Primary microstructure characterization of Co-20Ni-9Al-7W-3Re-2Ti superalloy

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Abstract

The characterization of the primary microstructure of the new Co-based superalloy of Co-20Ni-9Al-7W-3Re-2Ti type was shown in this article. The investigated alloy was manufactured by induction melting process from pure feedstock materials. The fundamental technological problem related to Co-Al-W-X multicomponent alloys' casting process is a strong susceptibility to interdendritic segregation of alloying elements, especially tungsten and rhenium. The performed analysis revealed that the observed effect of alloying elements segregation is detectable and much stronger than for Co-9Al-9W and Co-20Ni-7Al-7W alloys, related to titanium, nickel and aluminium migration to inter-dendritic spaces. Consequently, the tungsten concentration gradient between dendritic and interdendritic zones is higher than for Co-9Al-9W and Co-20Ni-7Al-7W alloys. The same situation is in the case of rhenium and cobalt, but Co's concentration in the interdendritic zone is only slightly lower.

Key words: Co-Al-W alloys, new Co-based superalloys, primary microstructure, interdendritic segregation

1. INTRODUCTION

Superalloys based on Ni or Co are high-performance materials usually used in high-temperature elements of land-based and aircraft turbines such as discs, blades, rotating shafts, nozzle guide vanes, and combustor liners [1]. Between them, the Co-based superalloys have applications as critical turbine engine parts, where hot corrosion, wear, and oxidation resistance is required [2-4]. Due to relatively low mechanical properties, especially at high temperature, the conventional Co-based superalloys are not dedicated to high-performance structural elements of turbines such as blades and disk. However, they can be used for static-loaded parts, e.g., vanes. The lower applications possibilities of carbides strengthened Co-based superalloys is related to temperature-depended limitation of strengthening effect by carbides precipitation in Co-based matrix [2]. The most popular and widely used alloys from this group are Haynes 188, Mar-M and stellite. Those alloys are strengthened by solid solution Coss and carbides of refractory elements. Still, its high-temperature properties, such as creep resistance, are lower than Ni-based superalloys due to lack of $\gamma/\gamma'$ structure [5-7].

Recent investigations showed that there is the possibility of beneficial $\gamma/\gamma'$ structure creation in Co-based superalloys. In the Co-Al system, the phase Co$_3$Al (similar to Ni$_3$Al phase in Ni-based systems) generally does not exist, and precipitation of an equilibrium B2-CoAl phase is more likely [8,9]. However, the Co$_3$Al phase with L1$_2$ type of lattice was detected occasionally in some of the grains of Co-Al ferromagnetic shape memory alloys [10]. Simultaneously in the Co-X (X=W, Nb, Ta) systems, compounds Co$_3$X with ordered L1$_2$ structure ($\gamma'$) has been reported [11-14], but these phases are not stable at the higher temperature (> 600 °C) [10,15-17]. The Co$_3$X L1$_2$ ordered phases are characterized by cuboidal shape, similar to Ni$_3$(Al,
Ti) phase in the Ni-based superalloys [18] and transform at the higher temperature to equilibrium disordered form with the same formula Co3X but with topological close-packed morphology D019 type of lattice) [19-21]. The metastability of Co3X phases with refractory elements can be weakened by forming triple phases such as Co3(Al, X). The presences of this type of compound were detected in the analysis of alloys form the Co-Al-W system. The additive and the appropriate proportion of Al and W in the structure, thereby stabilizing the L12 ordered structure of Co3(Al, W) phase up to 900 °C [15,16]. Mo's addition should get similar structural effects with additional decreasing of alloys density as an alloying element. However, the maximal level of Mo replacement is only up to 3 at %, because with the higher content of this alloying element, the formation of equilibrium Co3Mo phase with ordered D019 type of lattice structure is expected. This type of precipitates is characterized by specific needle-like morphology favoring the cracking phenomena with a strongly brittle character [22].

Compared to Co3(Al, W), no data confirmed Co3(Al, Mo) phase with L12 type of structure. L12 ordering does not take place on ageing between 600 °C and 800 °C [16]. This transformation was detected in the cases of quaternary alloys of Co-Al-Mo-Nb/Ta type. It was revealed that Nb or Ta's small addition plays a critical role in stabilizing of γ-γ' microstructure [18,22,23]. First principle calculations of Co3(Al, Mo, Nb) phase with the L12 structure revealed that this phase is mechanically stable and possesses intrinsic ductility. It is found additionally that the shear and Young's moduli of Co3(Al, Mo, Nb) are smaller than those of Co3(Al, W) [24].

