A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 59 2014 Issue 3
DOI: 10.2478/amm-2014-0164

P. BAŁA*,**

THE DILATOMETRIC ANALYSIS OF THE HIGH CARBON ALLOYS FROM Ni-Ta-Al-M SYSTEM

BADANIA DYLATOMETRYCZNE WYSOKOWĘGLOWYCH STOPÓW Z UKŁADU Ni-Ta-Al-M

In the following work presents results of high carbon alloys from the Ni-Ta-Al-M system are presented. The alloys have been designed to have a good tribological properties at elevated temperatures. Despite availability of numerous hot work tool materials there is still a growing need for new alloys showing unique properties, which could be used under heavy duty conditions, i.e. at high temperatures, in a chemically aggressive environment and under heavy wear conditions. A characteristic, coarse-grained dendritic microstructure occurs in the investigated alloys in the as-cast condition. Primary dendrites with secondary branches can be observed. Tantalum carbides of MC type and graphite precipitations are distributed in interdendritic spaces in the Ni-Ta-Al-C and Ni-Ta-Al-C-Co alloys, while Tantalum carbides of MC type and Chromium carbides of M_7C_3 type appeared in the Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys. In all alloys γ' phase is present, however, its volume fraction in the Ni-Ta-Al-C and Ni-Ta-Al-C-Co alloys is small.

During heating from as-cast state in Ni-Ta-Al-C and Ni-Ta-Al-C-Co alloys, the beginning of the tantalum carbides precipitation process (MC type) followed (or simultaneous) by the intermetallic phase precipitation (γ' – Ni_3(AlTa)) was stated, while in Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys, besides Tantalum carbides also the Chromium carbides precipitation occurred. It means that the investigated alloys were partially supersaturated in as-cast state. Above 1050°C in all investigated alloys the γ' phase is dissolving. In addition, the precipitation of secondary carbides during slow cooling was occured.

Keywords: Ni-based alloys, phase transformation, dilatometric analysis, gamma prime phase, carbides

W pracy przedstawiono wyniki badań nowych stopów z układu Ni-Ta-Al-M o dużym stężeniu węgla. Stopy te zostały zaprojektowane do pracy w wysokiej temperaturze i w warunkach silnego zużycia tribologicznego. Pomimo, że istnieje wiele materiałów narzędziowych do pracy na gorąco wciąż istnieje silna potrzeba poszukiwania nowych materiałów o unikatowych wł asnościach, które mogłyby pracować w bardzo trudnych warunkach, tj. wysokiej temperaturze, agresywnym chemicznie środowisku i w warunkach silnego zużycia tribologicznego.

W stanie po odlaniu badane stopy cechują się charakterystyczną budową dendrytyczną. Widoczne są pierwszo i drugorzędowe dendryty. W stopach Ni-Ta-Al-C i Ni-Ta-Al-C-Co w obszarach międzydendrytycznych rozmieszczone są węgliki tantalu typu MC oraz grafit, natomiast w stopach Ni-Ta-Al-C-Co-Cr i Ni-Ta-Al-C-Cr węgliki tantalu typu MC oraz węgliki chromu typu Cr_7C_3. We wszystkich stopach występuje faza γ', choć jej udział objętościowy w stopach Ni-Ta-Al-C i Ni-Ta-Al-C-Co jest nieduży.

Podczas nagrzewania ze stanu lanego w stopach Ni-Ta-Al-C i Ni-Ta-Al-C-Co stwierdzono wydzielanie węglików wtórnych tantalu typu MC z następnym (lub równoczesnym) wydzielaniem fazy (γ' – Ni_3(AlTa)). Natomiast w stopach Ni-Ta-Al-C-Co-Cr i Ni-Ta-Al-C-Cr oprócz węglików wtórnych tantalu wydzielają się węgliki wtórne chromu. Oznacza to, że badane stopy w stanie po odlaniu były w stanie częściowego przesycenia. Powyżej 1050°C we wszystkich badanych stopach rozpuszczają się wydzielenia fazy γ'. Wtórne wydzielanie węglików stwierdzono również podczas wolnego chłodzenia od temperatury 1200°C.

1. Introduction

A typical material for tools production are steels. For high temperatures application a hot-work and high speed steels, are applied [1÷5]. Usually, the most important attribute of the steel is high impact resistant, which is required for long service life. Therefore, their microstructures do not include a primary or secondary carbides. Tools made of these steels obtain high service properties by toughening, it is by combining quenching with medium or high tempering [1,2]. Some tools have to operate at temperatures above 600°C, sometimes even at 1000°C, at which quenched and tempered steels soften. Causing that, a lifespan of tools rapidly decreases.

