



New tool materials based on Ni alloys strengthened by intermetallic compounds with a high carbon content

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ABSTRACT

Purpose: The concept of new tool materials, based on Ni alloys strengthened by intermetallic compounds, intended for operations in high temperatures is presented in the hereby paper. The proposed chemical composition and the results of microstructure investigations as well as hardness testing in as-cast condition – are given.

Design/methodology/approach: A test melt of a mass of approximately 1 kg was done in a vacuum furnace, and cast into a ceramic mould. The microstructure of the investigated material was examined by a light microscope Axiovert 200 MAT and the scanning electron microscope FIB Zeiss NEON 40EsB CrossBeam. Dilatometric experiment was performed by means of the Adamel Lhomargy DT 1000 dilatometer .

Findings: The main components of the microstructure of the nickel-base investigated alloy are: the γ phase, which constitutes the matrix and the γ' phase. This γ' phase occurs as fine globular precipitates as well as in a form of primary Ta carbides of MC type. Primary carbides of irregular shapes are uniformly distributed not forming agglomerates. The assumed volume fraction of the primary carbides was achieved.

Research limitations/implications: Identification of microstructure components on Ni-based materials strengthened by particles of intermetallic phases of a high carbon content.

Practical implications: New tool material for hot-working.

Originality/value: The new chemical compositions of tool materials based on Ni alloys strengthened by intermetallic compounds with high carbon content.

Keywords: Tool materials; Ni-based alloys; Intermetallic compounds; Carbides

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MATERIALS

1. Introduction

Tool steels containing from 0.30 to 0.60% C, up to 5% Cr and Mo, W and V are universally applied as tool materials for operations in high temperatures. Tools made of these steels obtain functional qualities by means of a heat improvement, it is by

combining quenching procedures with medium or high tempering. Tempering of tool steels is usually done in the temperature range: 550 - 620 °C. Strengthening is achieved by precipitating alloy carbides of MC and M₂C (V, Mo and W) type [1-6].

Several tools have to operate at temperatures above 600 °C, sometimes even at 1000 °C, at which quenched and tempered steels soften and a lifespan of tools rapidly decreases.

The chemical composition of tool steels was, for many years, modified to improve their hot-working properties. The complex alloys Cr-Ni-Co-Fe with additions of W, Mo, Nb, in which a significant part of iron was substituted by Co were developed [7]. A group of alloys based on the Co matrix (Stellites) of good tribological properties intended for cutting tools was obtained. Those alloys can be divided into certain main groups: Co-Cr-W-C and Co-Cr-W/W-Ni/Fe-C with modifications Si+B [8,9]. Unfortunately the maximum temperature range in which those alloys can operate is 600 - 750 °C only.

A development of high temperature creep-resisting nickel-based alloys was mainly the modification of 80 % Ni and 20 % Cr alloy known for its good creep-resistance. On account of ineffectiveness of strengthening by carbides in high temperatures a hardening of Ni-based alloys was obtained by the intermetallic compound Ni₃(Ti, Al) marked as γ' [10,11].

Several alloys were developed on the concept of Ni-based matrix strengthened by the γ' phase, among others, the alloys of an increased carbon content and a complex chemical composition [12-22].

There are Ni-based alloys - intended for tools operating at temperatures above 600 °C - containing from 0.10 to 0.25 % C, from 8 to 25 % Cr, up to 25 % Co, up to 4 % Ti, up to 4% Al and additions of boron and/or zirconium. Alloys without Co were also developed which, apart from the already mentioned alloy components, contain up to 2.7 % Fe, 1 % Mn and 1 % Si. Those alloys allow to obtain a longer lifespan of tools than of steel tools, however their crack resistance, tendency to wrinkle formation and sticking on surfaces as well as a faster wearing at temperatures higher than 1000 °C, cause that their durability is not satisfactory [23].

There are known applications of Ni-based superalloys such as IN617, RR1000 [24, 25] or alloys of a complex composition [26] for tools operating in high temperatures. However, a carbon content in such alloys is low (not exceeding 0.1%) and as a result obtaining a large fraction of a carbide phase - which would allow to achieve good tribological properties of tools - is not possible.