Basing on those considerations, the new group of materials based on Co-Al-X systems (where X are refractory elements such as W – tungsten-containing alloys, and Mo, Nb or Ta – tungsten-free alloys) were developed [15,16,18,22,23]. The main strengthening element in those alloys is the ordered L12 phase with the overall formula Co3(Al, X). This new class of γ' precipitates strengthened Co-based materials revealed higher solidus and liquidus temperatures and less segregation during solidification than traditional Ni-based superalloys [25]. The γ' precipitates and the low-energy γ/γ' interface provide high-temperature strength and stability to these alloys similar to the Ni-based superalloys. Intensive investigations in alloying strategy (increasing γ' solvus temperature and growing strength and yield stress) get beneficial effects. At this moment, the creep properties and flow stress of tertiary, quaternary and quinary new Co-based superalloys are comparable to Ni-based superalloys of the first and second generation at a temperature approaching 900 °C [15,25]. But there are still challenges that require further research: decreasing the density of alloys and improving their creep and oxidation resistance [26,27].

In the case of increasing of γ' solvus temperature and increasing strength and yield stress, only data for Co-Al-W are present in the literature. It can be assumed that to increase the γ' solvus temperature and improve the microstructural stability, alloying elements, such as Ti, V, Ta, Nb, Mo, and Ni, should be added. Such elements increase the γ' solvus temperature in the following order: Ta→Nb→Ti→V→Mo→Ni [28,29]. The latest conclusion presented in [29] revealed that Nb greatly destabilized the γ' phase and is not suggested for alloy design in the Co-9Al-9W system. The morphologies and volume fractions of phases observed in these alloys' microstructures are highly sensitive to alloying with elements like Ni, Ti, Mo, B, Cr, and Ta [28, 30-33]. Co-based alloys' creep resistance is increased mainly with the addition of Cr, Mo, Ti, and Ta [34-36], and oxidation resistance can be improved primarily by expansion of Cr, Si and Ta [37-39]. The reduction of alloys density partially replaces W by Mo, Nb and Ta or developing tungsten free alloys.

The aim of the research is to characterize the primary microstructure of a new cobalt-based alloy with the addition of Re and Ti in as cast condition. The role of rhenium is to increase the melting point of the alloy, while titanium should increase the temperature of the L12 solvus. It was assumed that the dominant part of rhenium will be located in the cobalt solid solution, while titanium will form the L12 phase.

2. MATERIALS AND METHODS

The nominal composition of the new cobalt-based superalloy Co-20Ni-9Al-7W-3Re-2Ti used in this investigation was shown in Table 1. The induction vacuum process was used for alloy preparation. The
process was made in a VSG 02 Balzers type furnace, and the alloy was manufactured in Al₂O₃ crucible. The manually compacted molding sand Konmix MAP I was used to set the alumina crucible in the furnace coil. Argon of ALPHAGAZTM 1Ar (99,999% Ar) type was used to protection of liquid metal. Before the process starts, an operating chamber was washed by argon blowing (3 times). After this, the working pressure was decreased to a value of 10⁻³Tr (~0,13 Pa). The furnace chamber pressure was increased to 600 Tr (8x10⁴ Pa) by Ar filling in the next step. Technically pure metals were utilized as a stock material: electrolytic Co and Ni (both min. 99,98%), Al (purity 99,98%) and W, Re, Ti. Alloying Co, Ni, and Al elements were added to the crucible in the first step before the melting process. The other alloying elements – W, Re and Ti-was added to Co-Ni-Al’s liquid solution after its high-temperature homogenization (ca. 1600 °C). The final liquid alloy was thermally treated in a temperature range of 1650÷1750°C by 10 minutes. The final alloy was cast to the rods form under a protective argon atmosphere into cold graphite molds (Fig. 1). The actual composition of final alloy was shown at Tab. 2.

TABLE 1. Nominal composition of investigated alloy.

| Alloy | Co | Ni | Al | W  | Re | Ti |
|------|----|----|----|----|----|----|
| At. %|    | Bal. | 20.00 | 9.00 | 7.00 | 3.00 | 2.00 |
| Wt %|    | Bal. | 17.20 | 3.56 | 18.86 | 8.18 | 2.10 |

Fig.1. General view of final-cast from Co-20Ni-9Al-7W-3Re-2Ti alloy.

