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MICROSTRUCTURAL CHARACTERISTICS OF NEW TYPE γ-γ` Co-9Al-9W COBALT-BASED SUPERALLOYS IN AS-CAST STATE

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The paper presented deals primary with the structure characteristics of a new type of cobalt-based superalloys Co-9Al-9W type, casted via induction melting process with partially dosing of Common problems described in literature are focused on difficulties in obtaining uniform distribution of tungsten, particularly in interdendritic areas. That was the reason for the modified casting process to be applied. The method of tungsten dosing into liquid melts of Co and Al allows to obtain microstructure characterized by considerably decreased microsegregation. The material obtained was analyzed by standard methods such as light and scanning microscopy with analysis of chemical composition in micro-areas. Additionally, the detailed analysis of the sub-grain level was made by S/TEM on thin foils collected from equiaxed grains zone of the ingot.

Key words: Co-9Al-9W alloy, casting process, primary microstructure, Scanning Electron Microscopy (SEM) analysis, Scanning Transmission Electron Microscopy (STEM) analysis

INTRODUCTION

Conventional cobalt based superalloys are usually widely employed in various fields of industry eg., turbine engine constructions. The high-temperature applications of these alloys are the effect of stong fatigue strength as well as resistance to high temperature creep, oxidation and hot corrosion [1]. Usually the microstructure of standard Co alloys consists of Co based solid solution with different alloying elements. As a result the solid solution hardening effect can be observed. Next strengthening mechanism is related to precipitation phenomena of different types of carbides such as MC, $M_{23}C_6$ and M_7C_3. This mechanism gives the possibility for stable service of Co-based components up to approx 900 °C [2].

The new materials concept in the area of creep-resistant materials is the cobalt-based superalloys with γ/γ` structure, where strengthening phenomena is a consequence of the presence of γ` phase with $L1_2$ crystal structure. Co_3Al phase is not present in Co-Al system, due to the lack of thermal stability at room temperature. Thus it is observed only at high pressure. However, the different types of ternary compounds with overall formula γ`- $Co_3$(X, Y) exist in equilibrium state and are analogue to $Ni_3Al$ phase from structural point of view [3 - 5]. In 2006, Sato discovered the possibility of $Co_3Al$ phase formation in stable form at room temperature as a result of tungsten alloying and γ`-Co_3(Al, W) formation. In this case, lattice mismatch reaches approx. 0,53 %, which is below the limit value (1 %) [6]. Furthermore, the γ`-$Co_3$(Al, W) phase is stable up to 990 °C, hence new possibilities of the development of new cobalt based superalloys with comparable properties to nickel-based analogues appear. The most important disadvantages of cobalt γ/γ` Co-Al-W superalloys is relatively low plasticity and high density. Additionally, the high content of W causes technological problems with effect of microsegregation in interdendritic areas in as-cast condition [7].

The basic aim of the presented paper is microstructural characterization of Co-9Al-9W alloy in as-cast state, with special attention focused on the distribution of alloying elements in dendritic and interdendritic areas.

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MATERIALS AND METHODS

The nominal and the final chemical composition (in the as-cast state) of the analyzed cobalt-based superalloy used in investigation are present in Table 1.

Table 1 **Nominal (N) and real (R) chemical composition of Co-9Al-9W alloy**

Element	Co	Al	W
N_at. %	82	9	9
R_at. %	81,7	9,1	9,2
N_wt. %	71,80	3,61	24,59
R_wt. %	70,2	3,7	26,1

The alloy was melted using induction vacuum furnace VSG 02 Balzers. The samples were melted in Al_2O_3 crucibles, set in a coil using manually compacted moulding sand Konmix MAPI. The melting process was realized under argon Alphagaztm 1Ar (99,999 % Ar). Before melting, a chamber of furnace was washed three times by argon blowing, then the pressure was reduced to value of 10^{-3} Tr (~0,13 Pa) and subsequently, the chamber was gas filled to operating pressure 600 Tr (~800 hPa). Technically pure metals were used as a stock material, wherein the main components of alloys were: electrolytic cobalt (min. 99,98 % Co), aluminum 3N8 (99,98 % Al) and tungsten, which, due to its nature (pressed powder), was added with 20 % excess of the required weight.