Tool materials for operations in higher temperatures based on the matrix of intermetallic compounds, called NICRALC alloys, are also noteworthy. Those are Ni-Al-Cr-C alloys and their chemical composition is selected in such a way as to have the matrix constituted solely of the γ' phase [27]. However, obtaining the exactly determined chemical composition and observing strictly the crystallisation procedures, which provide the γ' phase as the matrix, can be difficult under actual industrial conditions.

The concept of new nickel based tool materials, strengthened by intermetallic phases intended for operations in high temperatures, is presented in this paper. The main aim of the endeavours was to determine the microstructural components of this, newly designed, tool material on the Ni matrix strengthened by intermetallic phase compounds.

2. Experimental procedure

The chemical composition of the new Ni-based alloy was designed in the Laboratory of Phase Transformations, Department of Physical and Powder Metallurgy, AGH University of Science and Technology.

The microstructure of the investigated material was examined by the light microscope Axiovert 200 MAT and the scanning electron microscope FIB Zeiss NEON 40EsB CrossBeam.

The measurements of hardness were performed with the Vickers HPO250 apparatus.

Dilatometric experiments were performed by means of the DT 1000 dilatometer made by Adamel, the French Company. Tests were made on samples of a size: $\varnothing 2 \times 12$ mm. The sample was heated to a temperature of 1200 °C with a rate of 0.08 °C/s and cooled to a room temperature with a rate of 0.33 °C/s.

The carbon content was measured by means of the LECO CS-125 analyser.

3. Material for investigations

The chemical composition of the investigated alloy is presented in Table 1. The chemical composition of this new material was designed in such a way as to obtain the matrix strengthening by precipitations of metallic compounds rich in Ni accompanied by a high carbide fraction. Carbides should remain stable in the microstructure - regardless of the heat treatment - since they favourably influence an abrasion resistance. It was assumed, when designing the alloy composition, that the primary Ta carbides of MC type will be formed. The Ta content was selected to bind carbon into a carbide form and to form the γ' phase together with Al and Ni. Zirconium was added to harden grain boundaries while cobalt to strengthen the γ solid solution and to obtain the microstructure stabilisation. The Ni matrix was chosen due to the lack of allotropic transformation, which could destabilise the microstructure and properties during a hot-working exploitation.

Table 1.
The chemical composition (wt. %) of the investigated alloy

C	Ta	Al	Zr	Co	P max	S max	Ni
0.88	6.0	3.0	0.2	20.0	0.01	0.01	Bal.

A test melt of a mass of approximately 1 kg was done in a vacuum furnace, and cast into a ceramic mould. The photograph of the investigated alloy casting together with the first cut sample (as an example) is shown in Figure 1. Samples were cut from the casting foot. Examinations were made on polished sections parallel and perpendicular to the casting surface.