A development of high temperature creep-resistant nickel-based alloys was mainly the modification of 80% Ni and 20% Cr alloy already known for its good creep-resistance. Considering an ineffectiveness of strengthening by carbides in high temperatures, a hardening of Ni-based alloys was obtained by the intermetallic compound Ni_3(Ti, Al) designated as γ' [6].

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND
** AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, ACADEMIC CENTRE FOR MATERIALS AND NANOTECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

Several alloys were developed on the concept of Ni-based matrix strengthened by γ' phase, among others, the alloys of an increased carbon content and a complex chemical composition [7,8].

Applications of Ni-based superalloys such as IN617, RR1000 [9,10] or alloys of a complex composition [11] for tools operating at high temperatures are common. However, a carbon content in such alloys is quite low (not exceeding 0.1%), so obtaining a large volume fraction of carbides, which would allow to achieve the good tribological properties of tools, is not possible. That's why there are still researches for the new materials with unique properties, such as the newly designed alloys from the Ni-Ta-Al-M system with very good tribological properties at elevated temperatures [12,13]. The problem always is the stability of their properties with increasing temperature. All the new groups of materials, such as metallic glasses [14,15] or nanomaterials [16] should be described in details before an industrial application. Therefore, the determination of microstructure stability of the new designed high carbon Ni-based alloys from the Ni-Ta-Al-M system and inclination to secondary precipitations were the purpose of the presented paper.

2. Material for investigations

The chemical compositions of the new Ni-based alloys (Table 1) were designed in the Laboratory of Phase Transformations, Department of Physical and Powder Metallurgy, AGH University of Science and Technology. Four Ni-Ta-Al-C-M alloys were designed and cast. Their chemical compositions were tailored to obtain the matrix strengthening by precipitation of the γ' phase and minimum 20 vol.% of primary carbides. The presence of a carbide eutectic in the given system is crucial. Carbides should remain stable in the microstructure regardless of heat treatment conditions in order to improve the wear resistance. It was decided to use Ni matrix due to the lack of allotropic transformations, which could destabilise the microstructure and properties during the high-temperature exploitation. It was assumed that primary Ta carbides (of MC type) and Cr carbides (in alloys containing Chromium) would be formed. The amount of Tantalum was calculated to bind carbon and form the γ' phase together with Aluminium and Nickel. The content of Aluminium and other elements (forming γ') were chosen to have the γ' solvus temperature between 1000 and 1100°C. Therefore, the content of Aluminium is only 3 mass%. The temperature range mentioned above allows working up to 1000°C and gives the possibility of solution heat treatment in the safe range without any partial melting in regions of the carbide eutectic occurrence.

In order to determine the stability of carbides in the presence of graphite, the composition of the Ni-Ta-Al-C alloy was chosen to obtain primary MC carbides, graphite and negligible volume fraction of γ' in the microstructure. The Ni-Ta-Al-C-Co alloy was designed in a similar way. In that case bigger volume fraction of γ' was expected to determine the stability of carbides in the presence of graphite, γ' and Cobalt (element, which does not create carbides). The Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys were designed to obtain both Tantalum (MC) and Chromium carbides and a large volume fraction of γ'.

TABLE 1
The chemical composition (wt. %) of the investigated alloys

	C	Cr	Ta	Al	Zr	Co	Ni
Ni-Ta-Al-C	0.815	–	5.9	2.7	0.2	–	balance
Ni-Ta-Al-C-Co	0.878	–	6.1	2.8	0.2	20.2	balance
Ni-Ta-Al-C-Co-Cr	0.898	20.5	6.3	2.9	0.2	19.5	balance
Ni-Ta-Al-C-Cr	0.834	19.4	6.1	2.8	0.2	–	balance

3. Experimental procedure

The melts of a mass of approximately 1 kg were made in a vacuum furnace, and cast into a ceramic moulds. Samples were cut from the casting foot.

The carbon content was measured using the LECO CS-125 analyser. The content of the others elements were measured by the EDS analysis.

The analysis of phase transformation was conducted by use of the high resolution Adamel-Lhomargy DT 1000 dilatometer. The samples were heated at the rate of 0.08°C/s up to 1200°C and next cooled (at the rate of 0.33°C/s) to the room temperature to check the inclination to secondary precipitations.