The scanning electron microscopy (SEM-Hitachi S-3400N) was used for the characterization of microstructural elements of alloys, as well as the chemical composition in micro-areas (EDS - Thermo NORAN System Seven), and phase identification (EBSD - INCA HKL Nordlys II, Channel 5). To ensure excitation of spectral lines of all analyzed elements during EDS analysis, the primary electron beam’s variable energy was used. Phase identification is the EBSD method was based on comparing the experimental Kikuchi pattern with the theoretical pattern. The “macro” phase constituent analysis of the investigated alloy was developed by X-ray diffraction method using X’Pert 3 diffractometer. The light microscopic analysis of microstructure was made on Nikon Eclipse MA200 microscopy. The final sample was cut from the central part of the rod, then a metallographic sample was prepared, and the plates were
ground, polished and etched. The electrolytic etching in a solution containing 25 ml H₂O, 50 ml HCl, 15 g FeCl₃ and 3 g CuCl₂ × NH₄Cl × 2H₂O was used to microstructure disclosure.

3. RESULTS AND DISCUSSION

The phase composition analysis of Co-20Ni-9Al-7W-3Re-2Ti alloy in the as-cast state (obtained by XRD measurement) showed diffraction peaks corresponding only to Co solid solution lattice - ICDD pattern no 15-0806 (Fig. 2). No peaks ordered to expected compounds of Co-W, Co-Ti or other types were identified.

![Fig. 2. Phase constituent of Co-20Ni-9Al-7W-3Re-2Ti alloy – XRD analysis.](image)

**TABLE 2.** Actual composition of investigated alloy.

| Alloy | Co  | Ni  | Al  | W   | Re  | Ti  |
|-------|-----|-----|-----|-----|-----|-----|
| At. % | Bal.19.58 | 8.75 | 7.11 | 2.87 | 2.10 |
| Wt %  | Bal.15.99 | 3.01 | 19.35 | 7.58 | 2.15 |

The primary microstructure (Fig. 3), visible in the longitudinal cross-section, consists of a very thin, peripheral chill zone (not shown in figure 3), and a wide columnar grain zone stretching to the core of the primary cast rod. The direction of columnar crystals growth is following the direction of heat dissipation from solidifying ingot. The rode's centre is occupied by a thick zone of refined, equiaxed grains, crystallized ahead of the columnar front.
Fig.3. LM picture of the primary microstructure of Co-20Ni-9Al-7W-3Re-2Ti alloy. The primarily revealed microstructure is typical for fast and directionally solidifying processes with heat dissipation effect, usually observed for casting into cold graphite molds. Detailed morphology of primary microstructure is visible in Fig. 4 and 5. Special attention was taken to characterize the inter-dendritic area, as the zones important from the point of view of chemical composition homogenization during heat treatment processes.

Fig.4. SEM picture of the primary microstructure of Co-20Ni-9Al-7W-3Re-2Ti alloy with visible precipitates in the interdendritic zones.

Fig.5. Alloying element maps of Co-20Ni-9Al-7W-3Re-2Ti alloy with a visible chemical constituent of precipitates in the interdendritic zones.

SEM analysis identified the small precipitates in interdendritic zones with a relatively high density of presences. Generally, those precipitates can be classified as W, Ti and Re containing carbides and Al-Ti intermetallic phases. Those observations were confirmed by EDS analysis in micro-areas presented in Fig. 6 and 7 (in the form of line distribution of alloying elements and point analysis, respectively), where zones rich in W and Ti were found (EDS analysis also revealed C presence, but this method is not adequate to carbon
analysis. Additionally, the areas affluent to Al and Ti were found as well. It suggests the presence of carbides of W and Ti (eventually Re) and Ti-Al compounds.

Fig. 6. Chemical composition in micro-areas of Co-20Ni-9Al-7W-3Re-2Ti alloy – EDS line analysis.

| Point 1 | Wt % | At % |
|---------|------|------|
| Al      | 02.34| 06.61|
| W       | 28.69| 11.90|
| Re      | 09.16| 03.75|
| Ti      | 01.00| 01.59|
| Co      | 44.72| 57.85|
| Ni      | 14.09| 18.30|

| Point 2 | Wt % | At % |
|---------|------|------|
| Al      | 04.26| 09.76|
| W       | 13.80| 04.63|
| Re      | 02.47| 00.82|
| Ti      | 06.12| 07.89|
| Co      | 50.99| 53.40|
| Ni      | 22.36| 23.50|

Fig. 7. Chemical composition in micro-areas of Co-20Ni-9Al-7W-3Re-2Ti alloy – EDS point analysis – average value from 10 random points.