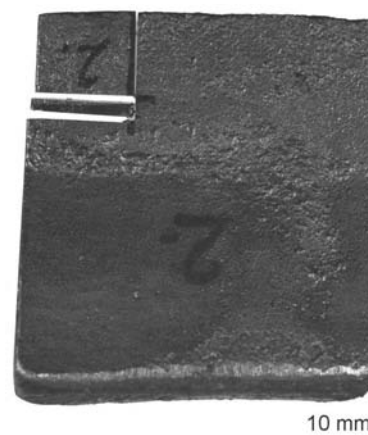


Fig. 1. Photograph of the investigated alloy casting

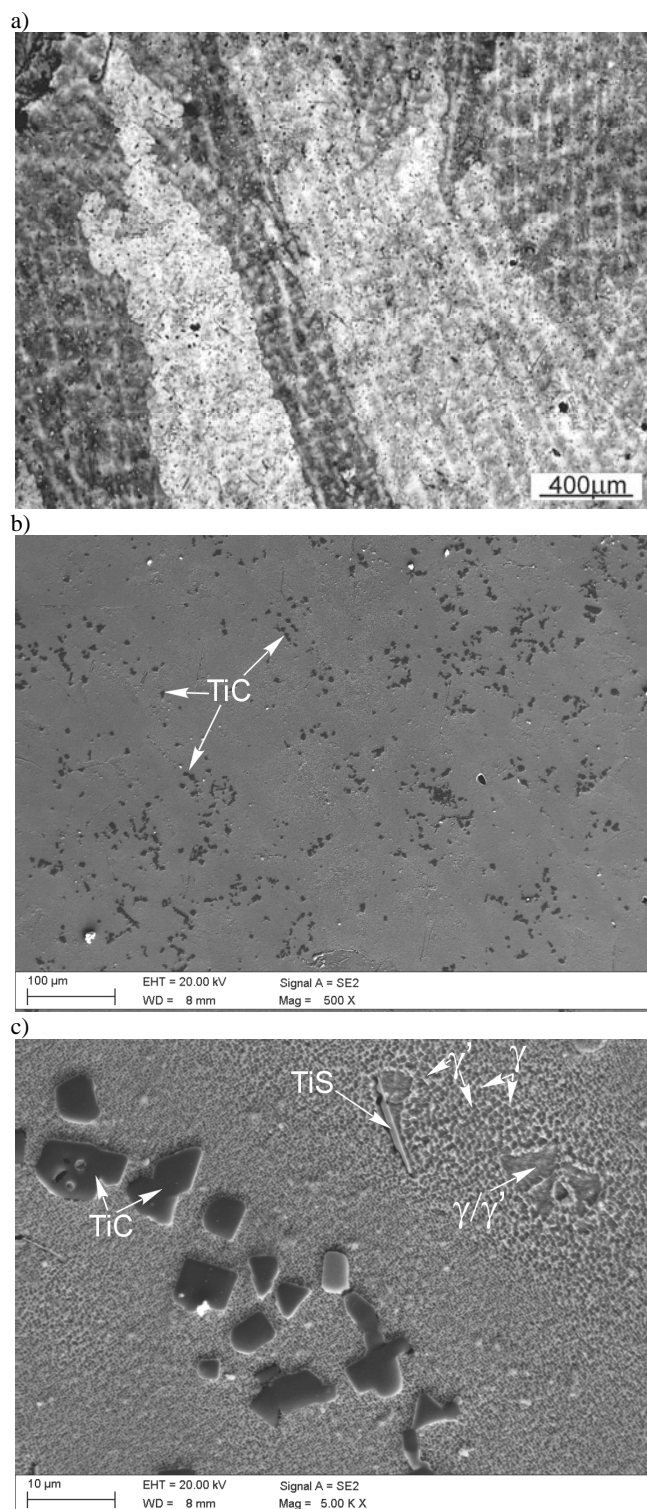


Fig. 2. The microstructure of the Ni-based alloy with Ti and Fe
 a) Morphology of grains from the casting in the light microscope;
 b) Morphology of carbides, SEM c) Phases occurring in the microstructure, SEM [28]

The investigated alloy is a modification of the alloy presented and described by the author in the reference [28]. Ti was added as a carbide forming element. When designing the chemical composition it was assumed that primary Ti carbides of MC type will be formed. The Ti content was selected in such a way that this element will bind carbon as a carbide and form the γ' phase together with Al and Ni. Iron was also used, due to metallurgical reasons, to facilitate an introduction of more carbon and to decrease alloy costs. Example of this alloy microstructure in as-cast state are shown in Figure 2. The main components of the microstructure of the nickel-based alloy with Ti were: the γ phase, which constitutes the matrix and the γ' phase. This γ' phase occurs in a small volume fraction as globular precipitates and, in the majority of cases, in a form of irregular precipitates in narrow matrix channels as well as in a form of primary Ti carbides of MC type. Primary carbides of irregular shapes are uniformly distributed not forming agglomerates however, some clusters were also seen.

4. Research results and discussion

The microstructures of the investigated alloy in as-cast state are shown in Figure 3. Large grains, characteristic for as-cast state material, are visible (Fig. 3a). Dendritic areas are exhibited inside these grains (Fig. 3b). Primary dendrites with secondary branches are seen. Tantalum carbides of MC type are distributed in interdendritic areas (Fig. 3c). carbides were identified by the EDS analysis.

The volume fraction of carbides, which is equal 23.8%, was estimated by the point-count method. Primary carbides of irregular oblong shapes and various sizes (Figs. 3c and f) are distributed uniformly not forming aggregates. Nevertheless, contrary to the alloy with titanium, described in reference [28] where carbides were in the total volume of material (Figs. 2a and b), they are in interdendritic areas. In addition, a small amount of graphite was found (Figs. 3d and e).