Cobalt and aluminum were directly placed into crucible before melting, whereas tungsten was being added to liquid solution after its homogenization (dosing during melting process). The base alloy was melted in temperature range 1 650 ÷ 1 750 °C in time of approx. 10 minutes. Co-based alloy was casted under argon atmosphere into cold graphite molds. The final products of casting process were rods of size ø 20 × 100 mm. Phase composition of alloy was investigated by X - Ray diffraction analysis using X′Pert 3 Powder diffractometer. SEM imaging of microstructure and chemical state of surfaces were carried out on a Hitachi S - 4 200N, equipped with an Energy Dispersive X - Ray Spectroscopy (EDS), whereas TEM analysis were carried out on STEM HITACHI HD - 2 300 A. The optical microscopic observations of cross section were performed on Nikon Eclipse MA 200 optical microscopy.

RESULTS

In the first stage of investigations the chemical and phase composition analyses were made. The chemical constituent was showed in Table 1, where very good accordance between nominal and real composition was found. Those data showed the technological correctness of the applied process. The phase composition of alloy in as-cast state revealed the presence of diffraction peaks adequate to Co based solid solution $Co(Al,W)_{ss}$ with no sign of segregation areas rich in Al or W (Figure 1).

The basic part of investigations was related to characterization of primary microstructure and microsegregation effect of tungsten and aluminum, which is typical technological problem concerning tungsten-rich alloys. Firstly, evaluation of proper etchant, which allows to reveal a dendritic structure of alloy in as-cast state was realized. In this case, the electrolytic etching in solution con-

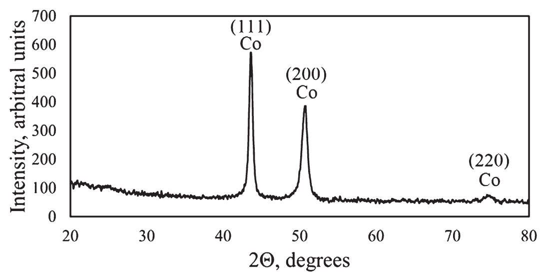


Figure 1 Diffraction pattern of Co-9Al-9W alloy

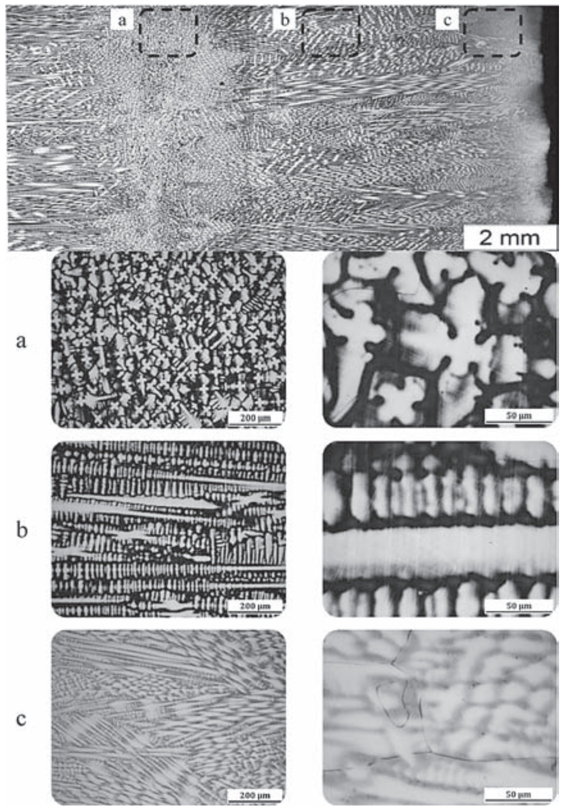


Figure 2 View of dendritic microstructure (up) and detailed picture (a, b, c) of Co-9Al-9W alloy on longitudinal section