The microstructures of the dilatometric samples were investigated by use of the scanning electron microscope FIB Zeiss NEON 40EsB CrossBeam.

4. Results and discussion

A characteristic, coarse-grained dendritic microstructure occurs in the investigated alloys in the as-cast condition (Fig. 1). Primary dendrites with secondary branches can be observed. Tantalum carbides of MC type and graphite are distributed in interdendritic spaces in the Ni-Ta-Al-C and

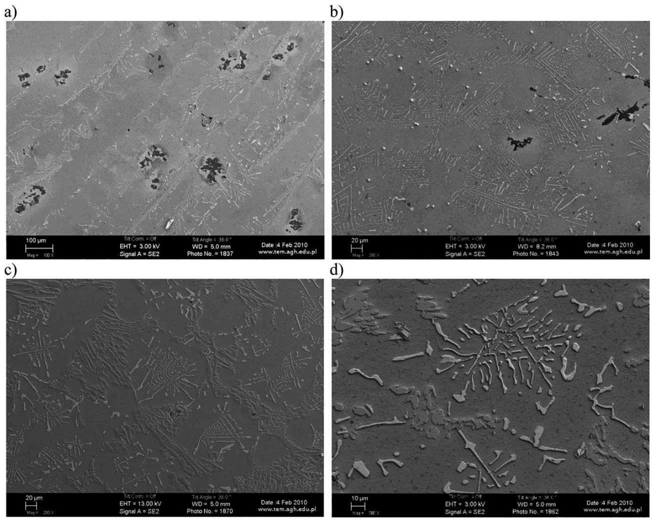

Fig. 1. Microstructures of investigated alloys in as-cast state:
a) Ni-Ta-Al-C alloy; b) Ni-Ta-Al-C-Co alloy; c) Ni-Ta-Al-C-Co-Cr alloy; d) Ni-Ta-Al-C-Cr alloy

Ni-Ta-Al-C-Co alloys, while Tantalum carbides of MC type and Chromium carbides of M_7C_3 type were observed in the Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys. In all alloys precipitations of γ' occurs, however, its volume fraction in the Ni-Ta-Al-C and Ni-Ta-Al-C-Co alloys is small. An example γ' phase morphology in Ni-Ta-Al-C-Co-Cr alloy is shown in Fig. 2.

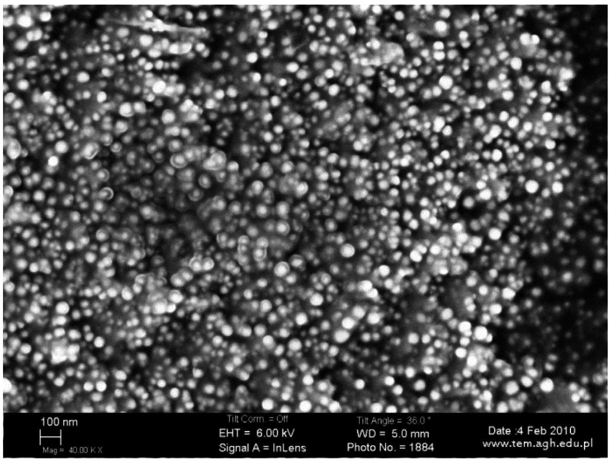

Fig. 2. Morphology of γ' in Ni-Ta-Al-C-Co-Cr alloy

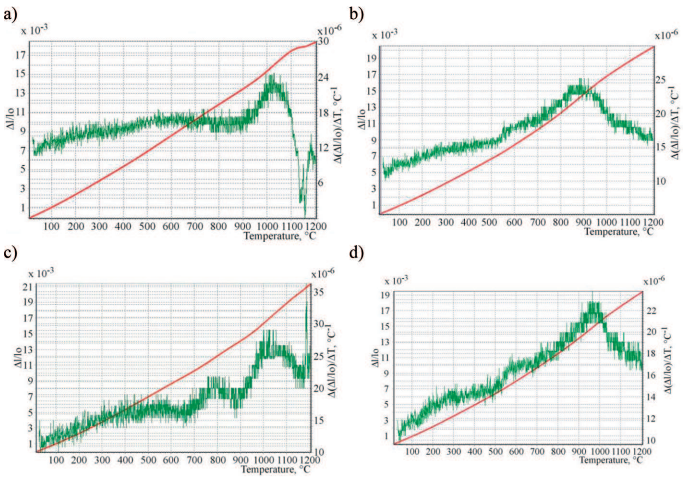

Fig. 3. Dilatograms of heating with the corresponding differential curves. Heating rate 0.08°C/s. a) Ni-Ta-Al-C alloy; b) Ni-Ta-Al-C-Co alloy; c) Ni-Ta-Al-C-Co-Cr alloy; d) Ni-Ta-Al-C-Cr alloy