Hardness measurements were carried out on samples taken from different places on the ingot cross-section. Hardness measured at the ingot surface equals 222 HV and increases in the direction of the casting axis to 243 HV. This is a result of alloying elements segregation in front of the crystallisation, however hardness differences are not large. Carbides and fine precipitates of the intermetallic phase in the γ matrix are seen in the photograph from the scanning electron microscopy (Fig. 3f). This intermetallic phase is so small that its identification was not possible by the EDS analysis. This phase is rich in nickel, aluminium, tantalum and cobalt. The most probably it is the γ' phase. However, it requires confirmation by means of the TEM. Assuming that the mentioned above phase is the γ' phase, substitution of titanium by tantalum caused the morphology change of both phases (compare Figs. 2 and 3). Simultaneously an alloy of a better purity - it means without sulphides and eutectic γ/γ' areas characteristic for nickel-based alloys in as-cast condition - was formed (see Fig. 2c). Such eutectic due to its brittleness is an undesirable component.

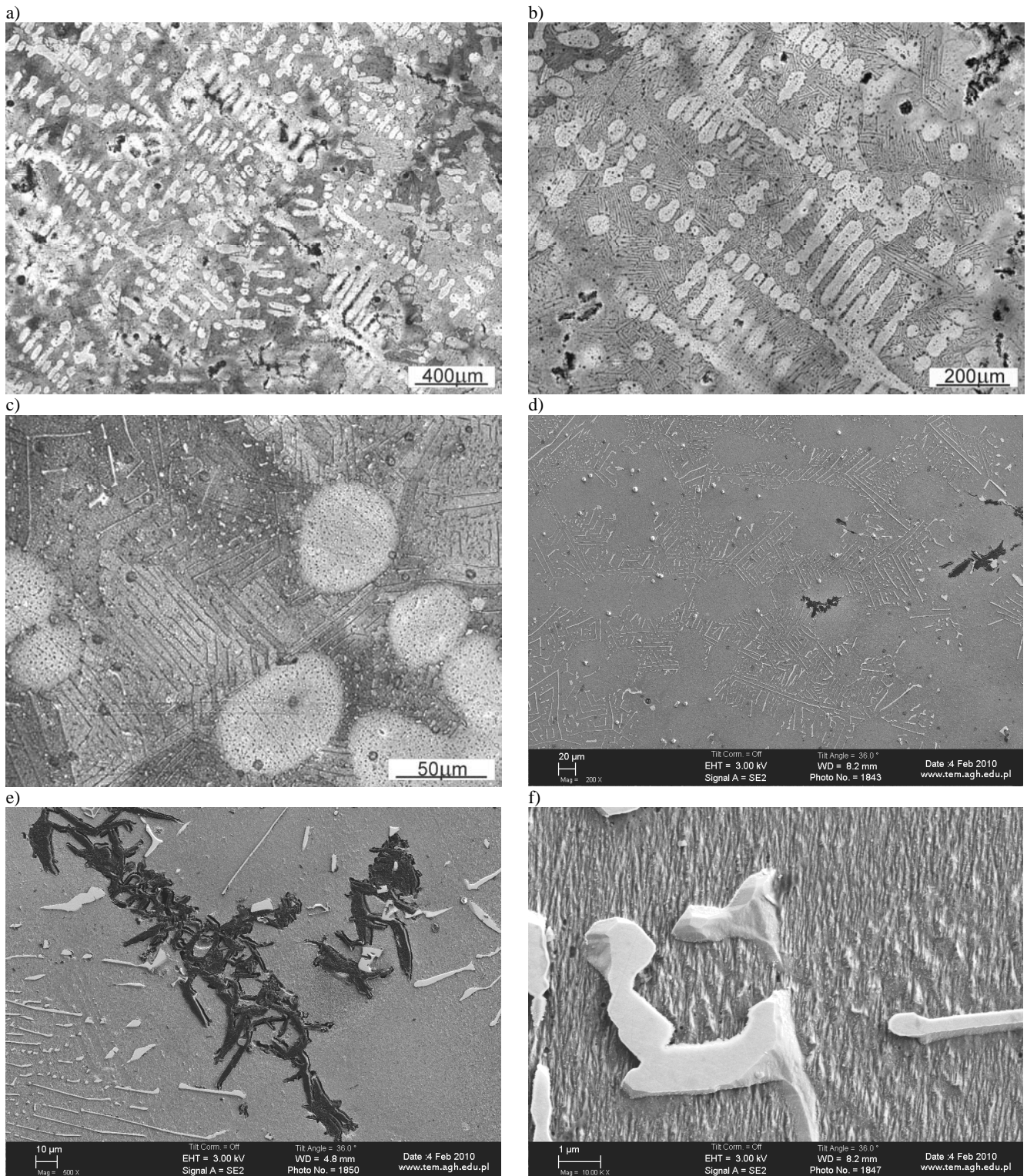
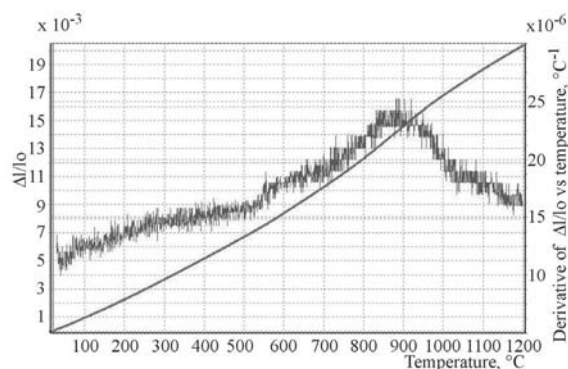