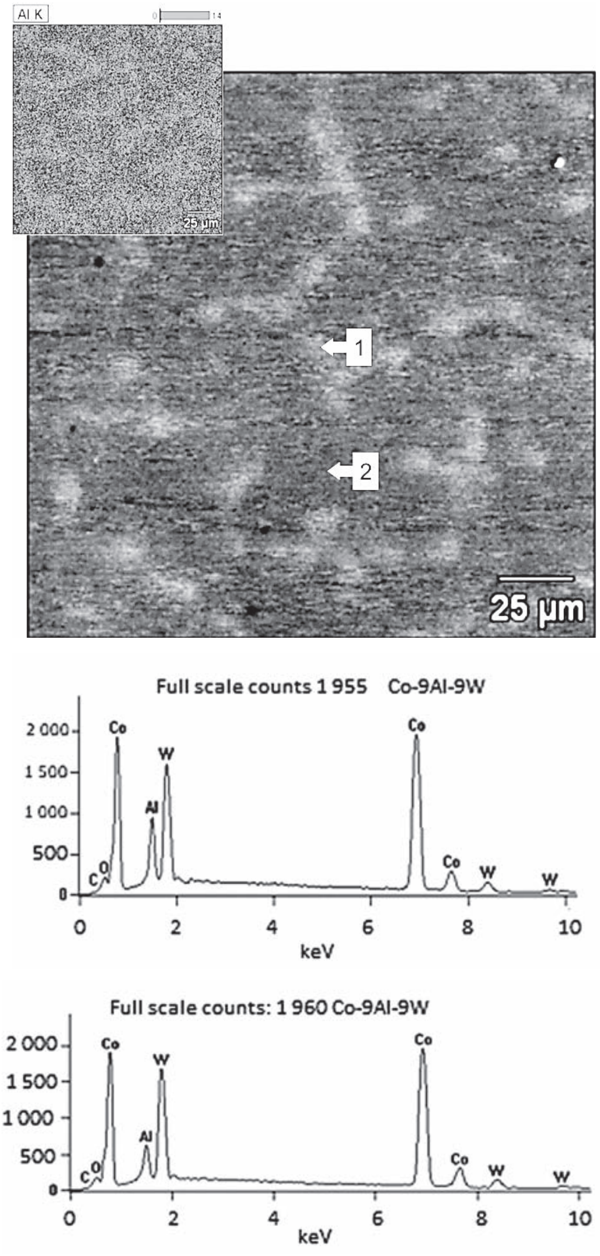
taining 25 ml H_2O, 50ml HCl, 15g $FeCl_3$ and 3g $CuCl_2 \times NH_4Cl \times 2H_2O$ was used. Primary structure of investigated superalloy at macroscale is shown in Figure 2.

The primary microstructure in longitudinal section consists of very thin, peripheral chill zone and wide columnar grains zone, as well as an equiaxed grains area. In this section the direction of columnar crystals growth is according to the direction of heat dissipation from solidifying ingot. Additionally, longitudinal section contains an area away from the bottom, where is present zone of fine, equiaxed grains, crystallized ahead of columnar front.

Revealed primary structure is characteristic for ingots solidifying in conditions of fast, directional heat dissipation - typical terms of casting into cold graphite molds. Morphology of grains present in all mentioned crystal zones is shown in Figure 3.

The columnar zone is made of highly elongated dendritic cells with visible first and second level dendrites, and ovules of third level dendrites. Equiaxed grains zone consists of fine crystals of poorly expanded dendrites oriented randomly to other dendrites and to the direction of heat dissipation. Considerable light contrast between dendrite cores and interdendritic areas is normally a sign of substantial dendritic microsegregation in alloys after casting.

