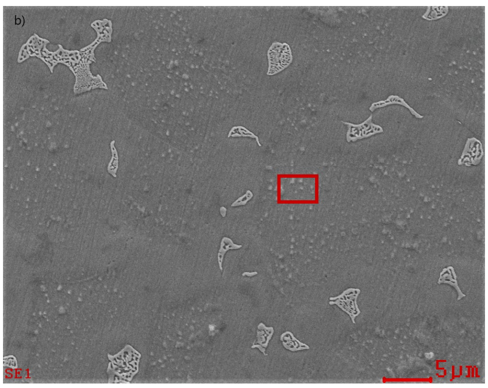


Fig. 4. Microstructure of the Co-10Al-5Mo-2Nb superalloy a) equiaxed crystals b) X-ray microanalysis results for selected areas of the alloy's structure (SEM)

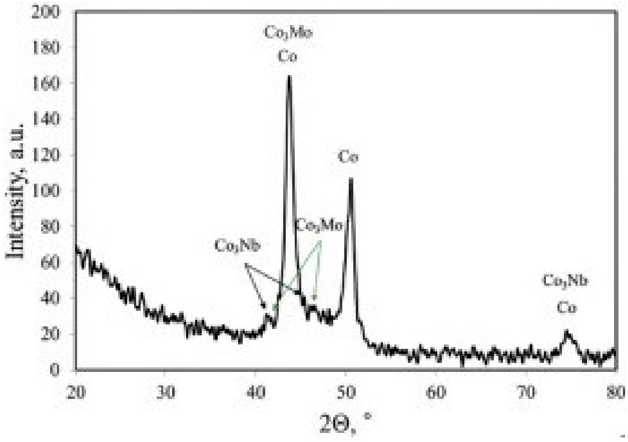


Fig. 5. X-ray diffraction pattern of Co-10Al-5Mo-2Nb superalloy in as-cast condition

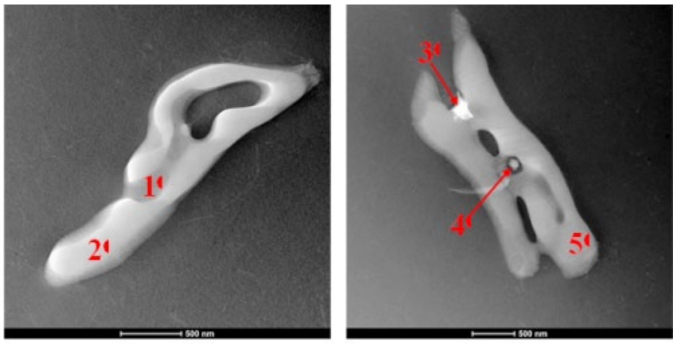
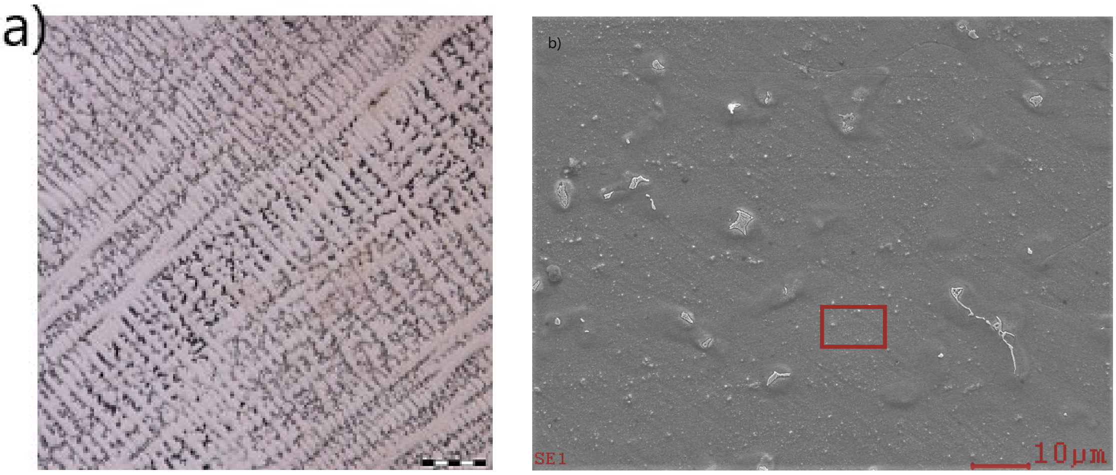


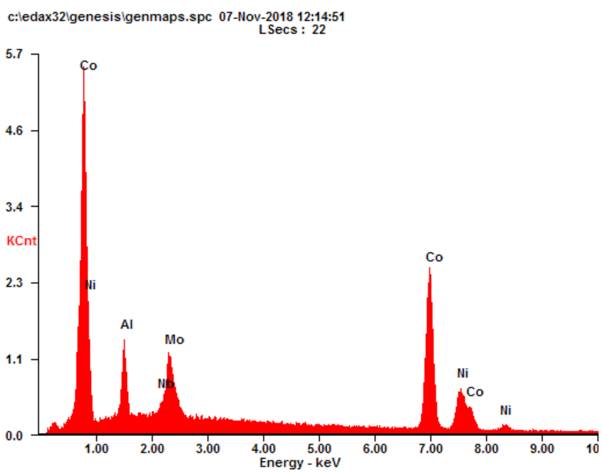
Fig. 6. Microstructure of the Co-10Al-5Mo-2Nb superalloy observed in TEM using an HAADF detector. The table presents the results of EDX microanalysis for selected measurement points