Fig. 3. Microstructures of the investigated alloy. a) Area of some grains, the light microscope, b) Dendrites within a single grain, the light microscope, c) Carbides in interdendritic areas, the light microscope, d) Carbide phase morphology, SEM, e) Graphite precipitations, SEM, f) Morphology of the carbide and intermetallic phases, SEM

The γ phase constitutes the matrix. The estimation of the γ' phase fraction in as-cast state is very difficult. According to [10] tantalum significantly diffuses into the γ' phase causing an increase of this fraction in the alloy. Strengthening of the γ' phase by tantalum is caused by large sizes of its atoms. However, on the basis of the presented hereby results, it seems that at a high carbon content (0.88 %) tantalum prefers the carbide phase which fraction is decisively higher than in alloy with Ti [28]. Therefore the γ' phase fraction in the investigated alloy seems smaller than in alloy with Ti (Fig. 2 and [28]).

Dilatometric curve of heating with a rate of 0.08 °C/s up to a temperature of 1200 °C are shown in Figure 4a, together with dilatometric curve of cooling with a rate of 0.33 °C/s to an ambient temperature (Fig. 4b). During heating, at a temperature of app. 540 °C, the dilatation positive effect, the most probably related to the tantalum carbide (of MC type) precipitation, was recorded. At a temperature of app. 760 °C the successive positive dilatation effect, the most probably related to the precipitation of intermetallic phases, superimposes. It is also possible, that both effects, it means the precipitation of carbides and intermetallic phases, start simultaneously and at 760 °C the change of their precipitation kinetics occurs. When a temperature increases both processes significantly intensify.

a)



b)

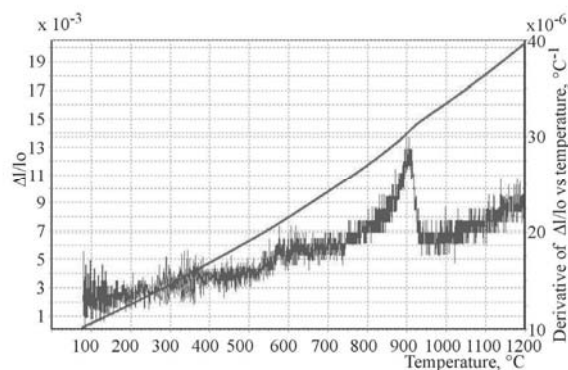


Fig. 4. a) Dilatometric curve of heating from as-cast condition with a rate of 0.08 °C/s, up to a temperature of 1200 °C/s; b) Dilatometric curve of cooling from a temperature of 1200 °C with a rate of 0.33 °C/s

At a temperature of app. 920 °C an expansion decrease (shrinkage on a differential curve), caused the most probably by dissolving of the intermetallic phases, occurs.

A negative dilatation effect, related probably to the precipitation of secondary tantalum carbides (of MC type), was recorded on the cooling curve (Fig. 4b). This effect was recorded in the temperature range 930-520 °C.

Linear expansion coefficients of the investigated alloy determined during heating and cooling processes are shown in Table 2. It is worth to mention that the highest values of the linear expansion coefficient are in the temperature range: 800-1000 °C. Taking into consideration the concept of applying the investigated material as a material to be used for operations in high temperatures, this last observation indicates that tools made of this alloy should not be heated up to this temperature range during work. The increase of the linear expansion coefficient is caused by phase transformations. Thus, such heat treatment technology of the investigated alloy, which would provide the stable microstructure (without phase transformations) in the temperature range of 800-1000 °C, should be developed. Another solution would constitute the chemical composition modification in such a way as to shift these transformations into higher temperatures (above 1000 °C).