Detailed results of investigations into chemical composition of equiaxed grains zone (where the strongest effects of microsegregation should be expected) by EDS method and cross-sectional distribution of tung-



Element	Al	Co	W
1_at. %	11,6	80,1	8,3
2_at. %	7,8	83,0	9,1
1_wt. %	4,8	72,0	23,2
2_wt. %	3,1	72,1	24,8

Figure 3 Chemical composition of dendritic and interdendritic regions in Co-9Al-9W alloy in area of crystals

sten, aluminum and cobalt are presented in Figure 3, respectively The diversity of tungsten concentration in dendrite cores and interdendritic areas did not exceed 2 % wt. (1 % at.). Substantially higher variations were observed in case of aluminum concentration, where value of difference between dendritic and interdendritic areas achieved even 4 % at. Cobalt behaved in analogue way to aluminum, resulting in increased concentration in dendrites. The difference reached even 3 % at. in the equiaxed grains zone.

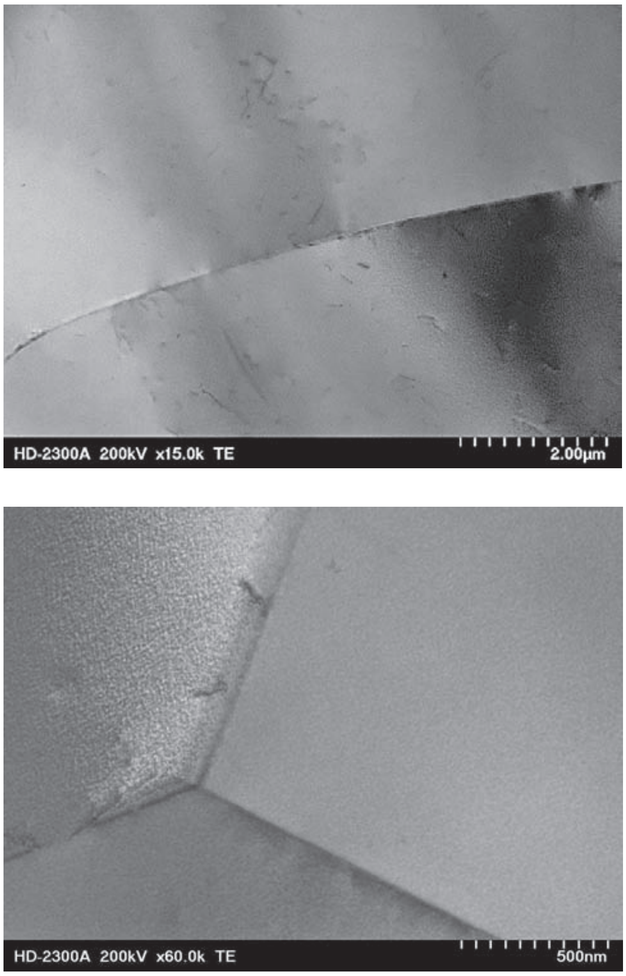


Figure 4 Electron image of the base Co-Al-W alloy in area of equiaxed crystals

However, the observations proved that the primary structure of the obtained cast is characterized by high homogeneity of chemical composition, although interdendritic areas exhibited local aluminum and cobalt enrichment.

In the final part of the presented investigations additional analysis of thin foils was made and sub-microstructural characterization of Co-9Al-9W alloy in ascasted state was presented (equiaxed grains area). Examples of structure on sub-grains level are shown in Figure 4, where high metallurgical quality of the obtained alloy is confirmed. The observations of equiaxed grains area by S/TEM method revealed the presence of clearly expressed grain boundaries as well as relatively small amount of single dislocations inside the grains. There was no precipitation on grain boundaries.

The analysis of chemical composition in micro-areas confirmed the presence of basic three alloying elements: Co, Al, W without significant effects of segregations (Figures 5 and 6).

CONCLUSIONS

- The performed investigation showed, that the applied technology of partial dosing of tungsten to liquid