Dilatometric curves of heating at a rate of 0.08°C/s up to a temperature of 1200°C are shown in Fig. 3. Additionally, in Fig. 4, an example dilatometric curve of cooling at a rate of 0.33°C/s to an ambient temperature for Ni-Ta-Al-C-Cr, is presented. During heating in all investigated alloys at a temperature of app. 500-540°C, the dilatation positive effect, the most probably related to the secondary Tantalum carbide (of MC type) precipitation, was recorded. In Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys it is also possible that the secondary Chromium carbides precipitate. Then, except Ni-Ta-Al-C alloy in which any significant effect was recorded, at a temperature of app. 700°C the successive positive dilatation effect, the most probably related to the precipitation of γ' phases superimposes. It is also possible, that both effects the precipitation of secondary carbides and the γ' phases, start simultaneously and at 700°C the change of their precipitation kinetics occurs. When a temperature increases both processes significantly intensify. Next, higher up 900°C in all investigated alloys a strong positive effects were recorded. These effects are the most probably related to the γ' precipitations growth. At a temperature of app. 1020°C an expansion decrease (shrinkage on a differential curve), caused the most probably by start dissolution of the precipitation of γ' phases. During cooling in all investigated alloys a negative dilatation effects, related to the precipitation of secondary Tantalum carbides of MC type (in Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys, additionally, the secondary Chromium carbides), were recorded.

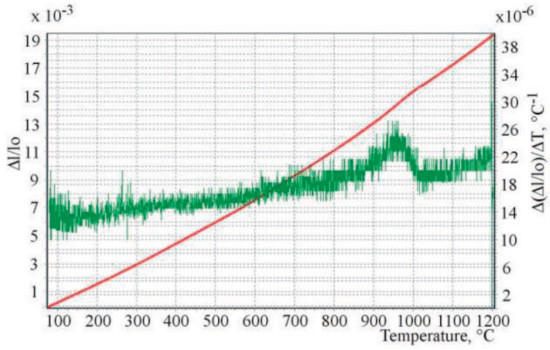

Fig. 4. Example dilatogram of cooling from 1200°C with the rate of 0.33°C for Ni-Ta-Al-C-Cr alloy

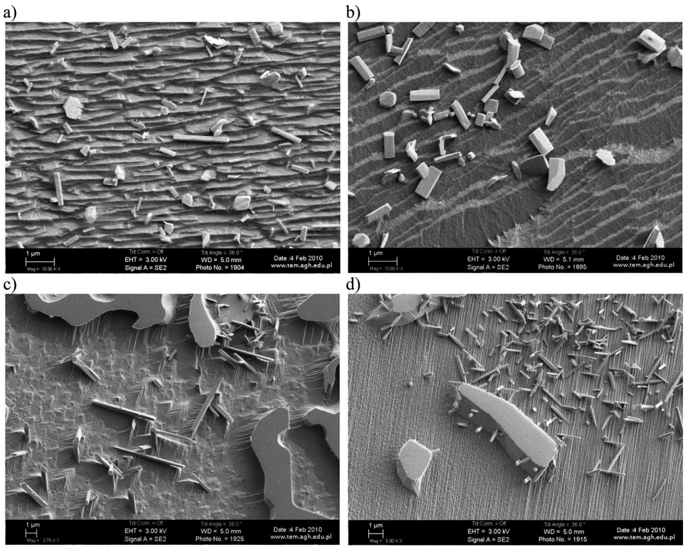

Fig. 5. Secondary carbides in investigated alloys after heat treatment in dilatometer: a) Ni-Ta-Al-C alloy; b) Ni-Ta-Al-C-Co alloy; c) Ni-Ta-Al-C-Co-Cr alloy; d) Ni-Ta-Al-C-Cr alloy

Microstructures of investigated alloys after heating and cooling procedures in dilatometer are shown in Fig. 5. 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 crystallization) were observed in the microstructure. Moreover, in microstructure the secondary carbides were observed. The secondary carbides are very fine and of irregular shapes. It should be mentioned, that only in Ni-Ta-Al-C-Cr alloys the secondary precipitation of the γ' phase were observed. In others investigated alloys the presence of the γ' phase, which was seen directly after casting, was not found in the microstructure. Heating up to

1200°C caused its dissolution. This provides the possibility of modifying alloys properties by further heat treatments such as solution heat treatment and aging. Heat treatment should be conducted because of microstructure instability in as-caste state.