Table 2.

Coefficient of linear expansion of the investigated alloy in the temperature range: 20 °C-1200 °C

	Temperature range, °C					
	20-100	100-200	200-300	300-400	400-500	500-600
heating	12.02	12.93	14.18	14.88	15.37	17.01
cooling	-	13.30	14.03	15.00	15.45	16.72
	Temperature range, °C					
	600-700	700-800	800-900	900-1000	1000-1100	1100-1200
heating	18.62	20.32	22.95	22.09	18.47	17.00
cooling	18.17	19.17	22.46	21.37	20.27	22.16

Photographs of microstructures of the investigated alloy after heating and cooling procedures in dilatometer are seen in Figures 5 and 6. As can be noticed (Fig. 5a) regardless of applying a slow heating (0.08 °C/s) up to a temperature of 1200 °C and a slow cooling (0.33 °C/s) residues of the primary structure (after crystallisation) can be seen in the microstructure. Primary tantalum carbides of MC type remained in the microstructure, all the same their solution process was initiated at a temperature of 1200 °C (compare Figs. 3d and f with Figs. 6a and c). The presence of the intermetallic phase, which was seen directly after casting, was not found in the microstructure. Heating up to 1200 °C caused its solving. On the bases of these two, given above, information it can be stated, that such selection of the temperature from which the investigated alloy will be superquenched - in order to remain the stable primary tantalum carbides (of MC type) and to dissolve the intermetallic phase (or phases) - is possible. This provides the possibility of modifying alloy properties by further heat treatments such as stabilisation and aging. On account of the expected applications of the investigated alloy it can be possible to simplify the heat treatment and limit it to two operations: hyperquenching and aging. The slow cooling (0.33 °C/s) after heating to 1200 °C was chosen in order to determine inclinations to secondary precipitates in the investigated alloy.