| Point 3 | Wt % | At % |
|---------|------|------|
| Al      | 10.15| 20.22|
| W       | 06.23| 01.82|
| Re      | 00.89| 00.26|
| Ti      | 10.31| 11.57|
| Co      | 48.57| 44.30|
| Ni      | 23.85| 21.83|

| Point 4 | Wt % | At % |
|---------|------|------|
| C       | 12.99| 48.70|
| Al      | 00.56| 00.93|
| W       | 41.82| 10.25|
| Ti      | 32.92| 30.96|
| Co      | 08.32| 06.55|
| Ni      | 03.41| 02.61|

More precisely, the phase constituent of precipitates in micro-areas was described by the EBSD method. Results of those investigations were shown in Fig 8. These investigations confirmed that the interdendritic
zones are rich in carbides precipitates of (W, Ti) C₂ type and intermetallic compounds such as TiAl, TiAl₂ and TiAl₃. The Ti-Al compounds have generally beneficial effect on high temperature properties of materials [40]. It should be assumed that interdendritic zones are characterized by a strongly lower concentration of tungsten and rhenium than the dendritic zone (assumption for solid solution). The same situation was detected in the case of cobalt, but the segregation effect was slightly lower. The contrary situation was observed for titanium distribution, where its concentration was ca. 3 times higher in the interdendritic zone (in at. %). In the case of Al, it is only ca. 0.5-time higher concentration. Ni concentration was only slightly higher. The effect of W, Al and Co segregation was practically not observed for as-cast Co-9Al-9W alloy [41]. A similar tendency to segregation of W, Al and Ni was observed in the case of Co-20Ni-7Al-7W alloy, but the scale of this effect was much lower [42].
Fig. 8. Phase’s composition in micro-areas of Co-20Ni-9Al-7W-3Re-2Ti alloy – EBSD point analysis.

4. CONCLUSIONS

The presented analysis revealed that multi-component alloy of Co-20Ni-9Al-7W-3Re-2Ti type obtained by vacuum induction casting process is characterized by the high level of homogeneity of chemical composition. The observed differences of alloying element concentration in dendrites core and interdendritic zone are detectable but generally negligible. The strongest tendency to interdendritic segregation was observed for titanium and much lower for nickel and aluminium. The main problem related to the segregation effect is the formation of W and Ti-rich carbides and intermetallic compounds from the Ti-Al system.