After casting, the Co-20Ni-10Al-5Mo-2Nb alloy is also characterised by a microstructure of a solid cobalt solution (austenitic) with a low content of primary precipitates in interdendritic regions. Light microscopy illustrates the morphology of columnar and equiaxed grains present in both dominant crystal zones. Scanning microscopy shows the four basic zones: three in interdendritic areas and one corresponding to dendrite cores.

The results of X-ray microanalysis for selected areas of the Co-20Ni-10Al-5Mo-2Nb alloy's structure are presented in Fig. 7.

Fig. 8 shows the four zones in the Co-20Ni-10Al-5Mo-2Nb alloy. The first of them consists of precipitates with morphology typical of a eutectic. Areas with a different chemical composition and coniferous morphology can be defined in the immediate vicinity of this component. This zone is probably related to the "cutting" of the microsections on the samples' cross sections. The morphology of the observed elements (Table 4) suggests





Element	Wt%	At%
Al	04.25	09.16
Nb	02.19	01.37
Mo	07.78	04.72
Co	65.13	64.29
Ni	20.65	20.46
Matrix	Correction	ZAF

Fig. 7. Microstructure of the Co-20Ni-10Al-5Mo-2Nb superalloy a) cross-section (LM) b) X-ray microanalysis results for selected areas of the alloy's structure (SEM)

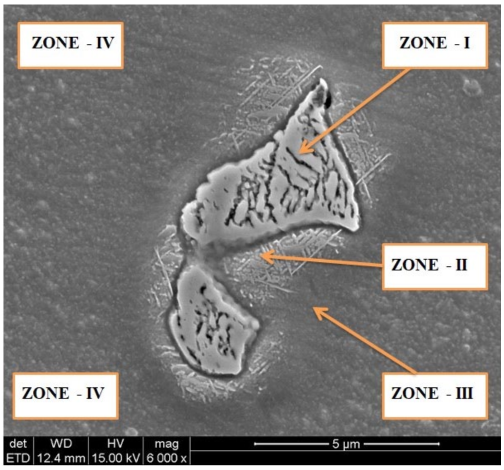


Fig. 8. Zones I-IV occurring in the Co-20Ni-10Al-5Mo-2Nb alloy in the as-cast state (SEM)

TABLE 4

Chemical composition of the analysed Co-20Ni-10Al-5Mo-2Nb alloy in four characteristic

Zone		Co	Ni	Al	Mo	Nb
I	at %	57.89	13.87	4.95	6.82	16.58
II		59.20 ↑	19.27 ↑	8.67 ↑	5.65 ↓	7.22 ↓
III		59.23 ↑	20.20 ↑	9.02 ↑	5.97 ↓	5.58 ↓
IV		62.72 ↑	21.31 ↑	9.52 ↑	4.88 ↓	1.58 ↓
I	wt %	52.01	12.43	2.04	9.99	23.53
II		57.51 ↑	18.65 ↑	3.86 ↑	8.94 ↓	11.05 ↓
III		58.07 ↑	19.73 ↑	4.05 ↑	9.53 ↓	8.62 ↓
IV		63.53 ↑	21.50 ↑	4.42 ↑	8.04 ↓	2.52 ↓

the presence of Co / Co_3 (Al, Mo, Nb) eutectic (first zone) with spheroidal Co_3Mo and / or Co_3Nb phase precipitates with a $D0_{19}$ lattice (second zone). The area marked as zone III is the coating (envelope) of zones I and II without the presence of a eutectic form, but with very fine-grained Co_3 (Al, Mo, Nb) precipitates, possibly of the primary $L1_2$ phase. The last identified morphological form (zone IV) is a Co-based solid solution as a matrix with fine-grained precipitates of probably the primary $L1_2$ phase with the formula Co_3(Al, Mo, Nb). Compared to the aforementioned fine-grained precipitates, in zone IV, this type of structure occupies a much larger area and consists of elements with a shape similar to spherical or cuboidal.