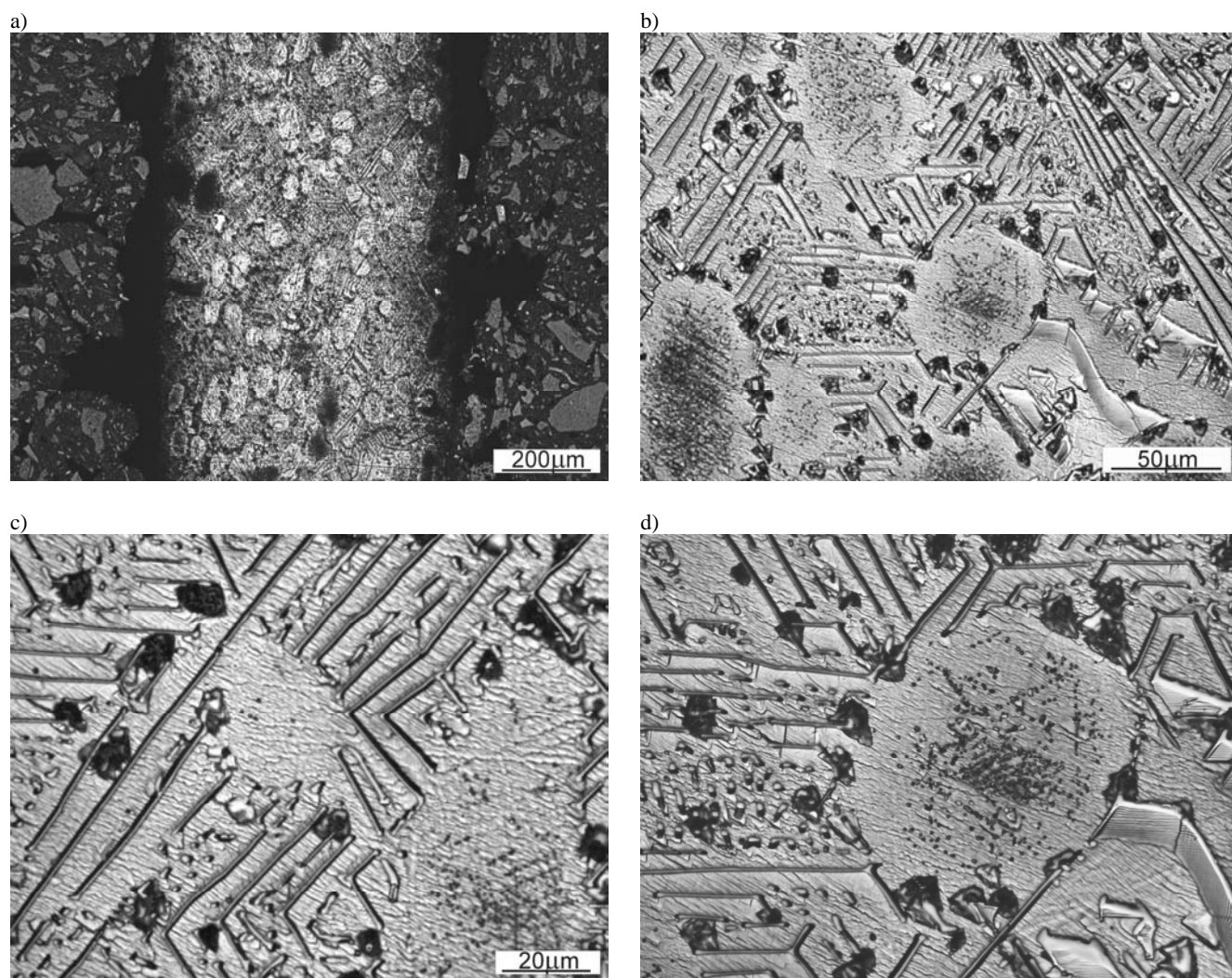


Fig. 5. Microstructures of the investigated alloy after the heat treatment carried out by means of the dilatometer (the light microscope). a) Remains of the primary structure, b) One grain area, c) Primary tantalum carbides morphology (MC type), d) Fine secondary tantalum carbides in the dendrite zone and surrounding primary carbides

The secondary tantalum carbides (MC type) precipitated during cooling from 1200 °C are shown in Figure 6d. Those carbides precipitate in dendritic zones. This indicates the necessity of application the higher cooling rate during hyperquenching. The secondary tantalum carbides are very fine and of irregular shapes.

However, it seems that at optimising the hyperquenching temperature in such a way as not to dissolve the primary tantalum carbides (while to dissolve the intermetallic phase) and to increase the cooling rate, the intensity of these effects should be limited. Nevertheless the problem of the carbide phase instability during aging (precipitation of carbides) still remains. Thus, the temperature and time of aging should be selected in such a way as either to bind total carbon into carbides or to modify the chemical composition by additions of other elements forming stable primary carbides. On account of a graphite presence in the

microstructure a much better solution seems to be the chemical composition modification.

Further studies on nickel-base tool alloys strengthened by the intermetallic phases with a high carbon content will be carried out in order to determine their tribological properties at an ambient temperature as well as at the expected temperature range of operations, eventual forging possibilities, optimization of their chemical composition and heat treatment. The modification of the chemical composition will consist of introducing elements increasing creep-resistance, it is: chromium and cobalt. It seems that due to a smaller volume fraction of the intermetallic phase as compared to the previous alloy with Ti [28] it will be necessary to design alloy with titanium and tantalum, to obtain intensive matrix strengthening (hardness) in result of the heat treatment.