5. Summary

During heating from as-cast state in Ni-Ta-Al-C and Ni-Ta-Al-C-Co alloys the beginning of the Tantalum carbides precipitation process (MC type) followed (or simultaneous) by the intermetallic phase precipitation (γ' – Ni_3(AlTa)) was stated, while in Ni-Ta-Al-C-Co-Cr and Ni-Ta-Al-C-Cr alloys, besides Tantalum carbides also the Chromium carbides precipitation occurred. It means that the investigated alloys in as-cast state were partially supersaturated. Above 1050°C in all investigated alloys the γ' phase is dissolving. It means that after casting the heat treatment (solution heat treatment and aging) should be processed because of microstructure instability.

In addition, the inclination to the precipitation of secondary carbides during slow cooling was found. This creates the need of high cooling rates application during solution heat treatment to avoid secondary precipitations.

REFERENCES

[1] A.K. S i n h a, Physical metallurgy handbook, The McGraw-Hill Companies, Inc., 2003.

[2] J. K r a w c z y k, P. B a ł a, J. P a c y n a, The effect of carbide precipitate morphology on fracture toughness on low-tempered steels containing Ni, Journal of Microscopy **237**, 411-415 (2010).

[3] M. M a d e j, Copper infiltrated high speed steel based composites with iron additions. Arch Metall Mater **54**, 1083-1091 (2009).

[4] R.W.K. H o n e y c o m b e, H.K.D.H. B h a d e s h i a, Steels. Microstructure and properties, 2nd ed. London: Edward Arnold, 1995.

[5] P. B a ł a, The kinetics of phase transformations during tempering of tool steels with different carbon content, Arch Metall Mater **54**, 491-498 (2009).

[6] J.R. D a v i e s, Metallurgy, Processing and Properties of Superalloys, ASM Speciality Handbook: Heat Resistant Materials, ASM International, 1997.

[7] M.J. D o n a c h i e, S.J. D o n a c h i e, Superalloys. A technical guide, ASM International, Materials Park OH, second edition, 2008.

[8] M. D u r a n d - C h a r r e, The microstructure of superalloys, CRC Press, 1997.

[9] Y. B i r o l, Thermal fatigue testing of Inconel 617 and Stellite 6 alloys as potential tooling materials for thixoforming of steels, Mat Sci Eng A **527**, 1938-1945 (2010).

[10] C. S t ö c k e r, M. Z i m m e r m a n n a, H.-J. C h r i s t, Z.-L. Z h a n b, C. C o r n e t, L.G. Z h a o, M.C. H a r d y, J. T o n g, Microstructural characterisation and constitutive behaviour of alloy RR1000 under fatigue and creep-fatigue loading conditions, Mat Sci Eng A **518**, 27-34 (2009).

[11] M. K o o r i, M. M o r i s h i t a, K. Y o s h i k a w a, O. T s u d a, Nickel-based heat-resistant alloy for dies. European Patent Application EP0460678.

[12] P. B a ł a, Microstructural characterization of the new tool Ni-based alloy with high carbon and chromium content, Arch Metall Mater **55**, 1053-1059 (2010).

[13] P. B a ł a, Microstructure characterization of high carbon alloy from the Ni-Ta-Al-Co-Cr system, Arch Metall Mater **57**, 937-941 (2012).

[14] K. Z i e w i e c, Z. K ę d z i e r s k i, The microstructure development in $Fe_{32}Cu_{20}Ni_{28}P_{10}Si_5B_5$ immiscible alloy and possibilities of formation of amorphous/crystalline composite, J. Alloys Compd. **480**, 306-310 (2009).

[15] T. K o z i e ł, Z. K ę d z i e r s k i, A. Z i e l i ń s k a - L i p i e c, J. L a t u c h, G. C i e s l a k, TEM studies of melt-spun alloys with liquid miscibility gap, J. Microsc. **237** , 267-270 (2010).

[16] B. D o u s t i, R. M o j a v e r, H.R. S h a h v e r d i, R.S. M a m o o r y, Microstructural evolution and chemical redistribution in Fe-Cr-W-Ti-Y2O3 nanostructured powders prepared by ball milling, J. Alloys Compd. **577**, 409-416 (2013).

Received: 10 January 2014.