The studies that were carried out with the use of transmission microscopy also showed that the alloy's matrix is made of an RSC cobalt solid solution, which was confirmed by selective area electron diffraction (Fig. 9). Areas rich in niobium, favouring the

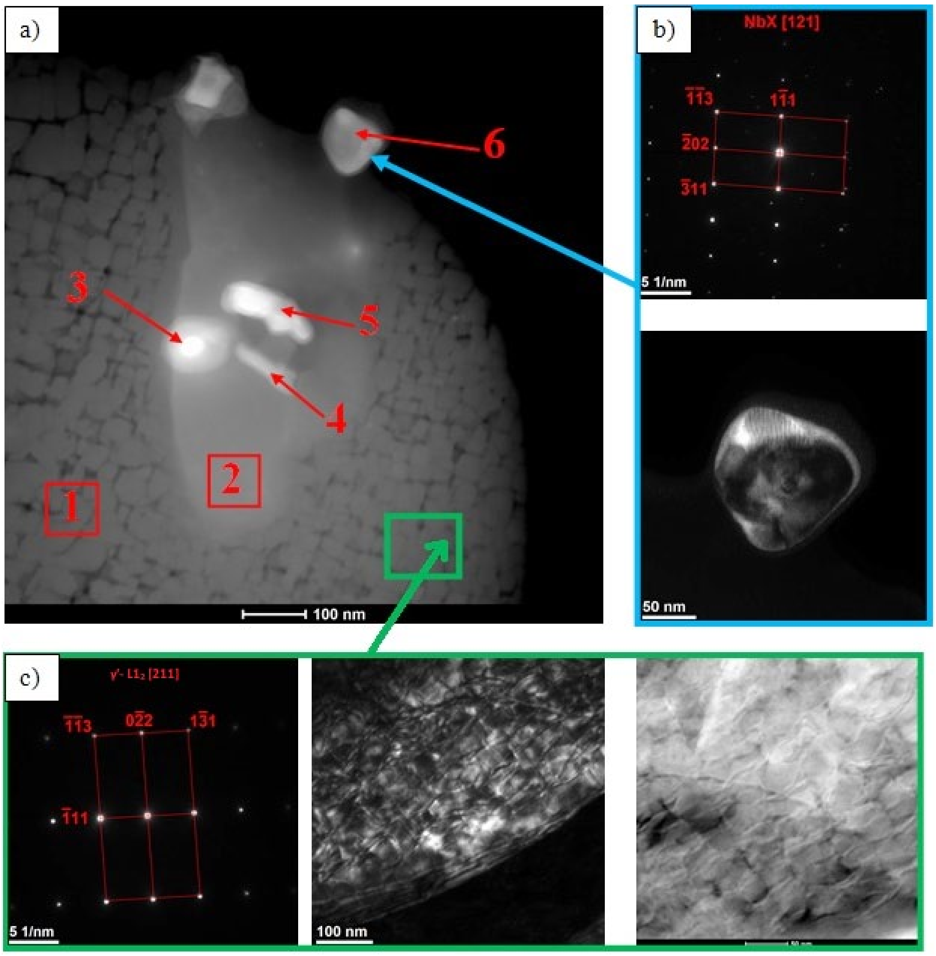


Fig. 9. Images of the microstructure of the Co-20Ni-10Al-5Mo-2Nb superalloy observed in S/TEM: a) fragment of the matrix with precipitates, b) diffraction and dark field from the marked precipitate, c) diffraction, dark field and HAADF image from Co matrix. The table presents the results of EDX microanalysis for selected measurement points

precipitation of Co_3 (Al, Mo, Nb) phases and NbX precipitates, were also observed.

TABLE 5

The results of EDX microanalysis for selected measurement points

Element	Wt [%]					
	1	2	3	4	5	6
Al	3.7	5.2	0.4	1.1	1.7	—
Co	58.3	40.4	39.7	35.4	22.6	0.6
Ni	19.2	7.4	7.8	12.8	10.2	0.1
Nb	5.4	31.4	42.0	45.5	62.9	99.1
Mo	13.4	15.6	10.1	5.2	2.6	0.2

5. Summary

The conducted research showed that the primary structure of the Co-10Al-5Mo-2Nb alloy is characterised by a homogeneous microstructure on the macro scale, consisting of the predominant content of columnar grains and a small amount of equiaxed grains. The obtained microstructure is unfavourable, and further development related to the development of the technological process is necessary. The main structural ingredient of the alloy is a Co solid solution with an addition of Al. Mo and Nb-rich eutectic particles was found in interdendritic areas. The results of the X-ray diffraction analysis suggest the possibility of Co_3Mo and Co_3Nb occurrence in these zones. However, the X-ray microanalysis shows the presence of complex multi-component Co_3(Al, Mo, Nb) and Co_3(Nb, Mo) phases.

The analysis of the primary microstructure of Co-20Ni-10Al-5Mo-2Nb showed that the solidification process in graphite forms had a strong influence on the segregation of alloying elements. The strongest tendency to interdendritic segregation was found for the addition of Nb. A much smaller tendency to segregate was observed in the case of the Mo alloying element. The formation of the Co_3Nb and Co_3Mo phases was probably observed in the interdendritic zone, as well as Coss /Co_3(Al, Mo, Nb) eutectic structures. Both structural components had different morphological forms. The formation of these structural elements causes the depletion of the solution in niobium and molybdenum (on a smaller scale) in the immediate vicinity and a reduction in the tendency for the formation of the primary Co_3 phase (Al, Mo, Nb). The dendrite core areas that are rich in Mo and Nb (in solid solution) showed a much stronger tendency to form the primary Co_3(Al, Mo, Nb) phase in a spherical/cuboidal form. The structure also includes MX precipitates based predominantly on niobium.

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