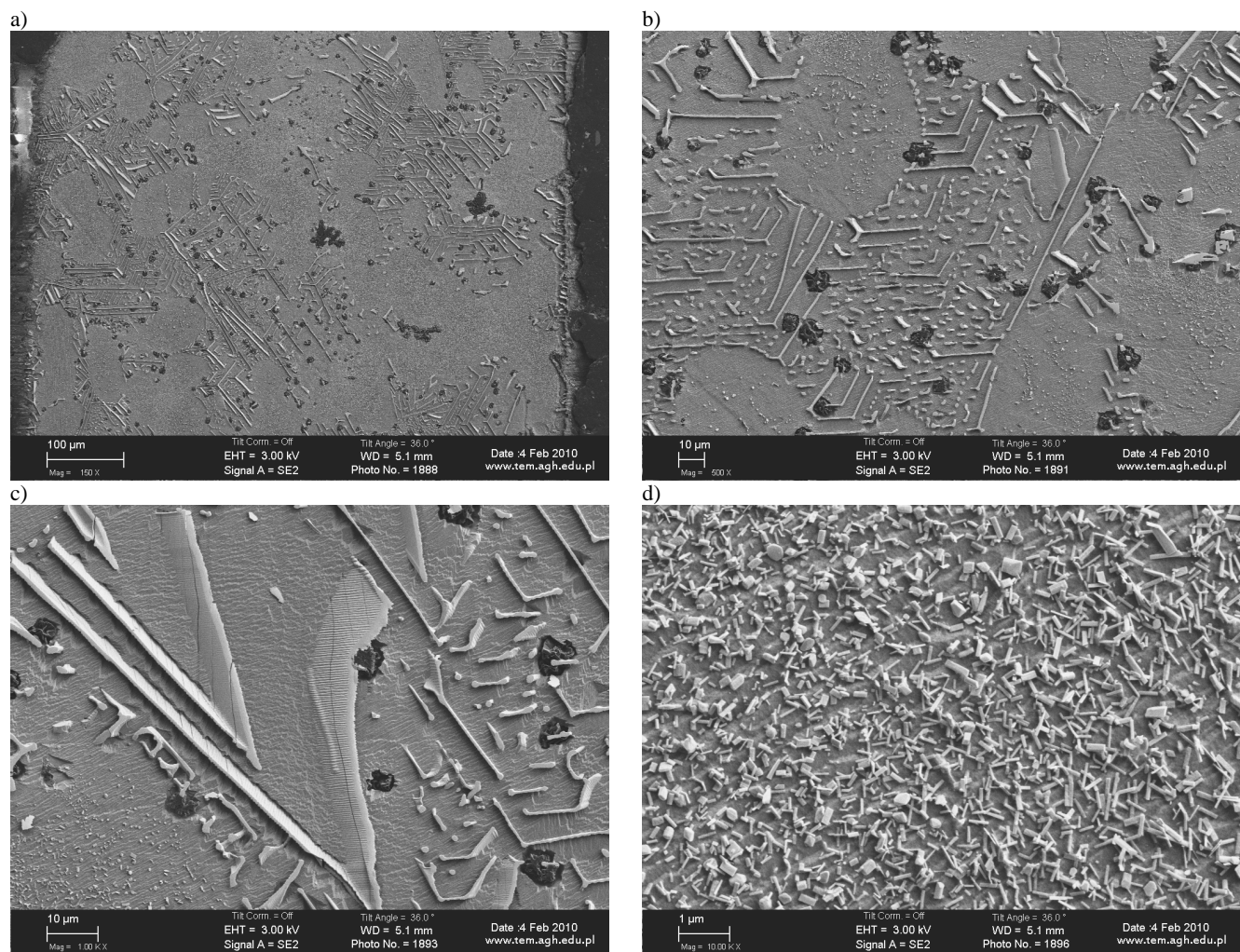


Fig. 6. Microstructures of the investigated alloy after the heat treatment (SEM). a) Area of a few grains, b) Primary and secondary tantalum carbides, c) Primary tantalum carbides of MC type, d) Secondary tantalum carbides, MC type, precipitated during cooling inside dendrites

5. Conclusions

The main microstructure components of the investigated Ni-based alloy of a high carbon content are: the γ phase, which constitutes a matrix, the γ' phase, which occurs as fine globular precipitates and the primary Ta carbides of MC type. The primary carbides of irregular shapes are distributed uniformly not forming agglomerates. The substitution of titanium by tantalum caused changes of the morphology both carbide and γ' phases. Simultaneously the new alloy of a better purity, it means without sulphides and zones of the γ/γ' eutectic characteristic for nickel-based alloys in as-cast condition.

During heating at a temperature of approximately 540 °C begins the tantalum carbides precipitation process (MC type) followed (or simultaneous) by the intermetallic phases precipitation.

Above a temperature of 920 °C the intermetallic phase (or phases) dissolves. The primary tantalum carbides of MC type

remained in the microstructure nevertheless their dissolving process was initiated at a temperature of 1200 °C. The presence of the intermetallic phase - which occurred directly after casting - was not found in the alloy microstructure after cooling. Heating up to 1200 °C caused its dissolving.

The precipitation of secondary carbides during cooling was found. These carbides are precipitating in dendritic zones. This indicates the necessity to apply higher cooling rates during hyperquenching. The secondary tantalum carbides are very fine and of irregular shapes.

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