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REFERENCES

[1] R.C. Reed, The Superalloys Fundamentals and Applications, Cambridge University Press, 2006.
[2] D. Coutsouradis, A. Davin, M. Lamberigts, Cobalt-based superalloys for applications in gas turbines, Materials Science and Engineering A 88 (1987) 11-19, doi.org/10.1016/0025-5416(87)90061-9
[3] D.L. Douglass, V.S. Bhide, E. Vineberg, The corrosion of some superalloys in contact with coal chars in coal gasifier atmospheres, Oxidation of Metals 16 (1981) 29-79, doi.org/10.1007/BF00603744
[4] N. Eliaz, G. Shemesh, R.M. Latanision, Hot corrosion in gas turbine components, Engineering Failure Analysis 9 (2002) 31-43, doi.org/10.1016/S1350-6307(00)00035-2
[5] S.-G. Kang and T. Kobayashi, Mechanical property of single phase Co-Ni-Cr-Mo based superalloy produced by cold working and recrystallization heat treatment, Materials Science Forum 449-452 (2004) 573-576, doi.org/10.4028/www.scientific.net/MSF.449-452.573
[6] W.H. Jiang, X.D. Yao, H.R. Guan, Z.Q. Hu, Secondary M6C precipitation in cobalt-base superalloy, Journal of Materials Science 4 (1999) 2859-2864, doi.org/10.1023/A:1004683301816
[7] W.H. Jiang, X.D. Yao, H.R. Guan, Z.Q. Hu, Carbide behavior during high-temperature low cycle fatigue in cobalt-base superalloy, Journal of Materials Science 4 (1999) 2859-2864, doi.org/10.1023/A:1004683301816
[8] P. Zieba, Microanalytical study of the discontinuous precipitation reaction in a Co–13 at.% Al alloy, Acta Materialia 46 (1998) 369–377, doi.org/10.1016/S1359-6454(97)00200-0
[9] T. Omori, Y. Sutou, K. Oikawa, R. Kainuma, K. Ishida, Shape memory effect in the ferromagnetic Co–14 at.% Al alloy, Scripta Materialia 52 (2005) 565–569, doi.org/10.1016/j.scriptamat.2004.12.001
[10] T. Omori, Y. Sutou, K. Oikawa, R. Kainuma, K. Ishida, Shape memory and magnetic properties of Co–Al ferromagnetic shape memory alloys, Materials Science and Engineering A 438 (2006) 1045–1049, doi.org/10.1016/j.msea.2005.12.068
[11] H. Okamoto, Co-W (Cobalt-Tungsten), Journal of Phase Equilibria and Diffusion 29 (2008), 119, doi.org/10.1007/s11669-007-9229-0
[12] H. Okamoto, Co-Mo (Cobalt–Molybdenum), Journal of Phase Equilibria and Diffusion 28 (2007) 300, doi.org/10.1007/s11669-007-9055-4
[13] K.P. Gupta, The Co-Nb-W (Cobalt–Niobium–Tungsten) system, Journal of Phase Equilibria 24 (2003) 82-85, doi.org/10.1007/s11669-003-0018-0
[14] K.P. Gupta, The Co-Mo-Ta (Cobalt–Molybdenum–Tantalum) system, Journal of Phase Equilibria 24 (2003) 186-189, doi.org/10.1361/105497103770330875
[15] J. Sato, T. Omori, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida, Cobalt-base high-temperature alloys, Science 312 (2006) 90-91, doi.org/10.1126/science.1121738
[16] C.S. Lee, Precipitation-hardening characteristics of ternary cobalt–aluminum–X alloys, University of Arizona, 1971.
[17] M. Korchynsky, R.W. Fountain, Precipitation phenomena in cobalt–tantalum alloys, Transactions of the Metallurgical Society of AIME 215 (1959) 1033-1043.
[18] S.K. Makineni, B. Nithin, K. Chattopadhyay, A new tungsten-free $\gamma'\gamma$ Co-Al-Mo-Nb-based superalloy, Scripta Materialia 98 (2015) 36-39, doi.org/10.1016/j.scriptamat.2014.11.009
[19] V.V. Kokorin, K.V. Chuistov, Initial stages of decomposition of supersaturated solid solutions Co–Ta and Co–Nb, Fiz Metallov Metalloved 21 (1966) 311–314.
[20] R.D. Dragsdorf, W.D. Foreing, The intermetallic phases in the cobalt–tantalum system, Acta Crystallographica 15 (1962) 531–536.
[21] J. Dutkiewicz, G. Kostorz, Structure of martensite in Co–W alloys, Materials Science Engineering A 132 (1991) 267–272, doi.org/10.1016/0921-5093(91)90383-X
[22] S.K. Makineni, A. Samanta, T. Rojhirunsakool, T. Alam, B. Nithin, A.K. Singh, R. Banerjee, K. Chattopadhyay, A new class of high strength high temperature cobalt based $\gamma'\gamma$ Co-Mo-Al alloys stabilized with Ta addition, Acta Materialia 97 (2015) 29-40, doi.org/10.1016/j.actamat.2015.06.034.
[23] S.K. Makineni, B. Nithin and K. Chattopadhyay, Synthesis of a new tungsten-free $\gamma'\gamma'$ cobalt-based superalloy by tuning alloying additions, Acta Materialia 85 (2015) 85-94, doi.org/10.1016/j.actamat.2014.11.016.
[24] Q. Yao, S.-L. Shang, Y.-J. Hu, Y. Wang, Y. Wang, Y.-H. Zhu, Z.-K. Liu, First-principles investigation of phase stability, elastic and thermodynamic properties in L1$_2$ Co$_3$(Al,Mo,Nb) phase, Intermetallics 78 (2016) 1-7, doi.org/10.1016/j.intermet.2016.08.002.
[25] T.M. Pollock, J. Dibbern, M. Tsunekane, J. Zhu, A. Suzuki, New Co-based gamma-gamma prime high-temperature alloys, JOM 62 (2010) 58-63, doi.org/10.1007/s11837-010-0013-y.
[26] L. Klein, A. Bauer, S. Neumeier, M. Göken, S. Virtanen, High temperature oxidation of $\gamma'/\gamma'$ -strengthened Co-based superalloys, Corrosion Science 53 (2011) 2027-2034, doi.org/10.1016/j.corsci.2011.02.033.
[27] H.-Y. Yan, V.A. Vorontsov, D. Dye, Effect of alloying on the oxidation behavior of Co-Al-W superalloys, Corrosion Science 83 (2014) 382-395, doi.org/10.1016/j.corsci.2014.03.002.
[28] M. Ooshima, K. Tanaka, N.L. Okamoto, K. Kishida, H. Inui, Effects of quaternary alloying elements on the $\gamma'$ solvus temperature of Co–Al–W based alloys with fcc/L1$_2$ two-phase microstructures, Journal of Alloys and Compounds 508 (2010) 71–78, doi.org/10.1016/j.jallcom.2010.08.050.