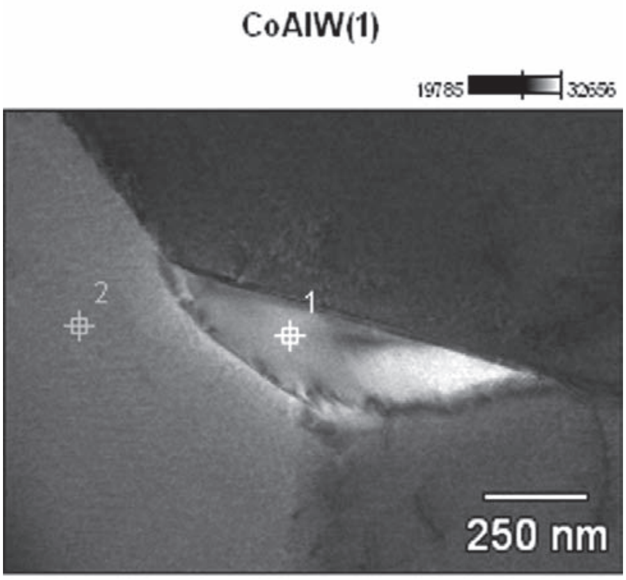


Figure 5 Electron image of the base Co-Al-W alloy in area of equiaxed crystals with the analysis points.

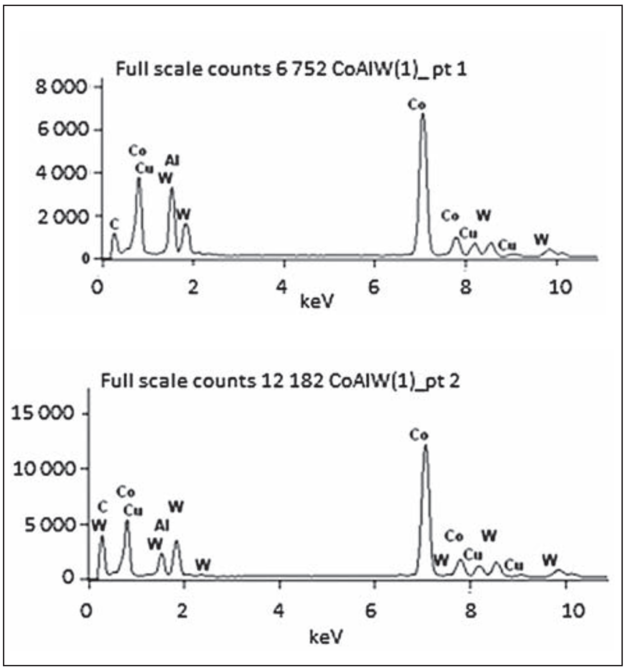


Figure 6 Chemical composition of dendritic and interdendritic regions in Co-9Al-9W alloy in area of equiaxed crystals

melt of cobalt and aluminum gives the possibility of formation of relatively uniform primary structure.

- The analysis of microsegregation effects showed slight differences in alloying elements such as aluminum and tungsten concentrations in dendritic and inter-dendritic zone.

- Detailed analysis of microstructure by S/TEM method confirmed very good metallurgical quality of as-cast material of Co-9Al-9W type, without significant segregation effect even on sub-grains level of microscopic observations.

Acknowledgments

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REFERENCES

[1] C. T. Sims, C.W. Hagel, The superalloys, John Wiley & Sons, New York, (1972).

[2] B. Lux, W. Bollmann, On the Mechanism of Carbide Precipitation in Cobalt Base Alloy 509, Cobalt 42 (1969), 3-13.

[3] C. T. Sims, N.S. Stoloff, W.C. Hagel, Superalloys II, John Wiley & Sons, New York (1987), 135–163.

[4] T. B. Massalski, H. Okamoto, P. R. Subramanian, L. Kacprzak, Binary Alloy Phase Diagrams Second Edition, 1, ASM International (1990), 137.

[5] M. Ellner, S. Kek, B. Predel, Zur existenz einer phase Co_3Al vom Cu_3Au-strukturtyp, Journal of Alloy and Compounds 189 (1992), 245–248.

[6] J. Sato, T. Omori, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida, Cobalt-base high-temperature alloys, Science. 312 (2006), 90–91.

[7] S.K. Makineni, B. Nithin, K. Chattopadhyay, A new tungsten-free *γ-γ`* Co–Al–Mo–Nb-based superalloy, Scripta Materialia 98 (2015), 36–39.

Note: Krajewska T. is responsible for English language, Katowice, Poland